

REMOVAL OF COPPER IONS BY A CATION-EXCHANGE RESIN IN A SEMIFLUIDIZED BED

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Abstract – The removal of copper ions was studied experimentally in a semifluidized bed charged with a strong cation-exchange resin, Amberlite 200C. The semifluidized bed system was formed by inserting a retaining grid in a packed bed and increasing the fluid velocity above U_{mf} . In this arrangement, the bed is separated into two sections; the upper packed bed section and the lower fluidized bed section. As the fluid velocity increases, the portion of the packed bed section becomes larger. As expected, the breakthrough curve obtained from the semifluidized bed lies between those from packed and fluidized beds. The breakthrough curves of copper ions were predicted reasonably well by using an axial dispersion model. In this paper, the effects of the liquid flowrate and the retaining grid height on the breakthrough behavior are extensively discussed.

Key words : Removal of Copper, Ion-Exchange, Semifluidized Bed, Wastewater Treatment

INTRODUCTION

A typical method for recovering metal ions from wastewater is a separation process using ion-exchange resins. The practical applications of ion-exchange resins in water and wastewater treatments can be found in Weber [1972] and Schweitzer [1979]. For this purpose, several different facilities such as packed, fluidized, and bubble columns have been used in many industrial processes [Davidson and Harrison, 1977]. Therefore, basic information on the effects of operating variables on the separation efficiency is basically required.

In general, a packed bed charged with resin particles has been used in removing metal ions from wastewater. However, the packed bed operation has some disadvantages, such as high pressure drop and channeling. Ion-exchange operations in fluidized or spout beds can eliminate these problems, particularly when resin particles are mobile. Recently, Biscans et al. [1988] studied the ion-exchange operation in a multi-stage, countercurrent fluidized bed. They found that the degree of separation is poor comparing with conventional packed bed operations even if the ion-exchange rate is high. Considering their practical aspects mentioned above, a semifluidized bed operation can be devised in order to take advantages of packed and fluidized bed operation.

A semifluidized bed can be formed by inserting a retaining grid in a packed bed and increasing the flowrate above U_{mf} . In this case, the bed is divided into sections, namely the lower fluidized section and the upper packed bed section. The portion of the upper packed bed section varies according to the flow rate and the position of the retaining grid. As the fluid velocity is increased above U_{mf} , the bed expansion is

restricted, resulting in a shorter fluidized section. The length of the fluidized section also depends on the position of the retaining grid. The particles in the upper section are slightly smaller and stagnant while those in the lower fluidized section are greater and mobile. This unique feature of semifluidized beds allows a wide range of practical applications by altering design parameters of the bed.

Fan et al. [1959] and Mydlarz [1987] studied the bed expansion in a semifluidized bed experimentally and proposed an empirical correlation for the relationship between the fluid flowrate and the height of packed section. Singh et al. [1980] obtained an empirical correlation for liquid-solid mass transfer coefficients and Fan et al. [1960] also obtained the mass transfer coefficient as a function of bed voidage in a water-benzoic acid system. Hwang and Lu [1990] studied the removal of copper ions from copper sulfate solution in a liquid-solid semifluidized bed and they found that the effluent concentration of heavy metal ions in the semifluidized bed is lower than that for the packed bed, but higher than that in the fluidized bed.

In this work, the mass transfer between liquid and ion-exchange resin particles was studied experimentally in a semifluidized bed, assuming that intraparticle diffusion of copper ions and ion-exchange rate are reasonably fast. The ion exchange of copper from dilute aqueous solutions of copper sulfate was carried out in a semifluidized bed packed with the strong cation-exchange resin, Amberlite 200C. Breakthrough curves of copper ion, variation of bed height, and pressure profiles were measured experimentally, and an axial dispersion model was used to simulate the exit concentration of copper ion. In particular, the effects of liquid flow rate, solid hold-up, and height of the retaining grid on the separation efficiency were rigorously discussed as well as the liquid to solid mass transfer characteristics.

