



On the optimization of the solid core radius of superficially porous particles for finite adsorption rate

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ABSTRACT

Packed chromatographic columns with the superficially porous particles (porous shell particles) guarantee higher efficiency. The theoretical equation of the Height Equivalent to a Theoretical Plate (HETP), for columns packed with spherical superficially porous particles, was used for the analysis of the column efficiency for finite rate of adsorption–desorption process. The HETP equation was calculated by the application of the moment analysis to elution peaks evaluated with the General Rate (GR) model. The optimal solid core radius for maximum column efficiency was estimated for a wide spectrum of internal and external mass transfer resistances, adsorption kinetic rate and axial dispersion. The separation power of the shell adsorbent for two component mixture, in analytical and preparative chromatography, was discussed. The conditions of the equivalence between the solutions of the General Rate model with slow adsorption kinetic and the Lumped Kinetic Model (LKM) or the Equilibrium Dispersive (ED) model were formulated.

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1. Introduction

In recent years the chromatographic columns technology was evolving in the direction of the use of smaller and smaller adsorbent particles. The reduction of the size of adsorbent causes the decrease of mass transfer resistances and increases the column efficiency. Further, reduction of mass transfer resistances and increase of the column efficiency was possible with introduction of superficially porous particles [1–4].

The performance of chromatographic columns, filled with different adsorbents, is conveniently compared on the basis of the values of their HETP. The theoretical equation of the HETP for columns packed with spherical particles was developed by Kucera and Kubin by application of the moment analysis to elution peaks calculated with the General Rate (GR) model [5–7].

Moulijn et al. [8] extended the Kubin–Kucera model by incorporating surface migration to the GR model.

The moment analysis was used recently for developing a plate height equation for monolith columns [9].

All these equations were obtained for the totally porous adsorbent and a finite adsorption–desorption rate process. For the shell adsorbent the theoretical equation of the HETP for instantaneous adsorption–desorption was presented in [10].

This model was next extended to shell adsorbent with finite rate of adsorption process by Li et al. [11].

The efficiency of the chromatographic column filled with a shell adsorbent, for an infinite adsorption rate, was investigated theoretically in [10,12]. It was proven that the highest efficiency can be obtained for shell thickness decreasing to zero. The more important measure of a chromatographic separation power is the resolution of components. Horváth et al. [12] has shown that the optimal shell thickness should be finite to guarantee a maximum resolution. The same conclusion was obtained analyzing maximum column productivity [10] for preparative separation.

Li et al. [11] has optimized the value of inert core radius for finite adsorption rate and linear adsorption isotherm. However, the optimization was restricted for minimizing HETP for capacity factors much higher than 1.

In the most of the papers devoted to chromatographic separation it was assumed that adsorption process is infinitely fast. However, in some cases adsorption rate is finite or it is convenient to assume that the effective adsorption rate is finite.

The group of Rodrigues has modeled the separation of proteins considering finite adsorption–desorption process [13–15].

Rizzi [16] reported two types of binding sites for microcrystalline cellulose triacetate that differ in their rates of adsorption and desorption. According to his model, one type of a sorption site is easily accessible, while the other site is sterically hindered.

Grebeyhannes and McGuffin [17] studied the separation of coumarin solutes on tris-(3,5-dimethylphenyl carbamate)

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amylose in the polar-organic mode. They have found that the adsorption–desorption rate is finite and that the rate of adsorption is always greater than the rate of desorption. The adsorption–desorption rates were found in interval between 0.04 and 11 L s⁻¹.

Puerta et al. [18,19] investigated adsorption kinetic of β -lactoglobulin on immunoadsorbents. The adsorption rate was between 0.13 and 1.5 L g⁻¹ s⁻¹ and desorption rate between 0 and 0.5 ms⁻¹ [19].

The aim of this work was to investigate the effect of the shell thickness on the column efficiency for a finite adsorption–desorption rate and any Henry constant. The optimal solid core radius was calculated to achieve minimum HETP in different process conditions. The analysis of the resolution in analytical chromatography and productivity in preparative chromatography on the shell thickness was presented.

