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ADSORPTION IN PERFECT MIXING TANK – COMPARISON OF EXACT AND APPROXIMATE KINETIC MODELS

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Periodic adsorption in a perfect mixing tank of a limited volume was considered. It was assumed that the adsorption rate is limited by diffusion resistance in a pellet. The approximate model of diffusion kinetics based on a continued fraction approximation was compared with the exact analytical solution. For the approximate model an algorithm was developed to determine a temporal variation of the adsorbate concentration in the pellet. The comparison was made for different values of the adsorbent load factor. In the numerical tests different shapes of pellets were considered. Both the numerical tests as well as our own experimental results showed that the approximate model provides results that are in good agreement with the exact solution. In the experimental part of this work adsorption of p-nitrophenol and acetic acid from aqueous solutions on cylindrical pellets of activated carbon was conducted.

Keywords: approximate kinetic equations, adsorption in vessel

1. INTRODUCTION

The adsorption rate is limited by the slowest step (steps) of a complex process which includes transport of adsorbate from the bulk of the liquid phase to the surface of an adsorbent pellet, diffusion in pellet macropores, diffusion in micropores, and the act of adsorption. In physical adsorption the final step is not generally dominant, and therefore the rate of adsorption is influenced mainly by the resistance caused by the transport of the adsorbate to the adsorption site. Kinetic relations describing the rate of adsorption that are based on the chemical reaction rate models such as the first or second order models (Haerifar and Azizian, 2013) are also known. A comparison of a kinetic model based on diffusion with the model based on a chemical reaction was published recently (Płaziński at al., 2013); the infinite slab-shaped and spherical adsorbent pellets were considered.

Partial differential equations with a space-coordinate and time as the independent variables constitute the exact model of the adsorption kinetics. Solving such a problem is time-consuming. The problem of the time-consuming solution is particularly important when the equations are repeatedly solved using a complex procedure. Simplification of the model can be achieved by eliminating the space-coordinate in the pellet and applying the so-called approximate kinetic equations, which have the form of ordinary differential equations.

There are many approximate kinetic equations. They are commonly used in modelling and design of adsorption processes. The most well-known approximate kinetic equation is the LDF equation

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(Glueckauf, 1955), which for adsorption in a spherical pellet and for the absence of external resistance has the form:

$$\frac{d\bar{q}_m}{dt} = 15\frac{D_s}{R^2}\left(q_m^* - \bar{q}_m\right) \tag{1}$$

This equation provides results which are quite consistent with the exact solution of the equation of diffusion and adsorption but only for sufficiently long duration of the process. The LDF equation fails for short times, which prevents its use for adsorption-desorption processes with short half-cycles. The approximate kinetic model based on a continued fraction approximation was recently presented by Lee and Kim (2011). Continued fractions are a useful tool in many approximation problems. This feature was used by these authors in their model. The model is based on the use of the Laplace transform for the equation of diffusion, bringing the solution to the form of a continued fraction, and cutting the resulting expression to the number of terms *n* that provides the required accuracy. As a result one must solve a system of *n* ordinary differential equations. Approximation of the first order ($n = 1$) corresponds to the LDF equation.

The Lee and Kim model was modified (Kupiec and Gwadera, 2013) in order to take into account not only the diffusion resistance in the pellet but also in the surrounding fluid. The modified approximate model of adsorption kinetics was compared with the exact solution for adsorption-desorption cycles and various shapes of pellets providing excellent agreement with the exact solution.

The aim of this study is to verify the approximate model based on continued fractions for adsorption in a limited volume tank for different shapes of adsorbent pellets. Numerical verification (comparison with the exact solution) and experimental verification were conducted. Systems with linear adsorption equilibrium and the absence of external mass transfer resistance were considered.

2. EXACT MODEL

It is convenient to introduce the diffusion and adsorption equation in a dimensionless form. The dimensionless adsorbate concentration in a pellet is defined as follows:

$$Q = \frac{q_m}{q_{m0}} \tag{2}$$

The average concentration is defined analogously:

$$\bar{Q} = \frac{\bar{q}_m}{q_{m0}} \tag{3}$$

Let us introduce the dimensionless space-coordinate:

$$\eta = \frac{x}{L} \tag{4}$$

and dimensionless time:

$$\tau = \frac{D_s t}{L^2} \tag{5}$$

The symbol *L* is a characteristic linear dimension (half the thickness of a slab, radius of a cylinder and sphere). The adsorption and diffusion equation has the form:

$$\frac{\partial Q}{\partial \tau} = \frac{\partial^2 Q}{\partial \eta^2} + \frac{\zeta}{\eta}\cdot\frac{\partial Q}{\partial \eta} \tag{6}$$

where ζ is a shape factor equal to 0, 1 or 2 for an infinite slab, infinite cylinder and sphere, respectively.

The initial condition for adsorbate-free pellets has the form:

$$\tau = 0 \quad Q = 0 \tag{7}$$

The first boundary condition concerns the symmetry of a pellet and takes the form:

$$\eta = 0; \quad \frac{\partial Q}{\partial \eta} = 0 \tag{8}$$

The form of the second boundary condition for pellet surface depends on the relationship between internal and external diffusion resistance. When the diffusion resistance outside pellets may be omitted, the condition has the form:

$$\eta = 1; \quad Q_1 = Q_1^* \tag{9}$$

which means that the dimensionless adsorbate concentration on the surface of a pellet is equal to the concentration in equilibrium to adsorbate concentration in the liquid phase.

A dimensionless concentration of adsorbate in the liquid phase is defined as follows:

$$Y = \frac{C}{C_0} \tag{10}$$

Since the equilibrium equation for linear adsorption has the form:

$$q_m^* = KC \tag{11}$$

and the concentration of adsorbate in a pellet being in equilibrium with the initial concentration in the liquid is:

$$q_{m0} = KC_0 \tag{12}$$

so after dividing both sides of the above equations by each other, one obtains:

$$Q^* = Y \tag{13}$$

Therefore, when the equilibrium is linear, then $Q_1^* = Y$ in the boundary condition (9). When the concentration in the liquid phase Y remains constant in time, then $Y = 1$ so $Q_1 = 1$. When the concentration in the liquid phase changes over time, the concentration at the surface of a pellet is also variable and less than unity. Then the model of the process should be supplemented by a balance equation for adsorbate in the liquid phase.