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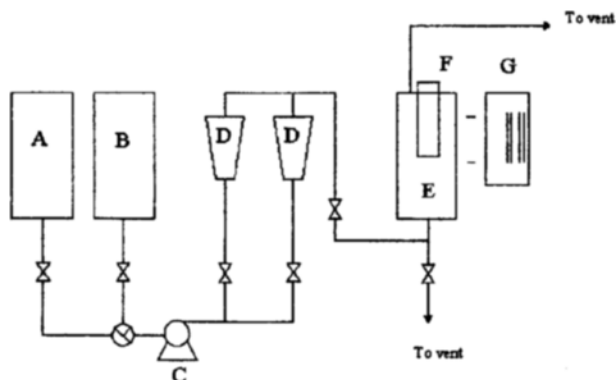


Fig. 1. Schematic diagram of experimental setup.

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|------------------------------------|----------------------|
| A: Water tank | E: Reactor |
| B: CuSO ₄ solution tank | F: Solution analyzer |
| C: Pump | G: Piezometer tube |
| D: Flow meter | |

EXPERIMENTS

The schematic diagram of the experimental apparatus used for the ion exchange is shown in Fig. 1. The bed was made of a transparent acrylic tube of 60 mm in diameter and 600 mm in length. The axial pressure profiles in the bed were measured using 16 pressure taps attached on the column wall. In the bottom section of the bed, glass particles of 3 mm in diameter were packed up to 150 mm as a liquid distributor and a 100 mesh stainless steel wire cloth was fixed to separate the glass particles from ion-exchange resin particles. The retaining grid for ion-exchange particles was also made of a 100 mesh wire cloth.

The exit concentrations of copper ion were analyzed using a solution analyzer (Solution Analyzer, Cole-Parmer) and an atomic absorption spectrometer (Philips). The strong cation-exchange resin, Amberlite 200C (Rohm and Hass Co.), was sieved in swollen state through standard sieves. Distilled water and aqueous solutions of copper sulfate, 100-500 ppm, were used in experiments and the temperature was kept at $22 \pm 2^\circ\text{C}$.

Batch sorption experiments were conducted to obtain the equilibrium distribution of copper ions between the ion-exchange resin and liquid phases. Amberlite 200C and CuSO₄ solution were equilibrated in a stirred tank at 22°C for 3 days. After equilibrium was established, the ion exchange resin particles and the solution were separated and the concentrations of copper ion in the liquid phase were measured by atomic absorption. The uptake amount of ion in the resin was evaluated from a material balance.

To carry out ion-exchange experiments in the semifluidized bed, a known amount of resin particles are loaded into the bed and a movable particle retaining grid is fixed at several predetermined positions. When a steady state condition is established after water is pumped into the bed, the axial pressure profile, bed expansion, and heights of lower fluidized and upper packed bed sections are measured. After these measurements, the flow of water is stopped and the copper sulfate solution is introduced into the bed, and the exit concentration of copper ion can be measured to get the breakthrough curve. The experiments were repeated by varying the

amount of resins in the bed and the height of the retaining grid. The procedures for the experiment in a fluidized bed are similar to that in a semifluidized bed except the retaining grid. The ion-exchange resins used are regenerated with 1N H₂SO₄ solution to reuse them.

