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External film control of the fixed bed adsorption

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Abstract

When the process of adsorption on the fixed bed of activated carbon is used to minimize the content of pollutants in a stream, e.g. in the technology of water treatment and renovation, the shape of the initial segment of the break-through curve of the so-called low concentration region is important. Usually, it is assumed that in this region the mass transfer is dominated by external film diffusion. The paper presents a theoretical analysis and experimental verification of this assumption. It was concluded that in the low concentration range, the process was determined by equilibrium parameters of the adsorption system and external mass transfer characterized by the intraparticle diffusion coefficient. Results of experimental investigations of phenol, *p*-nitrophenol and benzoic acid adsorption from aqueous solutions on a fixed bed of activated carbon AG-5 are presented. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fixed bed adsorption; Mass transfer in adsorption; Break-through curve; Activated carbon; Period of the bed protection

1. Introduction

Adsorption from water on a fixed bed of activated carbon is a process of unsteady-state mass transfer between the liquid and solid phase. The concentration of adsorbed substance in both phases is the function of both time and location in the bed. The general mathematical model of process dynamics contains mass balance equations for the adsorbate and equilibrium and adsorption kinetics equations. For a complete description a complex differential calculus and knowledge of various parameters that characterize the process and adsorption system are required [1].

To simplify solution of the problem some assumptions are taken, for instance for the needs of technological systems design and control with the use of adsorption. It is very important to determine the allowable range and conditions in which they can be used and to verify them experimentally.

One of the important applications of adsorption is the technology of water treatment and renovation. This process is applied to remove soluble organic compounds which are noxious even in trace amounts. Also in the wastewater treatment cycle, adsorption enables water recovery and closing of water-sewage cycles. In each case the initial concentration of pollutants is reduced earlier by other methods, and the aim of adsorption is to remove the remaining components and their further minimization.

When the process is carried out in a fixed-bed column, a number of assumptions are taken which are mostly in agreement with reality. One-component of the stream is absorbed. The stream moves in one direction at a constant velocity and its viscosity and density remain the same despite changing composition. The process is performed up to the moment when the concentration of adsorbed component in the effluent is lower than the value assumed as an allowable level of stream pollution. This moment is defined as a break through of the bed which loses its protective capabilities and requires regeneration. Usually, this concentration, i.e. the so-called break-through concentration, is very small, of the order of 1–5% as compared to the concentration in the inlet stream.

Thus, the main design parameter is the break-through time of a bed of defined height. In a previous study [2] a method for determination of protective time of the bed of sorbent for relative low concentrations of substance removed from a single-component solution was proposed. The next study [3] showed the application of this method to estimate working time of the bed through which a binary solution flows. This method was verified in model the adsorption systems obtaining very good agreement of experimental and calculated results (the error did not exceed 10%).

In the method described, an initial segment of the break-through curve was separated. This segment is formed in the bed during the residence time and then moves at constant velocity along the layer. In this region the adsorbent is free

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from adsorbate and reveals infinitely high absorptivity. Mass transfer resistance in the solid is negligibly small and the general process rate is determined by external diffusion. A driving force of the process is the difference of concentrations of the liquid on the interface and in the stream bulk. Each adsorbate portion which reaches the surface is immediately transported into the granule because of high absorptivity of the adsorbent. On the interface the adsorbate concentration is close to zero.

The output curve in the low concentration region (LCR) is described by the equation

$$\ln\frac{c}{c_0}=\frac{\beta_\mathrm{L}\cdot c_0\cdot\epsilon}{q_0\cdot\rho_\mathrm{n}}t-\frac{\beta_\mathrm{L}}{v}\cdot h \tag{1}$$

In the description of the method the notion of ''the range of low break-through curve concentrations'' was used. This range was assumed arbitrarily as the concentration range of the effluent from the column equal 5% of the inlet concentration. In order to apply the method to a greater extent the following questions should be answered:

- is it possible to determine the upper limit of the low concentration range without undertaking experimental investigations of column adsorption?
- on what does the upper limit of this range depend?