The average, dimensionless concentration of adsorbate in a pellet results from integration of a concentration profile. The formula for any pellet shape is as follows:

$$\overline{Q} = (\zeta + 1)\int_0^1 \eta^\zeta Q \, d\eta \tag{14}$$

3. ADSORPTION IN FINITE VOLUME TANK

In this work periodic adsorption in a finite-volume perfect-mixing tank is considered. Thus, during adsorption the concentration of adsorbate in the pellets increases, and in the liquid – decreases. In the case of the adsorbent pellets that initially do not contain adsorbate the mass balance for adsorption in a tank takes the form:

$$m_s \overline{q}_m = V\left(C_0 - C\right) \tag{15}$$

After introduction of the dimensionless variables, one obtains:

$$\overline{Q} = \alpha\left(1 - Y\right) \tag{16}$$

where the adsorbent load factor is given by the following formula:

$$\alpha = \frac{VC_0}{m_s q_{m0}} = \frac{V}{m_s K} \tag{17}$$

If adsorption time is long enough, the system reaches equilibrium and concentrations in both phases are not subject to further changes. Since, in accordance with (13), at equilibrium the dimensionless concentrations in both phases are the same, from combination of formulas (13) and (16) it follows that:

$$\lim_{\tau\to\infty} Y = \lim_{\tau\to\infty} \overline{Q} = \frac{\alpha}{1+\alpha} \tag{18}$$

The ratio of mass of adsorbed component at a given moment to the mass of adsorbed component at equilibrium amounts to:

$$\frac{m_t}{m_\infty} = \frac{\overline{Q}}{\lim\limits_{\tau\to\infty} \overline{Q}} = \frac{1+\alpha}{\alpha}\,\overline{Q} \tag{19}$$

Analytical solutions for the diffusion in pellets of different shapes in a finite-volume tank are known (Crank, 1956). They are presented in Appendix (A.1-A.4).

Taking into account formulas (16), (19) and (A.4), one can obtain:

$$Y = 1 - \frac{1}{1+\alpha}\left[1 - \sum_{i=1}^{\infty} \frac{2(1+\zeta)\alpha(1+\alpha)}{(1+\zeta)^2 + (1+\zeta)^2\alpha + \alpha^2\beta_i^2} \exp\left(-\beta_i^2\tau\right)\right] \tag{20}$$

The shorter the time, the series converge more slowly and more number of series terms should be included. However, solutions for short times that do not contain infinite series are known (Crank, 1956). They are presented in Appendix (A.5-A.7).

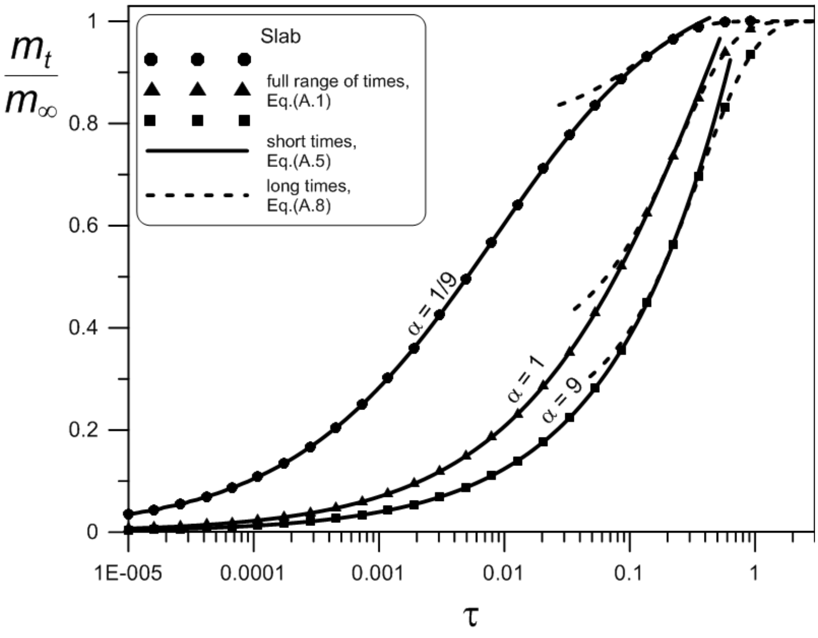

Fig. 1. Relationship between m_t/m_∞ and dimensionless time τ for slab

The consequence of reducing the necessary number of terms in the series with increasing τ is that only the first series term may be used for sufficiently long times (according to (A.4)). The appropriate relation for long times is presented in Appendix (A.8).

In Figs. 1, 2 and 3 the graphs of the relationship between m_t/m_∞ and dimensionless time for pellets of all the considered shapes were shown. On each of the graphs the results of solving the exact equation (A.4), the relationship for short periods of adsorption time ((A.5), (A.6) or (A.7)) and the relationship for long times (A.8) were presented. As can be seen, for each shape there are the maximum limit values of time above which the relationships for short times should not be used. Similarly, there are the minimum limits, below which the relationships for long periods of time lead to wrong results. These limit values are different for different shapes of pellets.