AXIAL DISPERSION MODEL

In developing the model, the following assumptions were made: (1) the liquid flow is a plug flow with axial dispersion, and (2) the particles in the fluidized and packed bed sections are uniformly distributed and particle swelling is neglected. The model obtained from the mass balance in the bed is as follows:

$$\frac{\partial C}{\partial t} + U_i \frac{\partial C}{\partial Z} + \frac{K_f a}{\varepsilon} (C^* - C) = E \frac{\partial^2 C}{\partial Z^2} \quad (1)$$

with boundary conditions for fixed and fluidized beds,

$$C=0 \quad 0 < Z < L, \quad t=0 \quad (2)$$

$$C=C_i \quad Z=0, \quad t > 0 \quad (3)$$

$$\frac{\partial C}{\partial Z} = 0 \quad Z=L, \quad t \geq 0 \quad (4)$$

Similarly with boundary conditions for a semifluidized bed,

$$C=0 \quad 0 < Z < L, \quad t=0 \quad (2')$$

$$U_f C_i = \left[U_f C_i - E_f \frac{\partial C}{\partial Z} \right]_{Z=0+} \quad Z=0, \quad t > 0 \quad (3')$$

$$\frac{\partial C}{\partial Z} = 0 \quad Z=L, \quad t \geq 0 \quad (4')$$

The interfacial boundary condition between the fluidized and fixed bed sections is

$$\varepsilon_f \left[U_f C - E_f \frac{\partial C}{\partial Z} \right]_{Z=H+} = \varepsilon_p \left[U_p C - E_p \frac{\partial C}{\partial Z} \right]_{Z=H+} \quad (5)$$

ε is the voidage, Z is the axial distance from the bottom of the bed, L is the height of the bed, K_f is the mass transfer coefficient, C^* is the equilibrium concentration of copper ion in liquid phase, and a is the specific surface area of the ion-exchange resin (This model is discussed in detail in elsewhere [Schweitzer, 1995]). Eqs. (1)-(5) could be reformulated into dimensionless forms and solved numerically by a finite element method.

RESULTS AND DISCUSSION

1. Hydrodynamics

The flow properties of particles and liquid are shown in Table 1. The mean diameter of the particles in swollen state is 0.77 mm. The density and viscosity of copper sulfate solution were 999.7 kg/m^3 and $0.956 \times 10^{-3} \text{ kg/m}\cdot\text{s}$, respectively. These values are practically the same with those for distilled water. U_{mf} and ε_{mf} were measured in the fluidized bed, and U_i was theoretically calculated [Davidson and Harrison, 1977].

The effect of liquid velocity on the heights of both fluidized bed (h_f) and packed bed (h_p) sections in the semifluidized

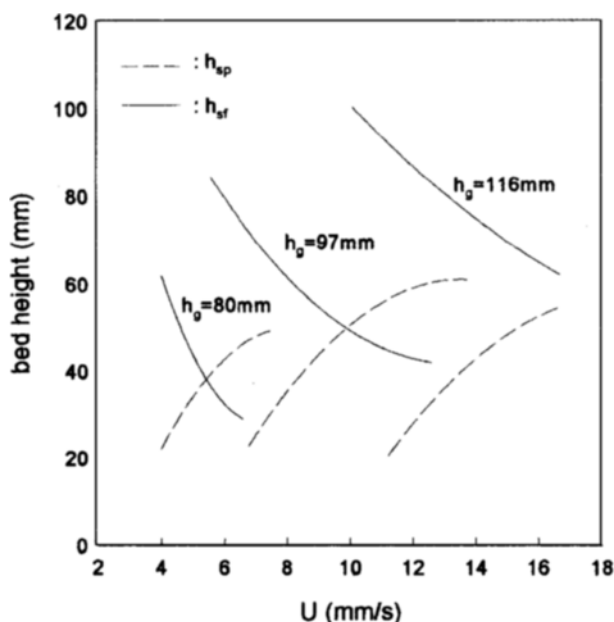


Fig. 2. Effect of fluid velocity on the heights of packed bed and fluidized bed sections in a semifluidized bed; $h_0=69.5$ mm, $h_g=80, 97, 116$ mm.

