Abstract

Computational models for adsorption in a tank are presented. The approximate model provides the same results as the exact model. The diffusion coefficient of a dye in an adsorbent pellet and the mass transfer coefficient in a fluid phase were determined on the basis of the measurements of dye adsorption on the activated carbon. It was determined how the fraction of the resistance to mass transfer in the fluid to the overall mass transfer resistance changes during adsorption. It was found that, for the examined system, the main resistance to mass transfer is located in the liquid phase.

Keywords: adsorption kinetics, resistance to mass transfer

Streszczenie

Przedstawiono modele obliczeniowe adsorpcji w zbiorniku. Stwierdzono, że model przybliżony daje identyczne wyniki z modelem ścisłym. Na podstawie przeprowadzonych pomiarów adsorpcji barwnika na węglu aktywnym określono wartość współczynnika dyfuzji w ziarnie oraz współczynnika wnikania masy w fazie ciekłej. Wyznaczono czasowe zmiany udziału oporu wnikania masy w fazie ciekłej w sumarycznym oporze przenoszenia masy w trakcie adsorpcji. Stwierdzono, że dla badanego układu główny opór przenoszenia masy jest zlokalizowany w fazie ciekłej.

Słowa kluczowe: kinetyka adsorpcji, opór przenoszenia masy

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* Ph.D. Eng. Monika Gwadera, Ph.D. Eng. Krzysztof Kupiec, prof. CUT; Faculty of Chemical Engineering and Technology, Cracow University of Technology.
1. Introduction

The presence of dyes from different branches of industry in water is a significant environmental problem. Even if a dye concentration is low, it affects the organisms living in water. Some of the dyes are carcinogenic or mutagenic.

Wastewater containing dyes comes from the following industries: food industry, fat industry, cosmetics industry and plastics industry. Such wastewater changes the color of water in a receiver, which leads to a reduction of its usefulness in industry and in households. The existing color reduces light transmittance, and thus interferes with the growth and biological activity of bacteria and delays the self-cleaning process. Furthermore, coloring substances consume oxygen dissolved in water, which results in chemical and biological changes of the aquatic environment. The consequence of dyes decomposition is the appearance of substances that are toxic, carcinogenic and mutagenic to living organisms.
Adsorption on activated carbon is one of the most effective and reliable technologies for the treatment of water and wastewater that contain hazardous compounds [1]. It is necessary to know the equilibrium and kinetics of adsorption in order to design an efficient installation for adsorption on activated carbon.

Adsorption in a liquid phase can be performed, for example, by contacting a mixture containing an adsorbate with adsorbent pellets in a mixing tank. Adsorption in a tank is an important step in the treatment of drinking water.

Most commercial adsorbents are porous and the rate of discharge of a component from a solution is limited by the adsorbate molecules diffusion to the interior of adsorbent pellets. An adsorbate must, however, first be transferred from the bulk of the fluid to the surface of a pellet. The relationship between internal and external mass transfer resistance is expressed by the Biot number $Bi$. When the resistance in a fluid phase can be neglected, then $Bi \rightarrow \infty$; otherwise $Bi$ has a finite value.

The purpose of this paper is to present the principles of modeling of adsorption in a tank of finite volume and to analyze the mass transfer resistance during this process. An exact model of the process based on a differential equation containing partial derivatives and an approximate model based on a system of ordinary differential equations are presented. Contributions of mass transfer resistances in both phases of the system were determined on the basis of the study of kinetics of dye adsorption on activated carbon. The dominant mass transfer resistance must be known for modeling and design of adsorption processes. Systems with linear adsorption equilibrium and adsorbent pellets with the shape of an infinite plate, infinite cylinder and sphere are considered.

2. An exact model of adsorption in a finite-volume tank

The equation of diffusion and adsorption will be presented in a dimensionless form. The dimensionless quantities are defined as follows: the concentration of an adsorbate in a pellet $Q = q_m/q_{m0}$, the average concentration in a pellet $\bar{Q} = \bar{q}_m/q_{m0}$, the spatial coordinate in a pellet $\eta = x/L$, time $= D_s t/L^2$, the concentration in a fluid $Y = C/C_0$. The formula that relates $Q$ and $\bar{Q}$ has the form:

$$
\bar{Q} = (\zeta + 1) \int_0^1 \eta Q \, d\eta 
$$

where the geometric factor is: for a slab $\zeta = 0$, for a cylinder $\zeta = 1$, for a sphere $\zeta = 2$. The equation of diffusion and adsorption is:

$$
\frac{\partial Q}{\partial \tau} = \frac{\partial^2 Q}{\partial \eta^2} + \frac{\zeta}{\eta} \frac{\partial Q}{\partial \eta}
$$