Moreover, the conditions of the equivalence between the solutions of the General Rate model with slow adsorption kinetic and Lumped Kinetic or Equilibrium Dispersive model were formulated.

2. Mathematical models

2.1. General Rate, Equilibrium Dispersive and Lumped Kinetic Model

The General Rate model used in the paper is the same as analyzed in [20,21].

It will be convenient to present this model in dimensionless form.

The dimensionless parameters used here are the following:

$$\begin{aligned} x &= \frac{z}{L}, \quad \tau = \frac{tu}{L\varepsilon_e}, \quad R = \frac{r}{R_e}, \quad y = \frac{C}{C_r}, \quad y_p = \frac{C_p}{C_r}, \quad \rho = \frac{R_i}{R_e}, \\ Q &= \frac{q}{C_r}, \quad Q_s = \frac{q_s}{C_r}, \quad Pe = \frac{uL}{D_L\varepsilon_e}, \quad St = \frac{3k_{ext}L\varepsilon_e}{Reu}, \\ Bi &= \frac{k_{ext}R_e}{D_{eff}}, \quad \Phi^2 = \frac{R_e^2 k'_{ads}}{D_{eff}} \end{aligned} \quad (1)$$

The meaning of the symbols is given in the notation.

The mass balance equation for mobile phase can be written as follows:

$$\frac{\delta y}{\delta \tau} + \frac{\delta y}{\delta x} = \frac{1}{Pe} \frac{\delta^2 y}{\delta x^2} - \frac{(1-\varepsilon_e)}{\varepsilon_e} St(t-t_p(R=1)) \quad (2)$$

The mass balance equation for adsorbent is:

$$\varepsilon_p \frac{\delta y_p}{\delta \tau} + (1-\varepsilon_p) \frac{\delta Q}{\delta \tau} = \frac{St}{3Bi} \frac{1}{R^2} \frac{\delta}{\delta R} \left(R^2 \frac{\delta y_p}{\delta R} \right) \quad (3)$$

When the adsorption–desorption process is not infinitely fast then the second term of Eq. (3) should be expressed by the adsorption–desorption kinetic. Assuming Langmuir kinetic model, the adsorption–desorption process in dimension form can be written as follows:

$$\frac{\partial q}{\partial t} = k_{ads}c_p(q_s - q) - k_{des}q = k_{ads}q_s \left(c_p - \frac{qc_p}{q_s} - \frac{q}{q_s K} \right) \quad (4a)$$

or

$$\frac{\partial q}{\partial t} = k'_{ads} \left(c_p - \frac{qc_p}{q_s} = \frac{q}{H} \right) \quad (4b)$$

where $k'_{ads} = k_{ads}q_s$ is the effective adsorption rate constant.

In dimensionless form Eq. (4b) is given by:

$$\frac{\partial Q}{\partial \tau} = \frac{\Phi^2 St}{3Bi} \left(y_p - \frac{Qy_p}{Q_s} - \frac{Q}{H} \right) \quad (5a)$$

or for linear isotherm

$$\frac{\partial Q}{\partial \tau} = \frac{\Phi^2 St}{3Bi} \left(y_p - \frac{Q}{H} \right) \quad (5b)$$

Eqs. (2)–(5) have to be coupled with the initial and boundary conditions:

The initial conditions (at $\tau=0$) are:

for $0 < x < 1$; $y(0, x) = y^0$;

for $0 < x < 1$; $0 < R < 1$;

$$y_p(0, R, x) = y_p^0(R, x); \quad Q(0, R, x) = Q^0(R, x) \quad (6)$$

The boundary conditions for the first mass balance equation are:

For $\tau > 0$; $x = 0$; $y'_f - y(\tau, 0) = -\frac{1}{Pe} \frac{\delta y(\tau, 0)}{\delta x}$