bed is shown in Fig. 2. The initial height of a loosely packed bed (h_0) was 69 mm, and the heights of the retaining grid (h_g) were 80, 97 and 116 mm, respectively. As the liquid velocity was increased above U_{mf} , bed expansion was observed. When the liquid velocity is increased above a certain value, the bed is separated into two sections: a fluidized bed in the lower section and a packed bed in the upper section. As shown in Fig. 2, the fluid velocity for bed separation is lower for the lower grid height. This figure also shows that the height of a fluidized bed section decreases as the liquid velocity is increased, while that for a packed bed section increases due to the particle transport from the fluidized bed section to the packed bed section. Under the experimental conditions of this study, the void region between the fluidized and packed bed sections is not clearly formed, but the particles near the top of the fluidized bed section move faster than those in the packed bed section. The particles in the two sections were collected separately and the size of the particles was measured from photographs taken using microscope and camera. The analysis of the photographs shows that the average diameter of the particles in the upper packed bed section is 0.74 mm, while that in the lower fluidized bed section is 0.79 mm.

The effect of liquid velocity on the pressure drops of the fluidized bed and packed bed sections in the semifluidized bed is shown in Fig. 3. The experimental conditions are the same as that shown in Fig. 2. This figure shows that the bed pressure drop through the upper packed bed section in the semifluidized bed is dominant especially as the liquid velocity is increased and the retaining grid height is decreased.

The voidage variation in the fluidized bed section was also measured. For this experiment, h_0 was 69 mm and h_g were 80, 97 and 116 mm, respectively. The effect of liquid velocity on the voidage variation of the fluidized bed was well represented by so-called Richardson-Zaki [1977] equation. However,

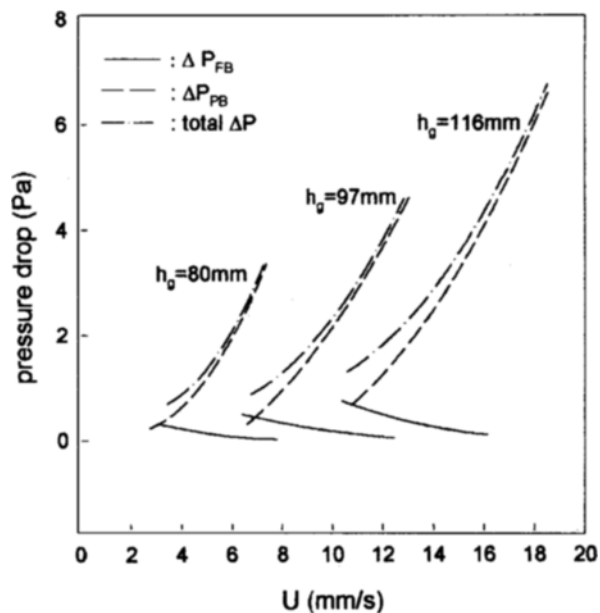


Fig. 3. Effect of fluid velocity on the pressure drop of packed bed and fluidized bed sections in a semifluidized bed; $h_0=69.5$ mm, $h_g=80, 97, 116$ mm.

the voidage of the fluidized bed section of a semifluidized bed is slightly lower than that of a conventional fluidized bed for the same flowrate. The voidage decreased with the grid height as expected.

The height of the packed bed section in the semifluidized bed was measured and compared with those from an experimental correlation shown in Fig. 4. As shown in this figure, the correlation by Mydlarz [1987], Eq. (6), and the modified Mydlarz equation, Eq. (7), represent our data reasonably well.