(2)
The initial condition for pellets that do not contain an adsorbate:

\[ \tau = 0 \quad Q = 0 \] (3)

One of the boundary conditions refers to the symmetry of a pellet:

\[ \eta = 0 \quad \frac{\partial Q}{\partial \eta} = 0 \] (4)

The form of a boundary condition at the surface of a pellet depends on the relation between the internal and external mass transfer resistance. When the resistance outside a pellet can be neglected \((\text{Bi} \to \infty)\), the condition has the form:

\[ \eta = 1 \quad Q = Y_b \] (5)

If the external resistance must also be taken into account, the boundary condition at the pellet surface is:

\[ \eta = 1 \quad \frac{\partial Q}{\partial \eta} = \text{Bi} \left( Y_b - Y \right) \] (6)

Values of \( Y_b \) are dimensionless concentrations of an adsorbate in the bulk of a fluid phase. For \( \text{Bi} \to \infty \) the concentration is constant i.e. it does not change with time. Then it is \( Y_b = 1 \) for adsorption and \( Y_b = 0 \) for desorption with an inert.

When a tank that contains a liquid has a finite volume, then concentration of an adsorbate in the liquid changes during adsorption. The model of the process must include not only the balance for a solid phase but also the balance of an adsorbate in a fluid. This equation has the form:

\[ \bar{Q} = \alpha (1 - Y) \] (7)

where the adsorbent load factor is given by the formula:

\[ \alpha = \frac{V}{m_s K} \] (8)

For the linear equilibrium of adsorption it can be proved that the ratio of mass of adsorbed component at a given moment \( m_t \) to the mass of adsorbed component at equilibrium \( m_\infty \) is:

\[ \frac{m_t}{m_\infty} = \frac{\bar{Q}}{\lim_{\tau \to \infty} \bar{Q}} = \frac{1 + \alpha}{\alpha} \bar{Q} \] (9)
For Bi → ∞ the analytical solutions for all the considered shapes can be written in the generalized form [2, 3, 7]:

\[
\frac{m_t}{m_\infty} = 1 - \sum_{i=1}^{\infty} \frac{2 (1 + \zeta) \alpha (1 + \alpha)}{(1 + \zeta)^2 + (1 + \zeta)^2 \alpha + \alpha^2 \beta_i^2} \exp(-\beta_i^2 \tau)
\]

(10)

where \(\beta_i\) are consecutive roots of the following algebraic equations. For a slab:

\[\tan \beta + \alpha \beta = 0\]

(10a)

For a cylinder:

\[\alpha \beta J_0(\beta) + 2 J_1(\beta) = 0\]

(10b)

For a sphere:

\[\tan \beta - \frac{3 \beta}{3 + \alpha \beta^2} = 0\]

(10c)

From formulas (7), (9) and (10) one can obtain:

\[Y = 1 - \frac{1}{1 + \alpha} \left[ 1 - \sum_{i=1}^{\infty} \frac{2 (1 + \zeta) \alpha (1 + \alpha)}{(1 + \zeta)^2 + (1 + \zeta)^2 \alpha + \alpha^2 \beta_i^2} \exp(-\beta_i^2 \tau) \right]\]

(11)

For short times the rates of convergence of the infinite series in equations (10), (11) are slow and a large number of terms must be taken into account, which is burdensome. However, in such cases, some other forms of solutions that do not contain infinite series may be used [2].

For Bi < \infty, i.e. when the resistances to mass transfer are in both phases, the analytical solution for adsorption in a finite volume tank is known only for a sphere.

Temporal variations of dimensionless concentrations of an adsorbate in a solid and liquid phases for different values of \(\alpha\) are presented in Fig. 1. The graph refers to spherical pellets and to the lack of the mass transfer resistance in a fluid. The courses (in the form of symbols) were determined on the basis of relations (11) and (7). After some time, the system reaches equilibrium and the dimensionless concentrations become equal to each other. The values of the equilibrium concentrations depend on the coefficient \(\alpha\).