2. Theoretical

Mass transfer during isothermal adsorption in a fixed bed, at negligible axial and radial diffusion, can be described by the following system of equations:

⇒mass balance for process dynamics:

$$\epsilon\left(\frac{\partial c}{\partial t}\right)_h+v\left(\frac{\partial c}{\partial h}\right)_t+\rho_\mathrm{n}\left(\frac{\partial\bar{q}}{\partial t}\right)_h=0 \tag{2}$$

with initial and boundary conditions

for t=0 and h=0, c=c_0;

for t=0 and h>0, c=0 and q=0

⇒process kinetic equation

$$\frac{\partial q}{\partial t}=\Phi(C,q,R) \tag{3}$$

with respective boundary conditions

⇒process equilibrium

$$q=f(c)_T \tag{4}$$

Mass accumulation in the adsorbent depends on the adsorbate penetration rate inside the particles. Two processes are identified:

- diffusion in the liquid phase which fills in sorbent pores; the diffusion is characterized by diffusion coefficients in the pores,
- diffusion in the phase adsorbed on the pore surface, determined by the surface diffusion coefficient.

The participation of these processes in mass transfer inside particles depends on the adsorbing system, process parameters and adsorbent saturation. In a mathematical description of the process rate the effective coefficient of intraparticle diffusion is used. It reflects the effect of either both processes of intraparticle mass transfer or only one of them – this which is more resistant to diffusional mass transfer.

In the case of adsorption of organic compounds from aqueous solutions on activated carbons of advanced microporous structure, the intraparticle diffusion is connected first of all with migration of the adsorbate in the adsorbed state [4]. The hydrophobic surface of carbon adsorbents reacts slightly with hydrophilic water particles. Active centres on the surface are not blocked by the solvent which facilitates diffusion of adsorbate particles [5,6].

At a predominating effect of surface diffusion the adsorption rate (Eq. (3)) has the following form

$$\frac{\partial q}{\partial t}=D_\mathrm{s}\left(\frac{\partial^2 q}{\partial r^2}+\frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{5}$$

at the initial conditions

where $t=0,\ C=0,\ q=0$

at the boundary conditions inside the particle

for $r=0,\quad \dfrac{\partial C}{\partial r}=0;\ \dfrac{\partial q}{\partial r}=0$

and on the particle surface

$$\text{for } r=R,\quad \beta_\mathrm{L}(c-c_\mathrm{s})=\frac{\rho_\mathrm{n}}{\epsilon}D_\mathrm{s}\left(\frac{\partial q}{\partial r}\right)_{r=R}. \tag{6}$$

When the bed of adsorbent is long enough to create conditions for a pseudo-steady-state mass transfer, and at a good sorptional affinity of the absorbed substance to the adsorbent surface, a simple method of Glueckauf and Coates [7] is often used. The model refers to the linear driving force of the process inside the particle. Thus, accumulation in the particle can be described by the equation

$$\frac{\partial\bar{q}}{\partial t}=\frac{15D_\mathrm{s}}{R^2}(q_i-\bar{q}). \tag{7}$$

A discussion on validity of the LDF model presented in study [8] limits its applicability to the case when intraparticle mass transfer is controlled just by the surface diffusion. Mass transfer in the external film is determined as follows:

$$\frac{\partial\bar{q}}{\partial t}=\beta_\mathrm{L}\frac{\epsilon}{\rho_\mathrm{n}}(c-c_i) \tag{8}$$