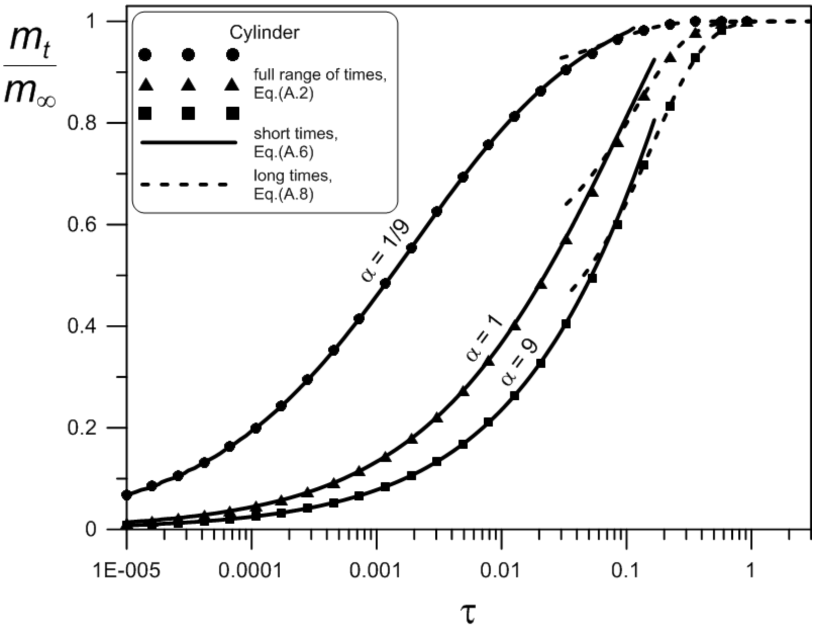

Fig. 2. Relationship between m_t/m_∞ and dimensionless time τ for cylinder

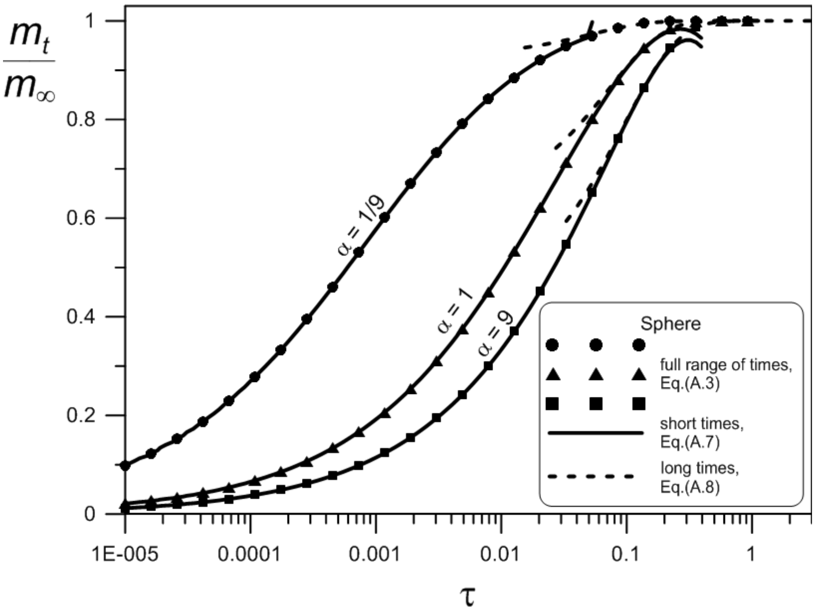

Fig. 3. Relationship between m_t/m_∞ and dimensionless time τ for sphere

4. APPROXIMATE KINETIC MODEL

In the approximate Lee and Kim model the average dimensionless concentration of an adsorbate in an adsorbent pellet after time τ is defined by the following equation (Lee and Kim, 2011):

$$\overline{Q} = \mathbf{qx} \tag{21}$$

where:

$$\mathbf{q} = \begin{bmatrix} q_1 & q_2 & \dots & q_n \end{bmatrix} \tag{22}$$

In order to determine the elements of the vector **x,** the following system of ordinary differential equations should be solved:

$$\dot{\mathbf{x}} = \mathbf{ax} + \mathbf{b}Q_1 \tag{23}$$

where the vectors $\dot{\mathbf{x}}$, **x** and **b** are defined as follows:

$$\dot{\mathbf{x}} = \begin{bmatrix} \dot{x}_1 & \dot{x}_2 & \dots & \dot{x}_n \end{bmatrix}^T \tag{24}$$

$$\mathbf{x} = \begin{bmatrix} x_1 & x_2 & \dots & x_n \end{bmatrix}^T \tag{25}$$

$$\mathbf{b} = \begin{bmatrix} \zeta + 1 & \zeta + 1 & \dots & \zeta + 1 \end{bmatrix}^T \tag{26}$$

and the elements of the matrix **a** are equal to:

$$a_{ij} = -p_i q_j \quad \text{for} \quad j > i \tag{27a}$$

$$a_{ij} = -p_j q_j \quad \text{for} \quad j < i \tag{27b}$$

$$a_{ij} = -p_i q_i \quad \text{for} \quad j = i \tag{27c}$$

where the values of p_i and q_i are defined as follows:

$$p_i = 2i^2 - i + \zeta i \tag{28}$$

$$q_i = 4i + \zeta - 1 \tag{29}$$

In the above formulas $i = 1, 2, \dots, n$.

The number of equations of system (23) is the order of approximation *n;* the higher the order, the higher the accuracy of approximation. The system of equations (23) should be solved with the initial condition which for a pellet that initially does not contain the adsorbate has the form:

$$\tau = 0; \;\; \mathbf{x} = 0 \tag{30}$$

Substituting $Q_1 = Y$ into (23) and considering Equation (16), one gets:

$$\dot{\mathbf{x}} = \mathbf{ax} + \mathbf{b}\left(1 - \frac{\overline{Q}}{\alpha}\right) \tag{31}$$

After transformations it was obtained that:

$$\dot{\mathbf{x}} = \mathbf{cx} + \mathbf{b} \tag{32}$$

where:

$$\mathbf{c} = \mathbf{a} - \frac{1}{\alpha}\mathbf{bq} \tag{33}$$

For an infinite volume of the tank it is α → ∞ so **c** = **a.**

The algorithm was as follows. Elements of the vectors **b**, **p**, **q,** matrix **a** and matrix **c** were determined for given values of α, ζ and n. Then the system of equations (32) was solved. Finally the function $\overline{Q}$ (τ) was obtained from formula (21).