The Bessel functions are present in the solution for an infinite cylinder instead of trigonometric functions occurring in the solutions for a slab and a sphere (eq. (10b)). Some difficulties lie in finding the roots of an equation that contains the Bessel function which are periodic functions with variable period. To find a root, the range in which it will be searched for should be determined. In order to do it, the zeroes of the Bessel function of order zero \(J_0(\beta) = 0\) should be known. The problem is illustrated in Fig. 2. The curves for the functions \(Y_1\) and \(Y_2\) defined as follows:

\[Y_1, Y_2 = \frac{\sin(\beta \tau) + \alpha \cos(\beta \tau)}{\alpha + 1}\]
Fig. 1. The effect of the parameter $\alpha$ on adsorbate concentrations in both phases in a finite-volume tank. Spherical pellets, $\text{Bi} \to \infty$.

Fig. 2. The roots of formula (10b)
\[ y_1 = -\frac{\alpha}{2} \beta J_0(\beta) \] (12a)

\[ y_2 = J_1(\beta) \] (12b)

are presented.

The shape of the function \( y_1 \) depends on the value of the parameter \( \alpha \); in Fig. 2 the graphs for \( \alpha = 1/9, \alpha = 1 \) and \( \alpha = 9 \) were presented. The zeroes of function \( y_1 \) (not shaded points) coincide with the zeros of function \( J_0(\beta) \). They are equal to: \( \beta_1 = 2.4048, \beta_2 = 5.5201; \beta_3 = 8.6537 \) etc. Therefore, the first solution of equation (10b) is in the range \((2.4048, 5.5201)\), the second is in the range \((5.5201, 8.6537)\) etc. Abscissae of the points of intersection of functions \( y_1(\beta) \) and \( y_2(\beta) \) are the sought roots of equation (10b) (shaded points). For example, for \( \alpha = 1/9 \) the first solution is 3.6374, for \( \alpha = 1 \) the first solution equals 2.9496, and for \( \alpha = 9 \) the first solution is 2.4922.

3. Computational relationships for the approximate model

In the approximate model of adsorption kinetics, based on the continued fractions approximation, the general form of the kinetic equation is as follows:

\[
\mathbf{\dot{x}} = \mathbf{d}^{-1} \left( \mathbf{a} - \frac{1}{\alpha} \mathbf{bq} \right) \mathbf{x} + \mathbf{d}^{-1} \mathbf{b}
\] (13)

Hence, a system of ordinary differential equations must be solved.

The vector \( \mathbf{b} \) is defined in the form: \( \mathbf{b} = [\zeta + 1, \zeta + 1, ..., \zeta + 1]^T \). The elements of matrix \( \mathbf{a} \) are: \( a_y = -p_i q_i \) for \( j \neq i \) and \( a_y = -p_i q_i \) for \( j < i \) and \( a_y = -p_i q_i \) for \( j = i \), where \( p_i \) and \( q_i \) are defined as follows: \( p_i = 2i^2 - i + \zeta i, q_i = 4i + \zeta - 1 \) where \( i = 1, 2, ..., n \). The elements of matrix \( \mathbf{d} \) depend on the Biot number: \( d_y = q_i / Bi \) for \( j \neq i \) and \( d_y = 1 + q_i / Bi \) for \( j = i \). The number of equations in system (13) is the order of approximation \( n \); the greater the order, the higher accuracy of approximation.

System of equations (13) has to be solved with the initial condition which for a pellet that do not contain an adsorbed component has the form:

\[
\tau = 0 \quad \mathbf{x} = \mathbf{0}
\] (14)

As a result of solving system (13), one gets a vector function \( \mathbf{x}(\tau) \) on the basis of which a scalar function \( \mathbf{Q}(\tau) \) can be determined:

\[
\mathbf{Q} = \mathbf{qx}
\] (15)
The form of a boundary condition at the pellet surface depends on the values of parameters $\alpha$ and $\text{Bi}$. Possible cases are discussed below. Since a linear form of adsorption equilibrium was assumed, it is $Q_1 = Y_1$ in each case.

In the simplest system, a pellet is contacted with a fluid of an infinite volume ($\alpha \rightarrow \infty$), which is mixed so intensely that the external mass transfer resistance can be neglected ($\text{Bi} \rightarrow \infty$). In this case, the concentration of an adsorbate in a fluid does not change over time and space. Therefore, it might be assumed that the surface of a pellet contacts with a fluid which has a constant and known concentration. The concentration at the pellet surface $Q_1$ (in equilibrium to the concentration of an adsorbate in a fluid that has a direct contact with the pellet surface) is also constant (Fig. 3a). The following equality is valid for such a case:

$$ Q_1 = Y_b = 1 $$

The approximate kinetic model simplifies to the form:

$$ \dot{x} = ax + b $$

(17)

Such a model was used by Lee and Kim [9].