The ratio of mass transfer units on the liquid and solid phases defines the Biot number in the form:

$$Bi=\frac{\beta_\mathrm{L}\cdot R^2}{D_\mathrm{s}\cdot K} \tag{9}$$

where parameter K is determined as:

$$K=\frac{q_0\cdot\rho_n}{c_0\cdot\epsilon} \tag{10}$$

Introducing the dimensionless concentrations in both phases:

$$X=\frac{c}{c_0},\ Y=\frac{q}{q_0}$$

we obtain

$$\frac{15}{Bi}[Y_i-Y]=X-X_i \tag{11}$$

If the break-through curve retains its shape and as Y and X have the same limits (viz. 0 and 1), for a constant pattern it follows that $X=Y$. We obtain the relationship:

$$\frac{15}{Bi}[Y_i(X_i)-X]=X-X_i \tag{12}$$

On the basis of Eq. (12) we can state that X_i depends on the concentration of the liquid phase, Biot number and adsorption equilibrium of the system, i.e. on the isotherm. An approximated solution of this equation assuming a Freundlich-type isotherm was given elsewhere [9]:

$$q=K_F\cdot c^n \tag{13}$$

with a hypothetical exponent $n=0.15$. Its other value or another type of isotherm, e.g. Langmuir's:

$$q=\frac{q_m\cdot b\cdot c}{1+b\cdot c} \tag{14}$$

would yield a different solution. Thus, it is better to keep the present form of this equation and to analyze it for a given isotherm basing on a graphical solution.

The analysis of relation $X-X_i=f(X)$ from Eq. (12) will allow us to identify the concentration region for which this approximation with a definite error is possible.

3. Experimental

Studies on adsorption from diluted, one-component aqueous solutions of *p*-nitrophenol (NP), phenol (P) and benzoic acid (BA) were carried out. The concentration of adsorbates in the solution was determined by a UV-spectrophotometric method. The adsorbent was a Polish activated carbon type AG5 whose parameters are given in Table 1. This is the product of carbonization of hard coal and is characterized by very good sorptional properties, developed microporous structure and good mechanical strength.

To identify sorption equilibrium, the isotherms were determined by the static method. A constant solution volume to carbon mass ratio was preserved changing the initial concentration of the solution in subsequent runs.

The kinetic study aiming at the determination of the effective coefficient of surface diffusion was performed in a mixer at the impeller speed which eliminated the effect of external diffusion. The experimental rig and methods of kinetic measurements were described elsewhere [6].

Adsorption dynamics was investigated under isothermal conditions in a column 3.5 cm in diameter, filled with a fixed bed of 100 g adsorbent. The initial concentration of solutions was constant and equal to about 2 moles/m^3. Three different flow rates of the solution were used: 1.125, 2.25 and 4.5 dm^3/h.

The concentration of effluent samples (sampling time 2 min) taken automatically every 757 s was analyzed. The change of effluent concentration in time in a broad spectrum of relative concentrations 10^{-4} to 1 relative to the inlet concentration was reported. Experimental parameters of dynamic measurements are given in the first part of Table 2.

4. Results and discussion

Adsorption equilibrium of the tested systems was described by sorption isotherms of Freundlich and Langmuir (Eq. (13) and Eq. (14)). Parameters of these equations, correlation coefficients and concentrations analyzed are given in Table 3. It follows from this table that for the experimental systems being tested a better correlation proves to be the Langmuir-type isotherm equation. To calculate coefficient K defined by Eq. (10), concentrations q_0 corresponding to concentrations c_0 were read out from experimental adsorption isotherms. The values of q_0 for the tested systems are given in Table 2.

The effective coefficients of surface diffusion D_s were obtained from kinetic measurements in a mixer. The kinetic curve illustrating the degree of adsorbent saturation as a function of process duration was determined experimentally. Then, it was compared with a theoretical curve obtained from the numerical solution of Eq. (5) at adequate boundary conditions. As kinetic investigations were carried out at a constant volume of the solution, the initial condi-

Table 1
Parameters of activated carbon type AG5

Apparent density ρ (kg/m^3)	Average bulk density ρ_n (kg/m^3)	Surface area of packing a (m^2/m^3)	Equivalent particle radius R (m)	Bed porosity ϵ (–)[a]
680	416	1500	5.2×10^{-4}	0.39

[a] Dimensionless.