5. NUMERICAL VERIFICATION OF APPROXIMATE KINETIC MODEL

In order to verify the approximate kinetic model numerically, calculations based on this model and the exact one have been conducted. Calculations were performed for different shapes of pellets and for different values of the adsorbent load factor. The calculation results are shown in Figs. 4-7. Dimensionless concentrations in both phases of the system are on the axis of ordinates. The decreasing curves define temporal variations of concentration in the liquid phase, and the increasing curves relate to the solid phase. In accordance with Equation (18), the curves converge for long times, which means that the system has reached the equilibrium. The values of the equilibrium concentrations depend on the parameter α, for example for $\alpha = 1$ equilibrium concentrations are (in accordance with (18)): $\lim\limits_{\tau\to\infty} Y = \lim\limits_{\tau\to\infty} \overline{Q} = 0.5$.

In Figs. 4, 5 and 6 adsorbate concentrations for a slab, cylinder and sphere were presented. Solid lines refer to the order of approximation $n = 10$, and dashed lines − to $n = 3$. It can be seen from the figures that for $n = 10$ the agreement between values calculated on the basis of the approximate and exact models is very good. Some deviations occur only for short times and small values of α; the differences are visible only for the liquid phase. In Fig. 7 temporal variations of concentrations for individual shapes of pellets and $\alpha = 1$ and $n = 10$ were shown. It should be remarked that in many cases much lower orders of approximation can be used e.g. for $\alpha > 1$ and $\tau > 0.01$ the third order approximation gives satisfactory results.

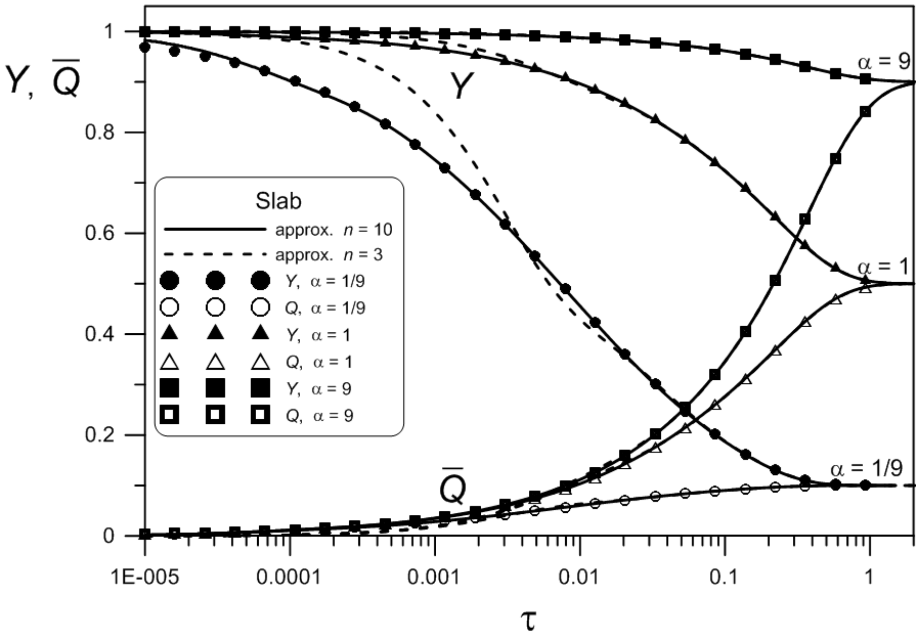

Fig. 4. Comparison of the graphs obtained for the approximate and exact models for the infinite slab

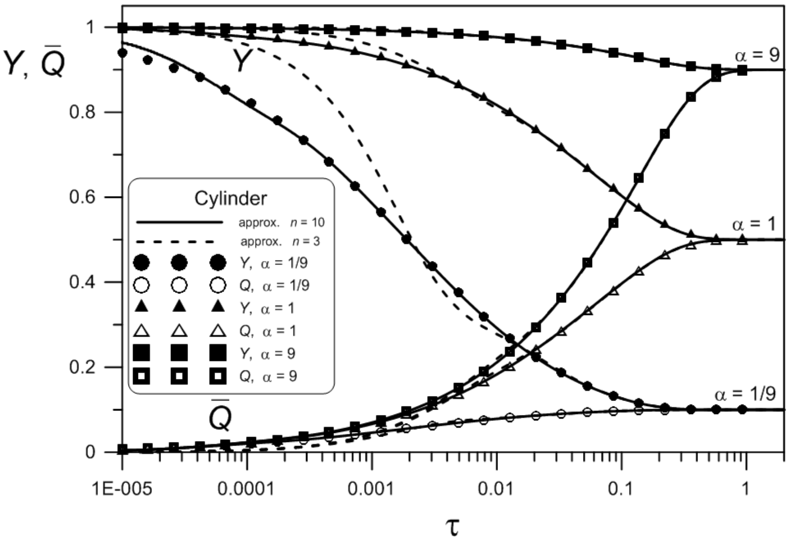

Fig. 5. Comparison of the graphs obtained for the approximate and exact models for the infinite cylinder