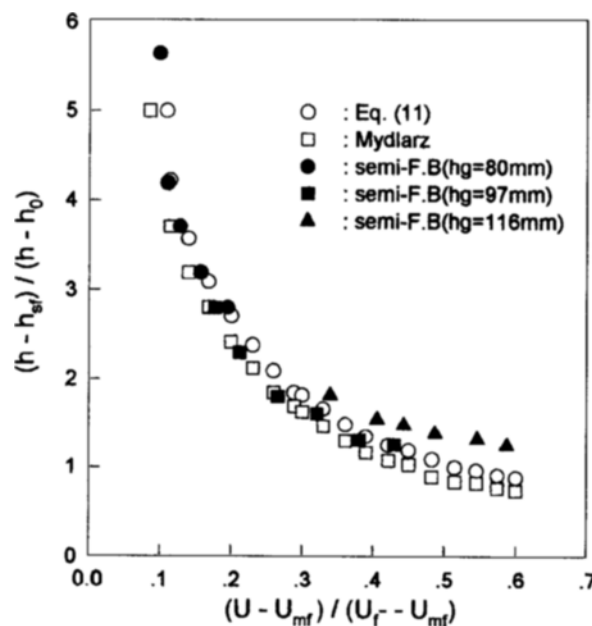


Fig. 4. Experimental data and correlations for the packed bed height in a semifluidized bed; $h_0=69.5$ mm, $h_g=80, 97, 116$ mm.

$$\frac{h - h_{sp}}{h - h_0} = 0.66 \left(\frac{U - U_{mf}}{U_i - U_{mf}} \right)^{-0.83} \quad (6)$$

$$\frac{h - h_{sp}}{h - h_0} = 0.71 \left(\frac{U - U_{mf}}{U_i - U_{mf}} \right)^{-0.85} \quad (7)$$

2. Equilibrium Isotherm

Equilibrium data obtained from batch experiments were fitted to the Langmuir equation and the isotherm parameters, *a* and *b*, are 4.65 and 0.00229, respectively.

$$Q = \frac{4.65 \times 0.00229C}{1 + 0.00229C} \quad (8)$$

Where *Q* is the equilibrium amount of copper ion per unit mass of resin (mg/g) and *C* is the concentration of copper ion in the liquid phase at equilibrium (mg/l).

3. Breakthrough Curves

Experimental breakthrough curves measured in the semifluidized bed are shown in Fig. 5. In these experiments, the loosely packed bed height was 61 mm, and the height of the retaining grid were varied from the fixed bed (*h*=61 mm) to fluidized bed conditions. The figure shows that the breakthrough curves obtained from the semifluidized bed lie between those obtained from fixed and fluidized beds.

The experimental breakthrough curves are compared with those calculated from the axial dispersion model shown in Fig. 6. In this case, the loosely packed bed height is 61 mm and the fluid velocity is 2.86 *U_{mf}*. In order to predict the breakthrough curves, ϵ was obtained from the Richardson and Zaki correlation [1977], the mass transfer coefficient was calculated from Eq. (9), and the measured specific surface area listed in Table 1 was used. As shown in Fig. 6, the axial dispersion model predicts the breakthrough curves reasonably well.

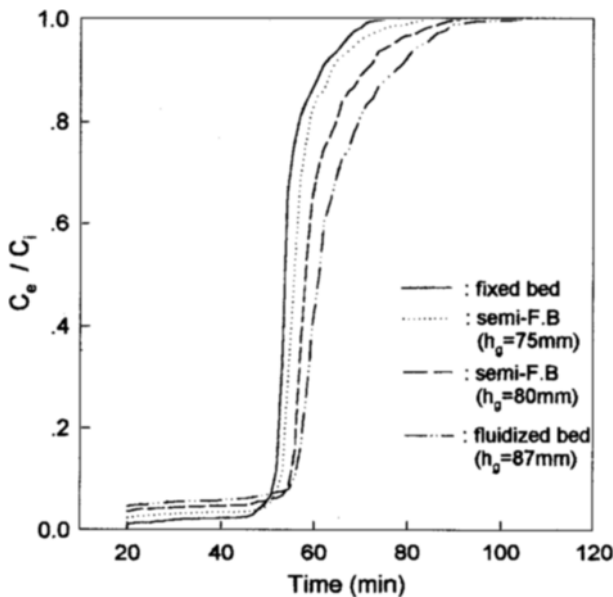


Fig. 5. Experimental breakthrough curves in the fixed, semifluidized and fluidized beds; *h₀*=61 mm, *C_i*=300 mg/L, *U*=3*U_{mf}*