Table 2
Experimental and calculated parameters of adsorption dynamics

Run number	Adsorbate	Linear apparent velocity $v \times 10^3$ (m/s)	Initial concentration c_0 (kg/m^3)	Equilibrium concentration in solid phase q_0 (kg/kg)	Effective surface diffusion coefficient $D_s \times 10^{12}$ (m^2/s)	Kinetic coefficient of external diffusion β_L (s^{-1})	Biot number Bi (–)[a]
1	NP	0.83				0.125	7.30
2		1.70	0.310	0.235	5.74	0.160	9.34
3		3.30				0.223	13.02
4	BA	0.83				0.0707	4.22
5		1.70	0.244	0.166	6.238	0.130	7.76
6		3.30				0.170	10.15
7	P	0.83				0.0694	4.86
8		1.70	0.188	0.110	6.141	0.119	8.33
9		3.30				0.239	16.73

Notation: NP – *p*-nitrophenol, BA – benzoic acid, P – phenol.
[a] Dimensionless.

tions are set up as follows:

for $t = 0,\ c = 0,\ q = 0,\ c_L = c_0.$

The boundary conditions describe mass transfer in the adsorbent granule:

for $r = 0,\ \dfrac{\partial c}{\partial r} = 0$

and on the external surface of the granule:

for $r = R,\ c = c_L.$

When main diffusion resistance is related to surface diffusion, the relationship of the concentration in the granules and in the liquid bulk, has the form:

$$-V_L \frac{dc_L}{dt} = \rho_p A_S D_S \left(\frac{\partial c}{\partial r}\right) \text{ dla } r = R. \qquad (15)$$

In the analysis of process dynamics experimental break-through curves obtained for each adsorption system are presented in the dimensionless system $X = c/c_0$, t/t_{st}. The value t_{st} was calculated as a coordinate of the centre of gravity in the graphical dependence of relative concentration of the effluent on time. The curves obtained at various liquid flow velocities are non-symmetrical, have different slopes and approximately common point of inflexion. Fig. 1 illustrates an exemplary system of break-through curves for *p*-nitrophenol adsorption at three flow rates of water phase through the fixed bed.

All experimental curves presented in the semi-logarithmic system are characterized by a linear initial segment, which can be described by Eq. (1). The external diffusion kinetic coefficients β_L were determined from this equation. The values are given in Table 2. This coefficient can be calculated independently from dimensionless equations for a laminar flow of liquid through the packing layer. It can be also determined experimentally on the so-called thin bed from the constant solution volume maintaining the same hydrodynamic conditions.

In Fig. 2 examples of experimental break-through curves for *p*-nitrophenol-water-AG5 carbon system are shown. For all adsorption systems tested, a so-called region of low concentrations can be identified which is a next verification of Eq. (1). The deviation of output curves from the lines presented in the semi-logarithmic system determines the upper range of concentrations. This value is different for individual sorption systems and changes with a change in the solution flow velocity through the bed.

For each measurement the Biot number defined by Eq. (9) was calculated and the results are given in Table 2. Data from Table 2 were used to draw graphs which illustrate the dependence of $X - X_i$ on X for various adsorption systems, isotherm equations and different values of the Biot number. The effect of adsorbate type is shown in Fig. 3 drawn for two Biot numbers 4 and 16. It is interesting to observe the initial range of the curves in which $X - X_i \cong X$ can be assumed, and accordingly the concentration difference in Eq. (8) can be substituted by a variable representing the

Table 3
Experimental values of parameters of isotherm equations on activated carbon for different adsorbates

Adsorbate	Concentration range c (kg/m^3)	Freundlich isotherm (Eq. (13))			Langmuir isotherm (Eq. (14))		
		K_F	n	r	a_m	b	r
NP	0.74	0.274	0.150	0.9822	0.253	61.7	0.9972
BA	1.3	0.203	0.151	0.9764	0.183	48.9	0.9988
P	0.96	0.140	0.172	0.9762	0.141	23.0	0.9992

Notation: NP – *p*-nitrophenol, BA – benzoic acid, P – phenol.