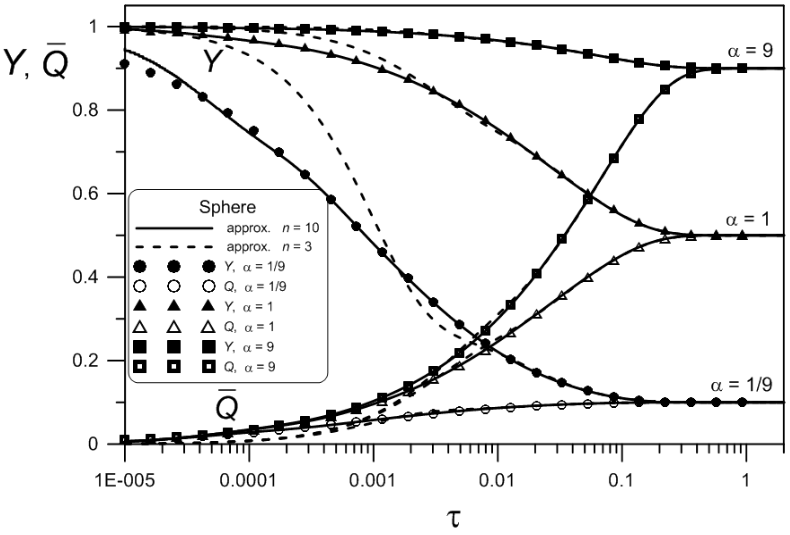

Fig. 6. Comparison of the graphs obtained for the approximate and exact models for the sphere

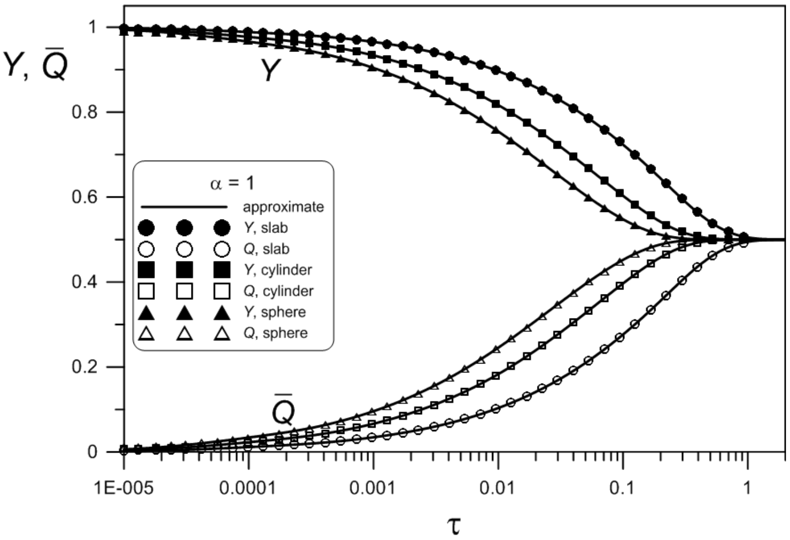

Fig. 7. Comparison of the graphs obtained on the basis of the approximate and exact models for different shapes of pellets

6. EXPERIMENTAL

Experimental studies of the kinetics of adsorption in a tank were conducted. Active carbon type Organosorb 10-CO (manufacturer Desotec) was used as an adsorbent. *p*-nitrophenol and acetic acid were adsorbed from aqueous solutions. The temperature was maintained at 23°C.

According to the adsorbent's manufacturer the physical properties of the adsorbent are as follows: apparent density of pellets 1058 kg/m^3, total pore volume 0.489 cm^3/g, average pore diameter 1.86 nm, volume fraction of micropores 74%. The adsorbent pellets were cylindrical. The radius of a pellet was 0.7 mm.

6.1. Adsorption of p-nitrophenol (PNP)

The concentration of PNP in an aqueous solution was determined using a spectrophotometer UV-VIS S2000 Miniature Fiber Optics (Ocean Optics) at a wavelength of 317 nm. PNP concentration range for which the measurements were conducted was 0.0123−0.0280 kg/m^3 (12.3−28.0 mg/dm^3). Calibration showed that the relationship between absorbance and concentration of the solution is linear in this range.

According to the literature (Chern and Chien, 2002) the adsorption equilibrium of PNP on activated carbon is linear if the PNP content is less than about 0.2 mol/m^3 (at 25°C). Therefore, one point on the equilibrium line is sufficient to determine the equilibrium relationship. The necessary measurements were conducted by contacting the PNP solution with activated carbon and determining concentration of PNP in both phases at equilibrium. The biphasic system was kept for 14 days at 23 °C and periodically mixed. Then, concentration of PNP in the solution was determined providing the result $C = 0.0280$ kg/m^3 ≈ 0.2 mol/m^3. Concentration of PNP in pellets was determined from the mass balance; the obtained values are sufficient to determine the adsorption equilibrium constant:

$$K = \frac{q_{m0}}{C_0} = \frac{0.452}{0.0280} = 16.3 \tag{34}$$

The kinetic measurements were conducted in a cylindrical glass tank with a magnetic stirrer. Pure *p*-nitrophenol class WSK (manufacturer POCh) was used to prepare the PNP solution. A sample weight of the substance was dissolved in distilled water. The resulting stock solution was used for preparation of dilute solutions. Before the current measurement, the sample weight of activated carbon was immersed in water to deaerate the adsorbent. The current measurement started by pouring the carbon to the PNP solution and starting the stirrer. The absorbance of the solution was determined at specified time intervals. During the measurements the temperature was maintained at 23°C. The measurements were performed for the volume of solution $V = 0.5\times10^{-3}$ m^3 and the adsorbent mass $m_s = 0.5\times10^{-3}$ kg. The adsorbent load factor was:

$$\alpha = \frac{V}{m_s K} = \frac{0.5\cdot10^{-3}}{0.5\cdot10^{-3}\cdot16.3} = 0.0615 \tag{35}$$

6.2. Adsorption of acetic acid

Concentration of acetic acid in aqueous solutions was determined by titration with 0.1 n NaOH solution in the presence of phenolphthalein. Automatic burette Titrette (manufacturer Brand, class A precision) was used.