With $y'_f = y_f$ for $\tau \in [0, \tau_p]$

and with $y'_f = 0$ for $\tau > \tau_p$

For $\tau > 0$; $x = 1$

$$\frac{\delta y(\tau, 1)}{\delta x} = 0 \quad (7)$$

The boundary conditions for the second mass balance equation are:

$$\text{For } t > 0; R = 1; \quad \frac{\delta y_p(\tau, R)}{\delta R} = Bi[y - y(\tau, R)] \quad (8)$$

$$\text{For } t > 0; R = 0; \quad \frac{\delta y_p(\tau, R)}{\delta R} = 0$$

The dimensionless mass balance equation for the Equilibrium Dispersive or the Lumped Kinetic Model is given by:

$$\frac{\delta y}{\delta \tau} + \frac{(1-\varepsilon_e)(1-\varepsilon_p)(1-\rho^3)}{\varepsilon_t} \frac{\delta Q}{\delta \tau} + \frac{\varepsilon_e}{\varepsilon_t} \frac{\delta y}{\delta x} = \frac{\delta}{\delta x} \left(\frac{1}{Pe_a} \frac{\delta y}{\delta x} \right) \quad (9)$$

where $\varepsilon_t = \varepsilon_e + (1-\varepsilon_e)\varepsilon_p(1-Q^3)$

$Pe_a = \frac{uL}{D_a\varepsilon_e}$ and D_a is the apparent dispersion coefficient.

The boundary and initial conditions are similar to those of the GR model.

Mass balance (9) is coupled with Eq. (5a) or (5b) (LKM) or Langmuir or linear isotherm (ED model).

2.2. HETP of chromatographic columns packed with a shell adsorbent

The performance of different chromatographic columns is conveniently compared on the basis of the values of their HETP. The HETP can be calculated as a ratio of the first absolute (μ_1) and the second central (μ'_2) moments:

$$\frac{\text{HETP}}{L} = \frac{\mu'_2}{\mu_1^2} \quad (10)$$

The following equations for the first and second moment, calculated with the scheme explained recently in [9] for the GR model (Eqs. (2), (3), (5b), and (6)–(8)), can be obtained, assuming the Dirac δ injection profile:

$$\mu_1 = (1+k_1) \frac{t}{\tau} \quad (11)$$

$$\begin{aligned} \mu'_2 &= \left(\frac{t}{\tau} \right)^2 \left\{ \frac{2}{Pe} (1+k_1)^2 + \frac{2(k_1)^2}{F'} \left[\frac{1}{St} + \frac{Bi}{5St} \right] \right. \\ &\quad \times \left(\frac{1+2\rho+3\rho^3-\rho^3-5\rho^4}{(1+\rho+\rho^2)^2} \right) \\ &\quad \left. + \frac{1}{(1-\varepsilon_p)(1-\rho^3)} \left(\frac{k_p}{1+k_p} \right)^2 \frac{3Bi}{St\Phi^2} \right\} \end{aligned} \quad (12)$$

where

$$k_1 = F'(\varepsilon_p + (1 - \varepsilon_p)H)(1 - \rho^3); \quad F' = \frac{1 - \varepsilon_e}{\varepsilon_e}; \quad k_p = \frac{1 - \varepsilon_p}{\varepsilon_p} H \quad (12a)$$

Finally, combination of Eqs. (10)–(12) gives the plate height equation:

$$\frac{\text{HETP}}{L} = \frac{2}{Pe} + \frac{2}{F'} \left(\frac{k_1}{1 + k_1} \right)^2 \left[\frac{1}{St} + \frac{Bi}{5St} * \right. \\ \times \left(\frac{1 + 2\rho + 3\rho^2 - \rho^3 - 5\rho^4}{(1 + \rho + \rho^2)^2} \right) \\ \left. + \frac{1}{(1 - \varepsilon_p)(1 - \rho^3)} \left(\frac{k_p}{1 + k_p} \right)^2 \frac{3Bi}{St\Phi^2} \right] \quad (13)$$

In the following the value of HETP will be referenced to unite column length.