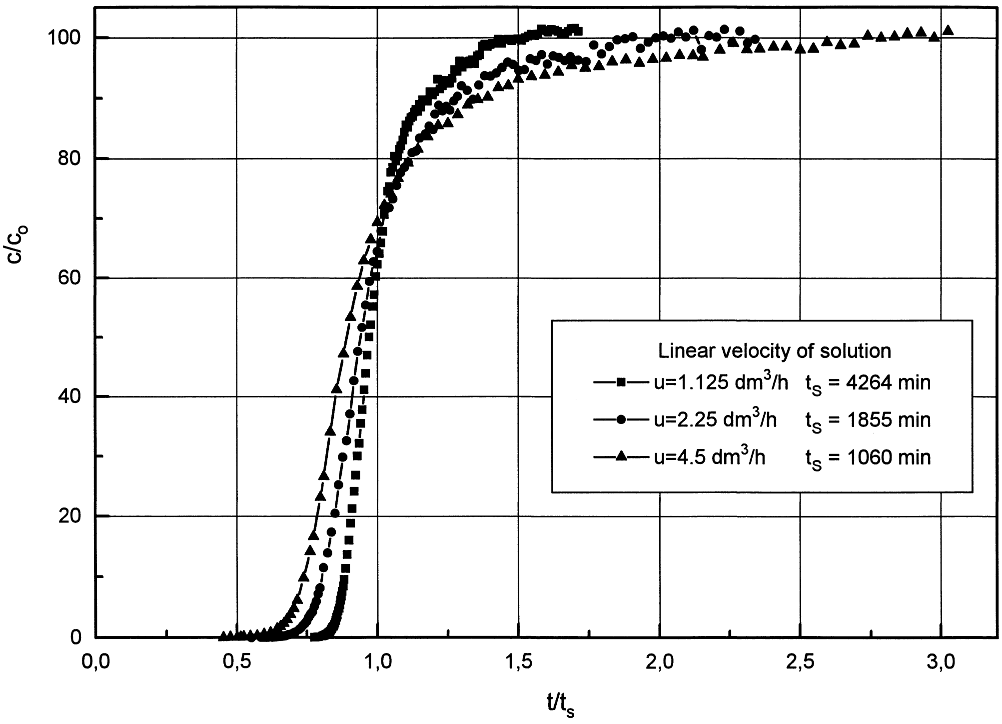

Fig. 1. Break-through curve for *p*-nitrophenol-water-activated carbon AG5 system at different solution flow velocities.

actual concentration in the liquid phase which corresponds to the low-concentration region. This concentration range depends on the adsorbate affinity to sorbent surface and thus the biggest one is for *p*-nitrophenol, while smaller for benzoic acid. It depends strongly on the value of *Bi*. Hence, for $Bi=4$ for both sorbents mentioned above the LCR can be defined for $X \leq 0.1$, while for $Bi=16$ only for *p*-nitrophenol. For phenol it is observed that LCR is impossible to identify in the scale in which the discussed graph is drawn.