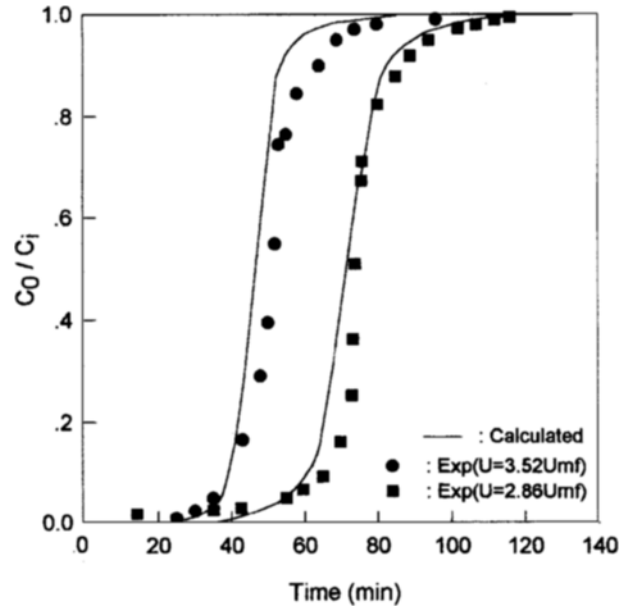


Fig. 6. Comparison of the calculated and experimental breakthrough curves in a semifluidized bed; *h₀*=69.5 mm, *h_g*=97 mm, *C_i*=300 mg/L.

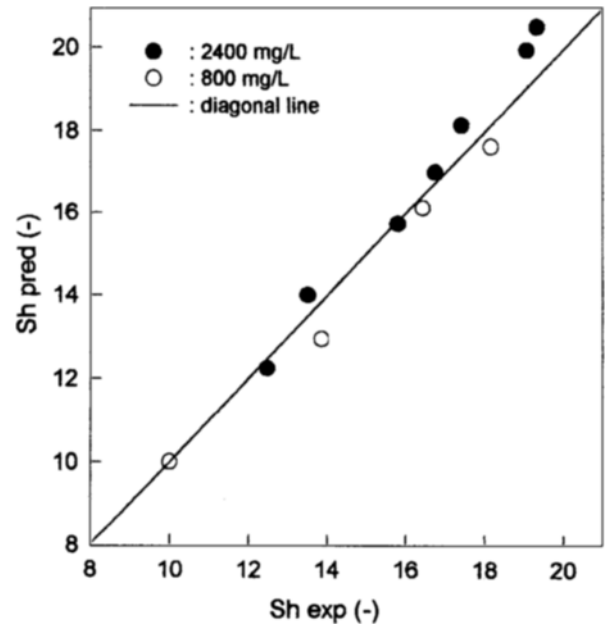


Fig. 7. Comparison of the predicted and experimental values of *Sh* in a fluidized bed.

4. Mass Transfer Coefficient

In order to study the mass transfer coefficient, *K_L*, in the fluidized and semifluidized beds, *K_L* was obtained from Eq. (9) in the initial period of the experiment, and the results are shown in Fig. 7.

$$K_L = \frac{V}{S} \ln \frac{C^* - C_i}{C^* - C_r} \quad (9)$$

In general, the mass transfer coefficient between liquid and solid has been correlated with a type of equation, *Sh*=*f*{*Re_p^a* *Sc^b* ϵ^c }. Mixon and Carberry [1960] and Snowdon and Turn-

Table 1. Experimental conditions : Dc=60 mm

dp (mm)	ρ_p (kg/m ³)	U_{mf} (mm/s)	U_t (mm/s)	ϵ_{mf} (-)	a (mm ⁻¹)
0.65	1,260	0.90	32.0	0.390	9.23
0.77	1,260	1.25	37.9	0.398	7.79

er [1967] reported Eqs. (10) and (11), respectively. Although they proposed these equations for similar experimental conditions in a fluidized bed, the effect of voidage on Sh is very different.