The study of adsorption equilibrium was conducted in a similar manner as for the *p*-nitrophenol. The solutions of different concentrations were contacted with activated carbon for sufficiently long time at a constant temperature of 23°C. The content was mixed from time to time. After equilibrium had been reached, acid concentration in the solution was determined. The results led to the conclusion that for the acid content $C_0 = 0.3$ kg/m^3 the equilibrium concentration in the solid phase is $q_{m0} = 0.046$ kg/kg, and the equilibrium for $C < 0.3$ kg/m^3 is approximately linear. The equilibrium constant in this case is:

$$K = \frac{q_{m0}}{C_0} = \frac{0.046}{0.3} = 0.153 \tag{36}$$

To prepare solutions of acetic acid, glacial acetic acid was used (manufacturer POCh). It was diluted with distilled water. The current measurement of the adsorption kinetics was initiated by pouring the previously weighed and deaerated carbon into the tank containing a solution of acid that had the initial concentration of $C_0 = 0.3$ kg/m^3. At specific time intervals 5 cm^3 of the solution was pipetted from the tank for acid-base analysis which was performed almost on-line. After concentration of the solution had been measured, the acid solution of the same amount and concentration as the previously analysed solution was poured into the tank. During the measurements the temperature was maintained at 23°C. The measurements were performed for the volume of solution $V = 1\times10^{-3}$ m^3 and the adsorbent mass $m_s = 7\times10^{-3}$ kg. The adsorbent load factor was:

$$\alpha = \frac{V}{m_s K} = \frac{1\cdot10^{-3}}{7\cdot10^{-3}\cdot0.153} = 0.934 \tag{37}$$

7. DETERMINATION OF DIFFUSION COEFFICIENT IN ADSORBENT PELLETS

The results of kinetic measurements were used in order to determine values of diffusion coefficient in pellets of activated carbon. These coefficients were determined on the basis of the approximate kinetic model (based on continued fractions approximation) and with the exact model. It was assumed that D_s = const. during the series of measurements. The following algorithm was applied, in which $t_D = R^2/D_s$ was used as a conversion factor that allowed one to calculate dimensionless time on the basis of its dimensional value (formula (5)). The procedure of t_D determination was as follows:

- A trial value of t_D was assumed,
- Concentrations of adsorbate in the solution $C_{k,calc}$ were calculated for the value of time for which experimental values $C_{k,\exp}$ were known for the given series of measurements. An appropriate model of the process (approximate or exact) was used.
- The sum of squared deviations between the calculation (*calc*) and experimental values (*exp*) was calculated in accordance to the formula:

$$SS = \sum_{k=1}^{l}\left(C_{k,exp} - C_{k,calc}\right)^2 \tag{38}$$

where $k = 1, 2,\ldots, l$; l − number of measurements.

The value of diffusion time constant t_D for which SS was the smallest, was considered to be the estimated value of t_D for the considered series of measurements. The diffusion coefficient was determined according to the formula $D_s = R^2/t_D$ (for the known value of the radius of the pellet $R = 0.0007$ m).

The results of measurement for adsorption of acetic acid were shown in Fig.9 as shaded symbols. Fig. 8 illustrates the search for the solid diffusion coefficient of acetic acid in the pellets. The sum of squared deviations defined by formula (38) is located on the vertical axis of the graph; the calculated values $C_{k,\mathrm{calc}}$ were determined on the basis of the approximate model. After several iterations conducted for different values of D_s, the diffusion coefficient $D_s = 2.62\times10^{-12}$ m^2/s (corresponding to the minimum value SS) was found. The procedure was repeated but $C_{k,\mathrm{calc}}$ was calculated in accordance to the exact model. The same value of D_s as for the approximate model was obtained.

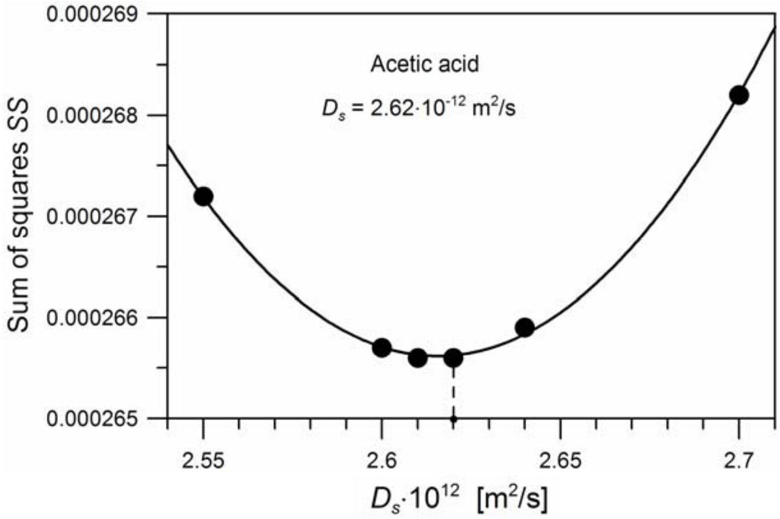

Fig. 8. Determination of the solid diffusion coefficient for acetic acid

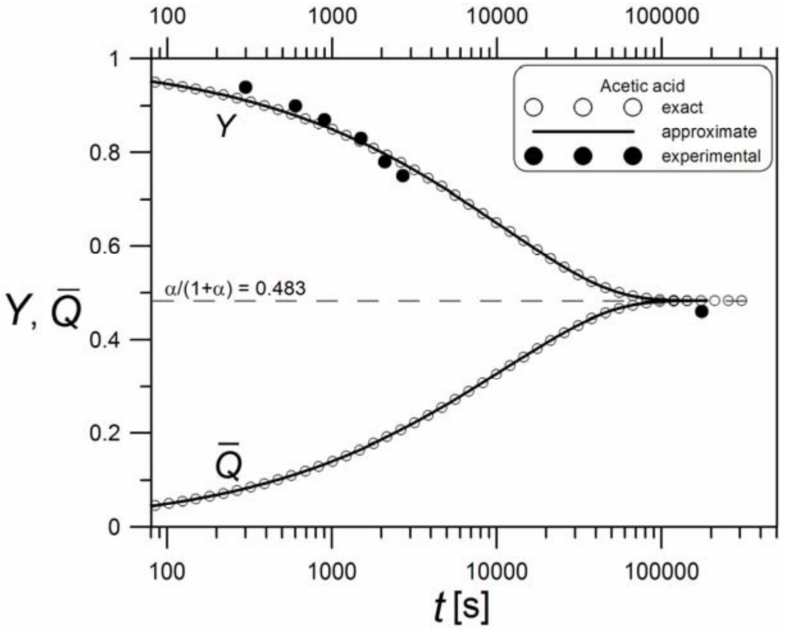

Fig. 9. Experimental and calculated courses of concentrations for adsorption of acetic acid on activated carbon in a tank with limited volume