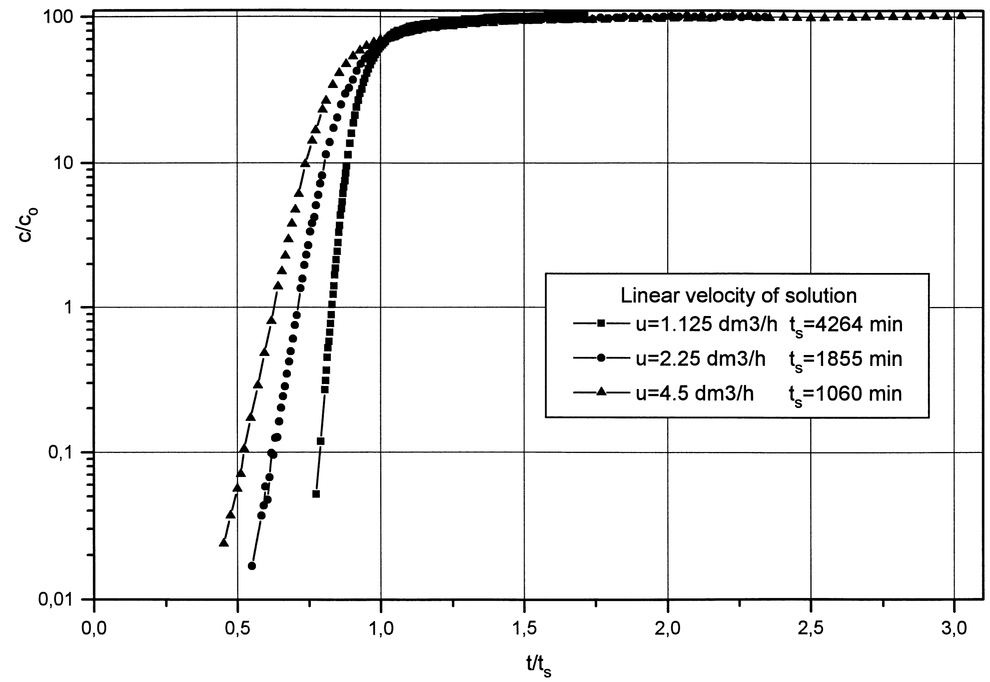

Fig. 2. Break-through curve for *p*-nitrophenol-water-activated carbon AG5 system at different solution flow velocities.

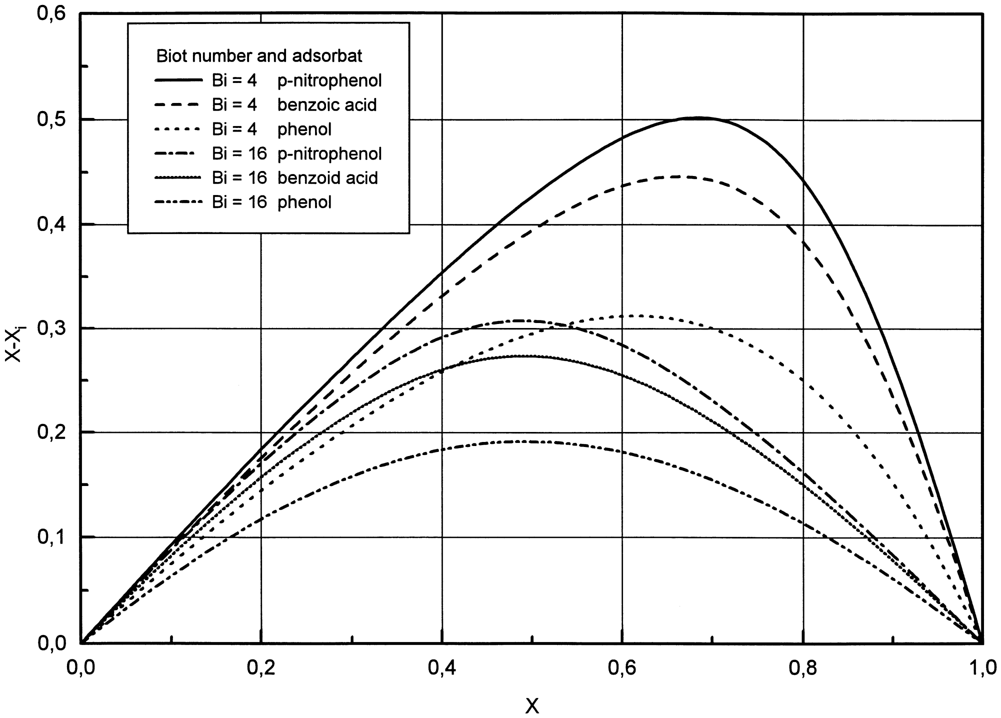

Fig. 3. Relation between dimensionless fluid-phase concentration driving force and dimensionless bulk liquid-phase concentration for Langmuir-type isotherm.