$$\text{Sh} = 0.974 \text{Re}_p^{0.5} \text{Sc}^{1/3} \epsilon^{-0.5} \quad (10)$$

$$\text{Sh} = 0.81 \text{Re}_p^{0.5} \text{Sc}^{1/3} \epsilon^{-1} \quad (11)$$

Also Dwivedi and Upadhyay's correlation [1977] for the mass transfer coefficients can be used.

$$\text{Sh} = 1.107 \text{Re}_p^{0.28} \text{Sc}^{1/3} \epsilon^{-1} \quad (12)$$

Eq. (12) shows that the effect of Re_p on Sh is smaller while the effect of ϵ is larger than that of Eq. (10). In the range of this experiment in a semifluidized bed, Eq. (10) represents our data reasonably well among the three equations. However, substantial improvement was obtained by changing the coefficient in Eq. (10) from 0.974 to 0.89.

$$\text{Sh} = 0.89 \text{Re}_p^{0.5} \text{Sc}^{1/3} \epsilon^{-0.5} \quad (13)$$

Sh calculated from Eq. (13) and experimental values are compared in Fig. 7. As shown in Fig. 7, Eq. (13) represents our data with a correlation coefficient of 0.94, and this equation was used in obtaining the mass transfer coefficient to predict the breakthrough curves.

CONCLUSIONS

The removal of copper ion from water using an ion-exchange resin was studied in a semifluidized bed, and the following results are obtained

1. The pressure drop in the packed bed section is dominant in a semifluidized bed.
2. The height of the fluidized bed section in the semifluidized bed is slightly lower than that of a conventional fluidized bed, and the height of the packed bed section can be correlated by Eq. (7).
3. Ion-exchange equilibrium data of copper ion on the cation-exchange resin, Amberlite 200C, were fitted to the Langmuir isotherm well.
4. The breakthrough curves obtained from the semifluidized bed lie between those from packed and fluidized beds and the axial dispersion model predicts the experimental data satisfactorily.
5. The liquid-solid mass transfer coefficient for the ion-exchange operation can be correlated by Eq. (13) with a correlation coefficient of 0.94.

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NOMENCLATURE

- a : specific surface area [mm⁻¹]
- C_e : effluent concentration of reactant [mN]
- C_i : inlet concentration of reactant [mN]
- C^* : equilibrium concentration in liquid phase [mN]
- D : diffusivity coefficient [mm]
- d_p : particle diameter [mm]
- E : axial dispersion coefficient [mm/s²]
- h : bed height [mm]
- h_f : height of the fluidized bed section [mm]
- h_g : height of the retaining grid [mm]
- h_o : initial static bed height [mm]
- h_p : height of the packed bed section [mm]
- h_{sf} : height of the fluidized bed in the semifluidized bed [mm]
- h_{sp} : height of the packed bed section in the semifluidized bed [mm]
- K_L : overall mass transfer coefficient [mm/s]
- ΔP_f : pressure drop in the fluidized bed [Pa]
- ΔP_{FB} : pressure drop in the fluidized bed section in the semifluidized bed [Pa]
- ΔP_{PB} : pressure drop in the packed bed section in the semifluidized bed [Pa]
- Re_p : Reynolds number [$U_d \rho_p d_p / \mu$]
- Sc : Schmidt number [$\mu / \rho D$]
- Sh : Sherwood number [$K_L d_p / D$]
- U : fluid velocity (superficial) in axial direction [mm/s]
- U_f, U_p : fluid velocity (interstitial) in the fluidized and packed bed sections [mm/s]
- U_{mf} : minimum fluidization velocity [mm/s]
- U_t : terminal velocity of the particle [mm/s]
- ϵ : bed voidage [-]
- ρ_p : particle density [kg/m³]
- μ : viscosity [kg/m · s]

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