For the value α = 0.934 numerical courses of the relationship between Y and τ and $\bar{Q}$ and τ, i.e. between the dimensionless concentrations and dimensionless time τ, were determined; for this purpose the approximate model was used. Then, as the value of D_s was known, the dimensionless time was recalculated into dimensional one in accordance with the relationship:

$$t = \frac{R^2}{D_s}\tau \tag{39}$$

The above calculations allowed construction of the graph plotted in Fig. 9, wherein the dimensional time is located on the horizontal axis. The figure shows that the dimensionless concentration in the liquid phase and in the pellets are close to each other and reach a state of equilibrium corresponding to, in lines with (18)), a value of 0.483. The experimental points are in good agreement with the solid line, which means that the estimated diffusion coefficient is well characterising the kinetics of the process. The calculation procedure is repeated to determine the time courses of Y and $\overline{Q}$ based on the exact model. The appropriate courses are also shown in Fig. 9 as not-shaded symbols. As can be seen, the courses corresponding to the approximate and exact models are identical.

Similar calculations were made with the use of the results obtained for the adsorption of PNP ($\alpha = 0.0615$). The results were shown as shaded symbols in Fig. 11. Fig. 10 presents the search for the solid diffusion coefficient: the value of D_s equal to 0.167×10^{-12} m^2/s is obtained with the approximate model.

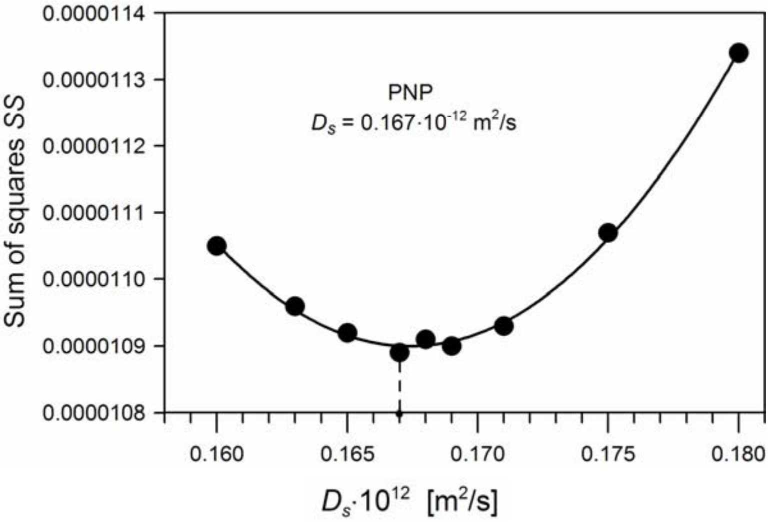

Fig. 10. Determination of solid diffusion coefficient for PNP

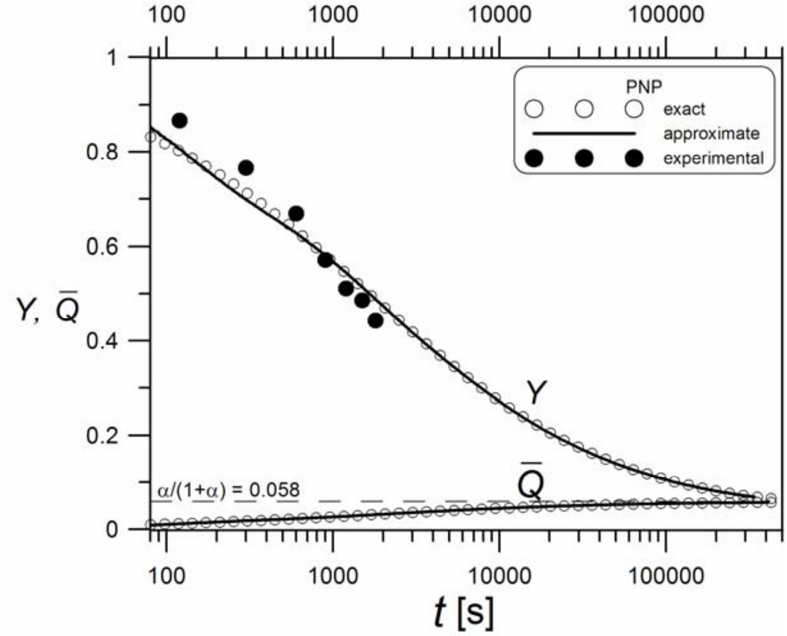

Fig. 11. Experimental and calculated courses of concentrations for adsorption of PNP on activated carbon in a tank with limited volume

In Fig.11, in addition to the experimental course of PNP concentration in the liquid phase, the calculated courses of concentrations in both phases were shown. The calculated approximate and exact courses match, but for the low concentrations slight variations were observed. This results in small differences of the estimated diffusion coefficients. The value of D_s obtained from the exact model was equal to 0.171×10^{-12} m^2/s. As stated in the numerical verification of the approximate model, a discrepancy in the courses occurs for short times and small α values. Precisely in this area the initial measurement points for the PNP adsorption are located. Due to the relatively high value of the equilibrium constant for PNP adsorption, the coefficient α is small resulting in a small increase of the adsorbate content in pellets and a significant decrease in the concentration of adsorbate in the liquid (Fig. 11). The dimensionless equilibrium concentration (Eq. (18)) is much lower (0.058) than that for the series of measurements with acetic acid (0.483).