3. Data selected for theoretical calculations

The performance of chromatographic columns, packed with shell particles, was investigated for a wide range of the changeability of dimensionless numbers. The Stanton number was taken from 100 up to 1,000,000. Stanton number express the external mass transfer resistances. For $St = 100$ the mass transport resistances are very large. For $St = 1,000,000$ the mass transport resistances are extremely low. Peclet number characterizing the dispersion was between 100 and 100,000. The higher is the Peclet number the lower is the peak broadening due to dispersion. Biot number was between 0.1 (a possible value for very low molecules with high molecular diffusivity) and 1000 (this value can be obtained for large proteins). Thiele modulus was chosen between 0.01 (very slow adsorption kinetic) up to 100,000 (practically instantaneous adsorption). Finally, the Henry constant was between 1 and 10,000.

To validate HETP model and analyze the column performance the GR model, the LKM model and the ED model were solved with orthogonal collocation on the finite elements method [22,23].

4. Results and discussion

4.1. Validation of the HETP model

The development of the HETP expression (Eq. (13)) is laborious. Eq. (13) is equivalent to the expression developed by Li et al. except the term $(1 - \varepsilon_p)$ in the last part of Eq. (13).

To validate the correctness of the plate height equation, the GR model was solved numerically for several combination of a dimensionless modulus: Bi , St , Pe and Φ . Next, for the obtained band profiles the first and second moments were calculated according to the expressions:

$$\mu_1 = \frac{\int C(t)tdt}{\int C(t)dt} \quad (14)$$

$$\mu_2' = \frac{\int C(t)(t - \mu_1)^2 dt}{\int C(t)dt} \quad (15)$$

and finally the HETP was estimated from Eq. (10). The estimated value of HETP was compared with one calculated from Eq. (13). The obtained results are summarized in Table 1. All simulations were performed for $\varepsilon_e = \varepsilon_p = 0.4$, $\rho = 0.8$ and the Henry constant $H = 5$. As can be seen, for extremely low external and internal mass transfer resistances ($St = 10^6$, $Bi = 0.1$) as well as for very large external

Table 1

Comparison of HETP calculated from the numerical solution of GR model and Eq. (13).

Pe	St	Bi	Φ	HETP ^a	HETP ^b
100,000	1,000,000	0.1	0.01	0.00543	0.00544
50,000	10,000	1	0.1	0.0542	0.0542
50,000	10,000	1	10	0.000118	0.000118
100	100	100	10	0.125	0.125

^a HETP calculated from Eq. (13).

^b HETP estimated from peaks calculated with GR model.

and internal mass transfer resistances ($St = Bi = 100$), for fast and slow adsorption kinetic, and for large and low dispersion, the calculated with both method HETPs are identical, what confirms the correctness of Eq. (13).

4.2. The optimal solid core radius – analytical chromatography

4.2.1. One component chromatography

It is well known that for the totally porous adsorbent and the instantaneous adsorption–desorption kinetic the HETP reaches minimum value when the solid core radius approaches the particle radius [10,12]. However, for finite adsorption rate the maximum column efficiency can be obtained for $\rho < 1$, what was shown by Li et al. [11]. Li et al. analyzed column efficiency for shell adsorbent only in the case of Henry constant $H \gg 1$. In the following the results of the investigation of the column efficiency for any Henry constant is presented.

The minimum value of HPLC as a function of ρ can be easily found using program Maple (Waterloo Maple Inc.) with help of function “minimize” implemented in this program. In this work the program Maple 13 was used. The optimum value of ρ was searched in the interval (0–0.97). The reason of the restriction of this interval to $\rho < 0.97$ is explained in the next section. All simulation were performed for $\varepsilon_p = \varepsilon_e = 0.4$. Values of other parameters are given in the captions to the figures.

In Fig. 1 the optimal solid core radius for the given Thiele modulus and Henry constant are presented for: (a) extremely low external and internal mass transfer resistances and dispersion, and (b) extremely high external and internal mass transfer resistances and dispersion. In Fig. 1c. the relative value of RHETP versus Φ and H , for high mass transfer resistances is illustrated. The RHETP is a ratio of HETP calculated for optimal solid core radius to HETP calculated for totally porous adsorbent.