For adsorption in a finite-volume tank ($\alpha < \infty$), the adsorbate concentration in a fluid contacting with the pellet surface changes over time, which results from changes of the adsorbate concentration in the bulk of a fluid. When diffusion resistance in a fluid is negligible ($\text{Bi} \rightarrow \infty$), the concentration of a component in a fluid at the solid-fluid boundary is equal to the bulk concentration (Fig. 3b). The following relationship is valid:

$$ Q_1 = Y_b \leq 1 $$

(18)

while the approximate kinetic model is:

$$ \dot{x} = \left( a - \frac{1}{\alpha} bq \right) x + b $$

(19)

Such a form of a kinetic model was used in the paper [7].

When mass transfer resistance in the fluid phase cannot be neglected ($\text{Bi} < \infty$), the concentrations of an adsorbate in the bulk of a fluid and at the phase boundary are not equal (for adsorption it is: $Y_1 < Y_b$). If the process is conducted in a tank of an infinite volume ($\alpha \rightarrow \infty$), the concentration of an adsorbate in the bulk of a fluid does not change over time ($Y_b = 1$). However, the concentration at the surface $Y_1 = Q_1$ varies over time. For such a case (Fig. 3c), the following relationship is valid:

$$ Q_1 \leq Y_b = 1 $$

(20)

The following system of equations constitutes the approximate kinetic model:

$$ \dot{x} = d^{-1} ax + d^{-1} b $$

(21)
Such a case was considered in the paper [6].

The most difficult case is when the mass transfer resistance in the liquid phase is significant and the bulk concentration changes. This occurs when adsorption is conducted in a finite-volume tank (\( \alpha < \infty \)) and the intensity of fluid stirring does not ensure that the bulk concentration and the phase boundary concentration are equal (\( \text{Bi} < \infty \)). The changes of the surface concentration result from the mass transfer resistance in a fluid and from reduction of an adsorbate concentration in the bulk of a fluid because of adsorption. It can be written that (Fig. 3d):

\[
Q_1 \leq Y_b \leq 1
\]  

(22)

The system of equations (13) without any simplifications is the approximate kinetic model.

Calculations were conducted to verify whether the approximate model gives results consistent with the exact model. A number of calculations are presented in the works of authors [4, 5, 6, 8]. The results of an exemplary calculation are also presented in Fig. 1.
The solid lines in this Figure denote values obtained on the basis of the approximate model. The compliance between this values and the values designated on the basis of an analytical solution (symbols) is very good.

4. Mass transfer resistance

In order to intensify the adsorption process, one should reduce the mass transfer resistance. The overall resistance is influenced by partial resistances in a fluid phase and adsorbent pellets. These resistances are connected in series so the greater resistance, which has the main impact on the overall resistance, should be reduced. If the main resistance is in the fluid it can be reduced e.g. by the increase of the flow velocity. When the resistance in pellets dominates, one should consider reduction of pellets size. By knowing the values of the mass transfer coefficient in a fluid and the diffusion coefficient in pellets, one can determine the contribution (fraction) of each resistance to the overall resistance and in this way the dominant resistance can be determined. However, it should be noticed that mass transfer during adsorption is usually a transient process so the relations between resistances change when adsorption is conducted.

For pellets with the considered shapes, the dimensionless equation of mass transfer in a liquid phase has the form:

$$\frac{d\bar{Q}}{d\tau} = (1 + \zeta) \text{Bi} (Y - Y_1)$$

(23)

The rate of mass transfer was determined by differentiation of equation (15):

$$\frac{d\bar{Q}}{d\tau} = q\dot{x}$$

(24)

From the above relationships, a concentration $Y_1 = Q_1$ at the phase boundary was calculated:

$$Y_1 = Y - \frac{1}{(1 + \zeta) \text{Bi}} q\dot{x}$$

(25)

In Fig. 4, the concentrations for adsorption in a finite-volume tank with mass transfer resistance in both phases are presented. The graph refers to spherical pellets and Bi = 10. Temporal variations in a liquid phase $Y$, solid phase $\bar{Q}$ and at the phase boundary $Y_1$ are presented. Since there is equilibrium at the phase boundary, so it is $Y_1 = Q_1$. Moreover the following relationships are valid: $Y > Y_1$ and $Q_1 > \bar{Q}$.