Therefore, for low X_i, when the Biot number is small, the intraparticle diffusion is fast and the influence of mass transfer resistance between the liquid and solid phase decreases. This causes an increase in LCR in which a parameter controlling the mass transfer is the external film.

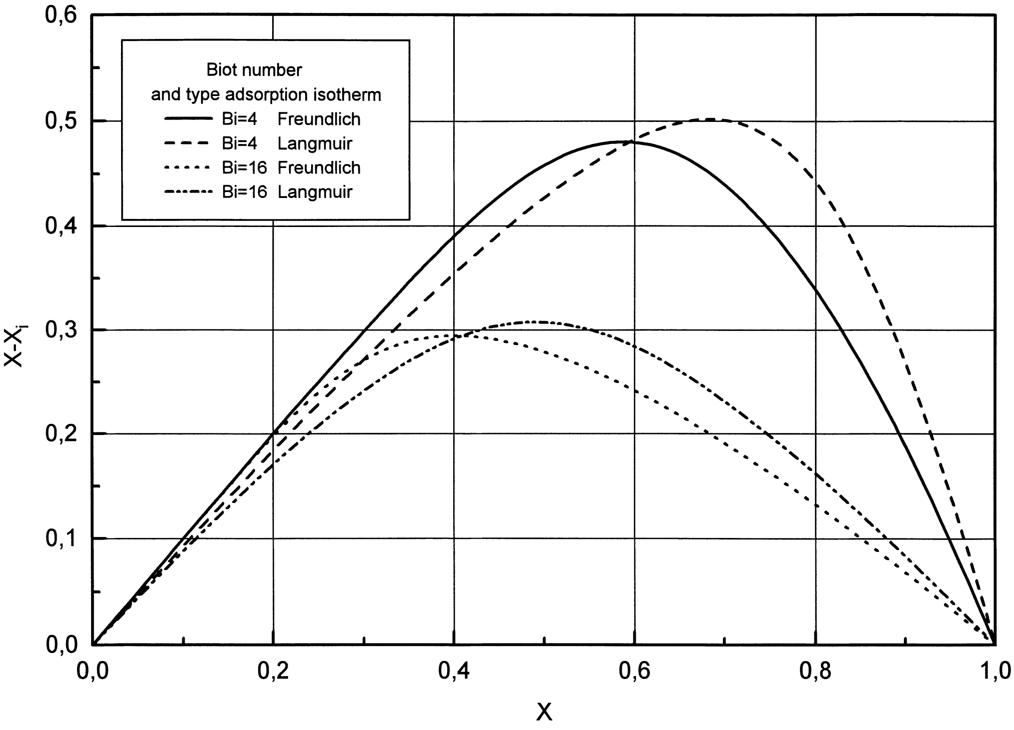

Fig. 4. Relation between dimensionless fluid-phase concentration driving force and dimensionless bulk liquid-phase concentration for p-nitrophenol-water-activated carbon AG5 system described by Freundlich-type and Langmuir-type isotherms.

Table 4
Comparison of the range of low-concentration regions, expressed as relative concentrations for experimental output curves and theoretical calculations

Adsorbate	Run number	LCR_e	LCR_F	LCR_L
NP	1	0.20	0.40	0.19
	2	0.18	0.35	0.15
	3	0.11	0.29	0.09
BA	4	0.18	0.32	0.17
	5	0.15	0.27	0.14
	6	0.12	0.25	0.13
P	7	0.03	0.38	0.04
	8	0.04	0.25	0.02
	9	0.01	0.2	–

NP – *p*-nitrophenol, BA – benzoic acid, P – phenol. LCR – low-concentration region.
Subscripts: e – determined from the experimental breakthrough curve, F – calculated for Freundlich-type isotherm, L – calculated for Langmuir-type isotherm.