8. CONCLUSIONS

- The model of adsorption kinetics based on the continued fractions approximation provides results consistent with the exact solution for periodic adsorption in a perfect mixing tank with a limited volume.
- The model has been successfully verified numerically for different pellet shapes and different values of the adsorbent load factor.
- The model was also verified experimentally for two different adsorption systems and various process conditions. Good agreement of the diffusion coefficient values determined from the approximate and the exact models was obtained.
- The approximate model is of crucial importance for investigating adsorption when analytical solution is not available.
- The use of the approximate kinetic equations significantly reduces the computation time in relation to the numerical calculations conducted when solving the exact model. In the approximate models ordinary differential equations (or systems of such equations) instead of equations with partial derivatives are solved. This is important when solving kinetic equations needs to be performed repeatedly in complex calculation procedures.

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SYMBOLS

C	adsorbate concentration in solution, kg/m^3
D_s	solid diffusion coefficient, m^2/s
$J_0(a)$	Bessel function of the first kind of order 0
$J_1(a)$	Bessel function of the first kind of order 1
K	adsorption equilibrium constant, m^3/kg
m_s	mass of adsorbent, kg
q_m	concentration of adsorbate in the solid, kg adsorbate/kg solid
q_{m0}	concentration in equilibrium to the initial concentration of adsorbate in liquid phase, kg adsorbate/kg solid
$\overline{q}_m$	concentration of adsorbate averaged over pellet volume, kg adsorbate/kg solid
Q	dimensionless adsorbate concentration in solid
L	characteristic geometric dimension of pellet, m
R	radius of pellet, m
t	time, s
V	volume of liquid solution, m^3

x	spatial coordinate, m
Y	dimensionless adsorbate concentration in liquid phase
α	adsorbent load factor
β_i	roots of algebraic equation
η	dimensionless spatial coordinate
τ	dimensionless time
ζ	geometric factor

Indexes

calc	calculation value
exp	experimental value
k	*k*-th measurement
0	initial value
1	pellet surface
‾	average value

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APPENDIX

Analytical solutions for the diffusion in pellets of different shapes in a finite-volume tank for full range of time are as follows. The solution for infinite slab-shaped pellets takes the form (Crank, 1956):

$$\frac{m_t}{m_\infty} = 1 - \sum_{i=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2\beta_i^2} exp\left(-\beta_i^2\tau\right) \tag{A.1}$$

where β_i are consecutive roots of the algebraic equation:

$$tan\,\beta + \alpha\beta = 0 \tag{A.1a}$$

The solution for infinite cylinder-shaped pellets is as follows (Crank, 1956):

$$\frac{m_t}{m_\infty} = 1 - \sum_{i=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2\beta_i^2}\, exp\left(-\beta_i^2\tau\right) \tag{A.2}$$

where β_i are consecutive roots of the algebraic equation:

$$\alpha\beta J_0(\beta) + 2J_1(\beta) = 0 \tag{A.2a}$$

A solution for spherical pellets is also known. It has the form (Crank, 1956; Do,1998; Petrus at al., 1998; Suzuki, 1990):

$$\frac{m_t}{m_\infty} = 1 - \sum_{i=1}^{\infty} \frac{6\alpha(1+\alpha)}{9+9\alpha+\alpha^2\beta_i^2}\, exp\left(-\beta_i^2\tau\right) \tag{A.3}$$

where β_i are consecutive roots of the algebraic equation:

$$tan\,\beta - \frac{3\beta}{3+\alpha\beta^2} = 0 \tag{A.3a}$$

The solutions for all the considered shapes can be written in the generalised form:

$$\frac{m_t}{m_\infty} = 1 - \sum_{i=1}^{\infty} \frac{2(1+\zeta)\alpha(1+\alpha)}{(1+\zeta)^2+(1+\zeta)^2\alpha+\alpha^2\beta_i^2}\, exp\left(-\beta_i^2\tau\right) \tag{A.4}$$

The solutions for short times have the following form (Crank, 1956). For an infinite slab:

$$\frac{m_t}{m_\infty} = (1+\alpha)\left[1 - exp\left(\frac{\tau}{\alpha^2}\right)\cdot erfc\left(\frac{\sqrt{\tau}}{\alpha}\right)\right] \tag{A.5}$$

For an infinite cylinder:

$$\frac{m_t}{m_\infty} = \frac{1+\alpha}{1+\frac{\alpha}{4}}\left\{1 - exp\left[4\left(1+\frac{\alpha}{4}\right)^2\frac{\tau}{\alpha^2}\right]\cdot erfc\left[2\left(1+\frac{\alpha}{4}\right)\frac{\sqrt{\tau}}{\alpha}\right]\right\} \tag{A.6}$$

For a sphere:

$$\frac{m_t}{m_\infty} = (1+\alpha)\left[1 - \frac{\gamma_1}{\gamma_1+\gamma_2}\cdot \mathrm{eerfc}\left(3\gamma_1\frac{\sqrt{\tau}}{\alpha}\right) - \frac{\gamma_2}{\gamma_1+\gamma_2}\cdot \mathrm{eerfc}\left(3\gamma_2\frac{\sqrt{\tau}}{\alpha}\right)\right] \tag{A.7}$$

$$\gamma_1 = \frac{1}{2}\left(\sqrt{1+\frac{4}{3}\alpha}+1\right) \tag{A.7a}$$

$$\gamma_2 = \gamma_1 - 1 \tag{A.7b}$$

$$\mathrm{eerfc}(z) = \exp\left(z^2\right)\cdot \mathrm{erfc}(z) \tag{A.7c}$$

The following relation is valid for long times and all the considered shapes**:**

$$\frac{m_t}{m_\infty} = 1 - \frac{2(1+\zeta)\alpha(1+\alpha)}{(1+\zeta)^2+(1+\zeta)^2\alpha+\alpha^2\beta_1^2}\exp\left(-\beta_1^2\tau\right) \tag{A.8}$$

where β_1 is the first root of equations (A.1a), (A.2a) or (A.3a) depending on the pellet shape.