A stream of an adsorbed component (component that is transferred from a liquid to a solid phase) is proportional to the mass transfer driving force and inversely proportional to the mass transfer resistance $R$. Comparison of the stream of a component transported in a liquid and the stream transferred between both phases leads to the formula:
Fig. 4. Temporal variations of concentrations in a fluid $Y$, pellets $\overline{Q}$ and at the phase boundary $Y_1 = Q_1$.

Fig. 5. The contribution of the mass transfer resistance in a fluid to the overall mass transfer resistance during adsorption in a tank

\[
\frac{Y - Y_1}{R_L} = \frac{Y - Y^*}{R_{\text{st}}}
\]  

(26)
Hence, the ratio between resistance to mass transfer in a liquid phase and the overall mass transfer resistance between phases $\chi = \frac{R_l}{R_{ol}}$ is:

$$\chi = \frac{Y - Y_1}{\bar{Q}}$$  (27)

where it was substituted that $Y^* = \bar{Q}$.

Temporal variations of the quantity $\chi$ for different values of $\alpha$ and Bi are presented in Fig. 5. The graphs refer to spherical pellets and the quantity $\chi$ was determined from formula (27). As can be seen, the contribution (fraction $\chi$) of the external resistance (in a liquid) to the overall resistance decreases. The greater the Biot number, the lower the fraction of the resistance to mass transfer in a liquid phase. For $\text{Bi} \to \infty$ resistance in a liquid phase disappears completely.

5. The analysis of measurement results

Experimental studies on kinetics of adsorption of a dye BR 200% from an aqueous solution on activated carbon BA-20 were conducted. The pellets had irregular shape, their average size was 2.0 mm. The experimental setup consisted of a tank with a stirrer, peristaltic pump and adsorber with a layer of adsorbent pellets of low height [8]. A dye concentration was measured by a UV-VIS Shimadzu spectrophotometer model UV-2600 at the 584 nm wavelength. A constant temperature of 23°C was kept during the measurements. The apparent velocity of the solution in the adsorber was $u = 0.0437$ m/s, adsorption equilibrium constant $K_{p_p} = 426$, solution volume 0.25 dm$^3$, pellets mass 2.30 g. The results of measurements are presented in the form of symbols in Fig. 6. The Figure illustrates the relationship between the dye concentration in pellets and time.

On the basis of the measurement results, the diffusion coefficient of the dye referred to the concentration in pellets $D_s$ and the mass transfer coefficient in the liquid phase $k_l$ were determined. The following values were obtained: $D_s = 92.5 \cdot 10^{-12}$ m$^2$/s, $k_l = 18.0 \cdot 10^{-6}$ m/s [8]. These values were used to determine the computational relationship that is presented in Fig. 6 as a solid line. The good agreement with the experimental values indicates that the model of the process based on the equation of diffusion and adsorption corresponds to reality.

In Fig. 7, the interpretation of the process based on the dimensionless concentrations is presented. The symbols denote experimental values. The graph refers to the following values of parameters: $\text{Bi} = 0.46$ and $\alpha = 0.27$ which were determined for the conditions under which the experiments were conducted. For sufficiently long time lines corresponding to the concentrations converge to the value that refers to the equilibrium. The values of the concentrations for which the lines converge result from the relationship $\bar{Q} = \bar{Y} = \alpha/(1 + \alpha)$. Temporal variations of the concentration at the phase boundary $Y_1$ and the contribution (fraction $\chi$) of the mass transfer resistance in liquid to the overall resistance are also presented in the Figure. In the whole considered range of $\chi > 0.9$ it is clear that, for the considered system, the main mass transfer resistance is located in the liquid phase.
6. Conclusions

Using the approximate model of adsorption kinetics, one can easily determine the contribution of mass transfer resistance in the individual phases of a system. If one knows the dominant resistance, they can take the proper steps to intensify the adsorption process. For adsorption of a dye BR 200% on activated carbon of an average size 2 mm, the main
mass transfer resistance is located in a liquid phase. Therefore, the overall rate of the process can be increased by the intensification of flow of the liquid that contacts with adsorbent pellets.

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References