The influence of the Biot number on $X-X_i$ was discussed for a Langmuir isotherm. To check if the type of isotherm equation affects the LCR, curves $X-X_i=f(X)$ were compared for an experimental adsorption system whose equilibrium was described by Langmuir and Freundlich isotherms. An example is Fig. 4 for *p*-nitrophenol. For the Freundlich-type isotherm for all adsorbates LCRs can be defined for $X\leq 0.2$, which was impossible for Langmuir-type isotherms – as followed from previous analyses. Thus, the possibility of defining LCR and using simplifications resulting from Eq. (1) would depend on the choice of equation to describe adsorption system equilibrium.

Experimental verification finally decides whether LCR can or cannot be defined. In the verification the series of dynamic measurements described earlier was used. Table 4 gives the LCR_e determined from the initial linear segments of output curves in the semi-logarithmic system (e.g. Fig. 2) and the one determined with a 5% error from relation $X=f(X_i)$, from which a graphic relation $X-X_i$, X was made, for the same *Bi* number for Freundlich-type (LCR_F) and Langmuir-type (LCR_L) isotherm. The Langmuir-type isotherm equation is a better approximation of experimental equilibrium data for all tested sorption systems. A method for determination of the equation parameters takes into account the lowest concentrations and not just these which are included in the LCR.

5. Conclusions

Irrespective of the isotherm shape, in the typical range of Biot number there is always a low relative concentration range X, when $X_i\cong 0$. In this range, the external film process controls mass transfer. If the allowable adsorbate concentration in the effluent from the fixed bed of adsorbent is within this range, the break-through curve can be described by Eq. (1). The time of protective action of the bed can be calculated if the equilibrium (isotherm) curve parameters and the kinetic coefficient of external diffusion are known.

On the basis of a simple mathematical analysis it was proved why the relative concentration X vs. time for small values of X depends only on kinetic coefficient β_L and not on the effective inner diffusion coefficient D_s.

Because $X_i\cong 0$ at low value of X, regardless of the value of D_s, the external film β_L parameter must control the mass transfer rate. Under conditions when $X\cong 0$ and $X_i\cong 0$, D_s has no effect on the fluid-phase driving. It should be stressed that, even when $X_i\cong 0$, the concentration Y_i can be quite substantial and significant concentration profile does exist in the particle phase. The validity of the assumptions made in this case depends on external diffusion kinetics of the process and can be determined as a function of the Biot number and isotherm constants which describe the system equilibrium for LCR in the best way.

6. Nomenclature

a	external surface area of adsorbent on a volume base (m^2/m^3)
A_s	area of the external surface of adsorbent granule (m^2)
c	solute concentration in liquid phase (kg adsorbate/m^3)
C	adsorbate concentration in solution inside the particle (kg adsorbate/m^3)
D_s	effective surface diffusion coefficient (m^2/s)
h	axial distance from the bed inlet (m)
K	parameter defined by Eq. (10) (dimensionless)
q	adsorbate loading (kg adsorbate/kg adsorbent)
r	radial position within particle (m)
R	equivalent radius of particle (m)
t	time (s)
t_{st}	stoichiometric time (s)
v	apparent linear velocity of liquid (m/s)
V_L	volume of adsorbate solution in the mixer (m^3)
X	dimensionless concentration in liquid phase (–)
Y	dimensionless concentration in particle phase (–)
Bi	Biot number (dimensionless)
β_L	kinetic coefficient of the external mass transfer (1/s)
ϵ	void fraction in the fixed bed (bed porosity) (dimensionless)
ρ_n	bulk density of the bed (kg/m^3)
ρ_p	adsorbent apparent density (kg/m^3)

Subscript and superscript

o	concentrations corresponding to feed conditions
s	concentrations at the fluid/solid interface

–	concentrations average over the particle
i	concentrations equilibrium

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