From simulations performed for very low mass transfer resistances follows that for $H < 1.9$ and any Φ value, or for Φ greater than about 30, the optimal value of the active shell thickness decreases to zero. For H greater than about 50 and Φ lower than 2, the column effectiveness reaches maximum for the totally porous adsorbent particle. For very low mass transfer resistances the minimum value of HETP for the shell adsorbent is no more than few percent smaller than HETP calculated for totally porous adsorbent.

Similar results were obtained for very high mass transfer resistances: for $H < 2.2$ and any Φ value, or for Φ greater than 45, the optimal value of active shell thickness decreases to zero. For H greater than about 25 and Φ lower than 2.3, the column effectiveness reaches maximum for the totally porous adsorbent particle. However, for high mass transfer resistances the HETP of the totally porous adsorbent can be several times greater than that obtained for an optimal core radius – see Fig. 1c). The effectiveness of shell adsorbent strongly increases with the adsorption rate (Thiele modulus) increase.

To sum up, it is evident that mass transfer resistances and dispersion do not influence considerably the position of optimal shell thickness. However, it should be noted, that with increasing mass transfer resistances (St decrease, Bi increase) the region with the

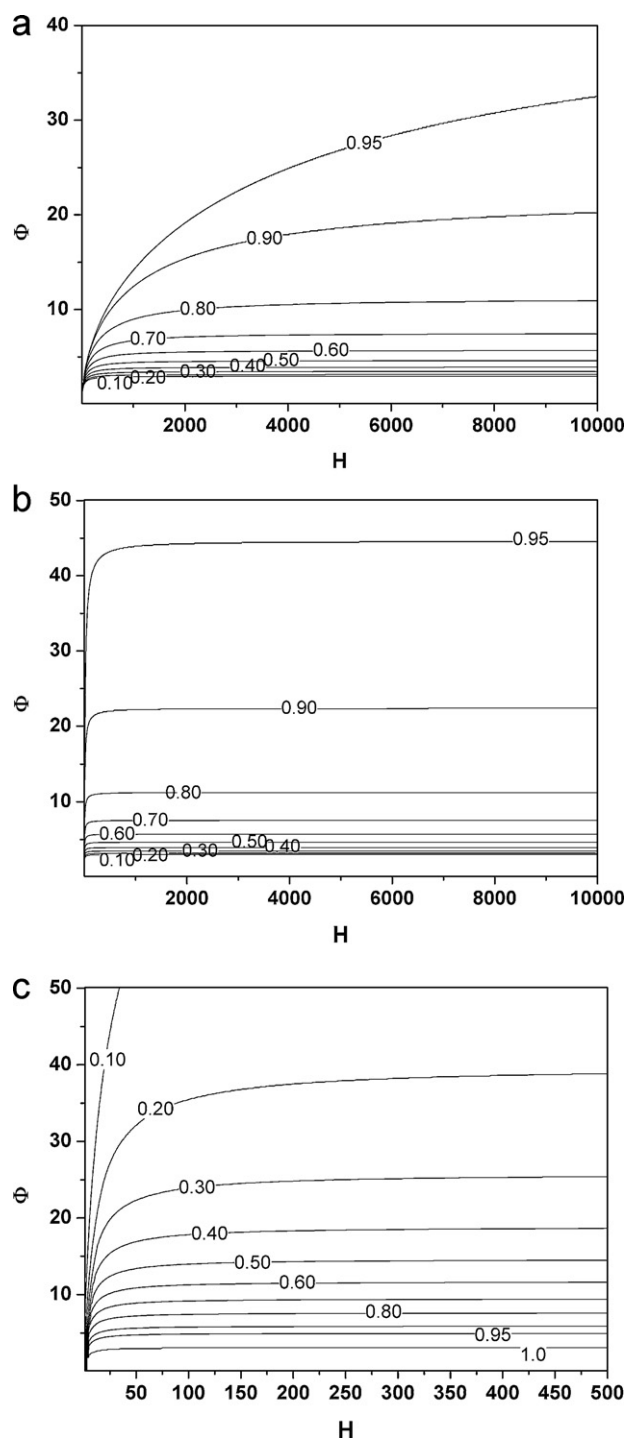


Fig. 1. The dependency of the optimal solid core radius (a), (b), and RHETP (c) on Thiele modulus and Henry constant. (a) $Pe = 10^5$, $St = 10^6$, $Bi = 0.1$. (b) and (c) $Pe = 100$, $St = 100$, $Bi = 10^3$.

optimal ρ value between 0 and 0.97 is wider, especially for a lower value of the Henry constant. The application of the shell adsorbent is favorable mainly for low Biot number and fast adsorption kinetic.

The calculation presented above, for optimal ρ value were performed assuming that $\rho < 0.97$. It is instructive to analyze the dependency of HETP versus dimensionless solid core radius ρ – see Fig. 2. The calculations were performed for typical value of St and Pe numbers for contemporary columns, $Pe = 50,000$, $St = 10,000$. Value of other parameters are: $Bi = 1000$, $\Phi = 10$.

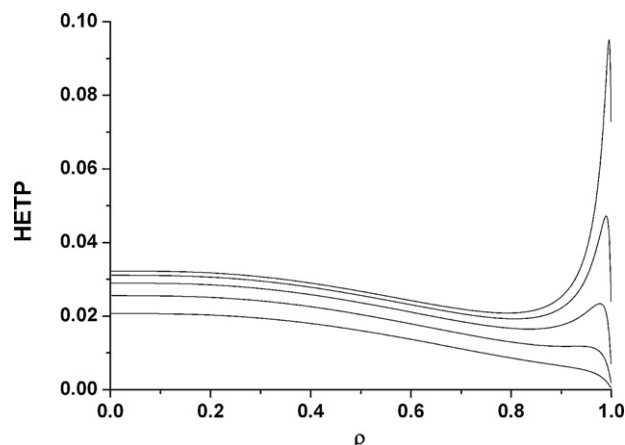


Fig. 2. The dependency of HETP on dimensionless solid core radius. $H = 4, 8, 16, 32, 64$ from bottom.

The curves $HETP = f(\rho)$ have in a general case two extremes: the local maximum near $\rho = 1$ and the local minimum. The maximum value of HETP can be even several times greater than its value in the local minimum. The local minimum is the more shifted towards smaller ρ values the higher Henry constant is and the smaller Thiele modulus. Moreover, the local minimum is more expressive for larger Biot number (larger internal mass transfer resistances). The global minimum is always for ρ approaching 1. However, infinitely low thickness of active layer is rather impractical because of the extremely low adsorbent capacities, so in previous calculation the optimal value of solid core was searched in the interval from 0 to 0.97.

4.2.2. Two component chromatography – the resolution of two component

In the previous section the optimal values of the adsorbent solid core radius, for which the HETP reaches minimum, were estimated. However, the most important measure of a chromatographic separation power is resolution, R_s , between different compounds.

The resolution, R_s , of two compounds can be calculated from the first and second moments of the chromatographic peaks as:

$$R_s = \frac{|\mu_{1a} - \mu_{1b}|}{2 \left(\sqrt{\mu'_{2a}} + \sqrt{\mu'_{2b}} \right)} \quad (16)$$

where a and b denote component a or b .

From Eq. (16) follows that resolution depends not only on column efficiency expressed by second moments, but also on the difference between the retention times of the compounds depicted by first moments.

To scrutinize the influence on Thiele modulus, Biot number and Henry constant on the optimal solid core radius for which the resolution is maximal, it is convenient to introduce the relative resolution factor, RR , as the ratio of the resolution factor R_s for shell adsorbent to the resolution factor of totally porous adsorbent. In the calculations the Peclet and Stanton numbers were assumed to be equal: $Pe = 50,000$ and $St = 10,000$.

In Fig. 3a and b the dependency of the optimal ρ value and relative resolution factor, RR , on Biot and Thiele modulus is presented. The H_a was equal to 3 and H_b was equal to 3.5. The same dependencies are presented in Fig. 4a and b but $H_a = 3000$ and $H_b = 3500$, values observed for strongly adsorbed proteins.

From analysis of presented figures and other not presented results of calculation follows that:

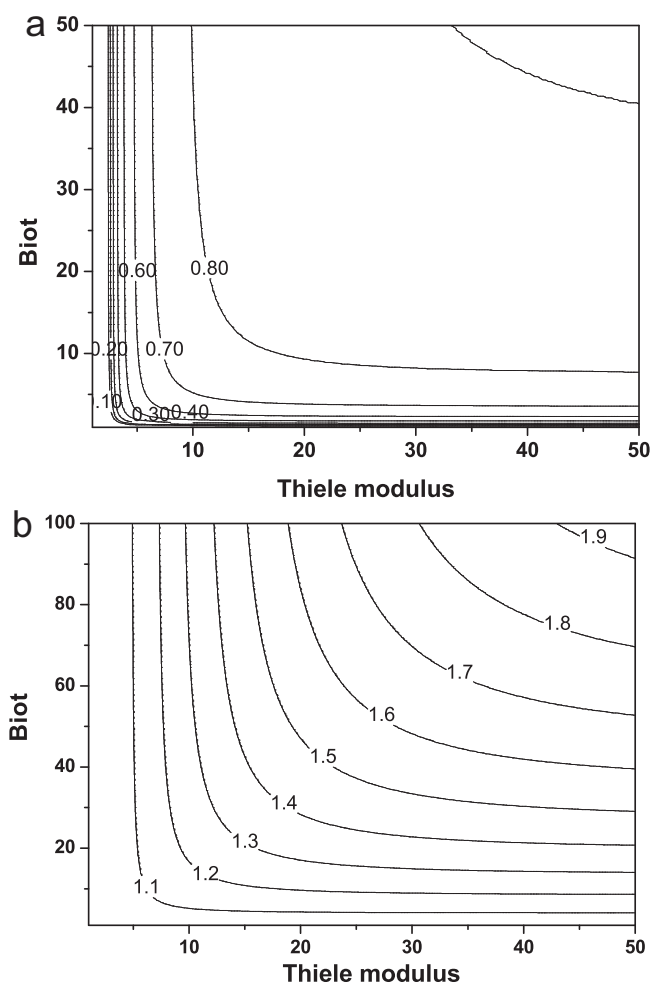


Fig. 3. The dependency of the optimal ρ value (a) and relative resolution factor, RR , (b) on Biot and Thiele modulus. $H_a = 3.0$ and $H_b = 3.5$.

- the relative resolution always decreases to zero for ρ increasing to one;
- the optimal solid core radius is shifted towards higher values when Thiele modulus or Biot number is increasing, however for very high Henry constant the position of optimal ρ value almost does not depend on Biot number;
- the maximum value of the relative resolution and optimal ρ value slightly depends on the Stanton number;
- the maximum value of relative resolution is generally increasing when Biot, Thiele modulus and Henry constant are increasing (keeping $H_b/H_a = \text{const}$).

In Fig. 5 the calculated optimal solid core radius, ρ , and the relative resolution factor, RR , obtained for optimal radius as a function of the Biot number and the Henry constant were presented. The Henry constant for component “b” was equal $H_b = 1.2 \cdot H_a$. The calculations were performed for instantaneous adsorption process ($\Phi = \infty$).

As can be seen, for Bi and H less than about 5, the optimal ρ value is less than about 0.7 and the relative resolution factor is less than 1.1. For Biot less than 1 the RR factor can be less than one (see Fig. 6), which means that application of shell adsorbent in this case has negative impact on the resolution.

The application of shell adsorbents is the more attractive the greater are Biot number and Henry constant. However, for $Bi > 10$ and $\Phi > 10$ the optimal shell thickness should be very thin, less than

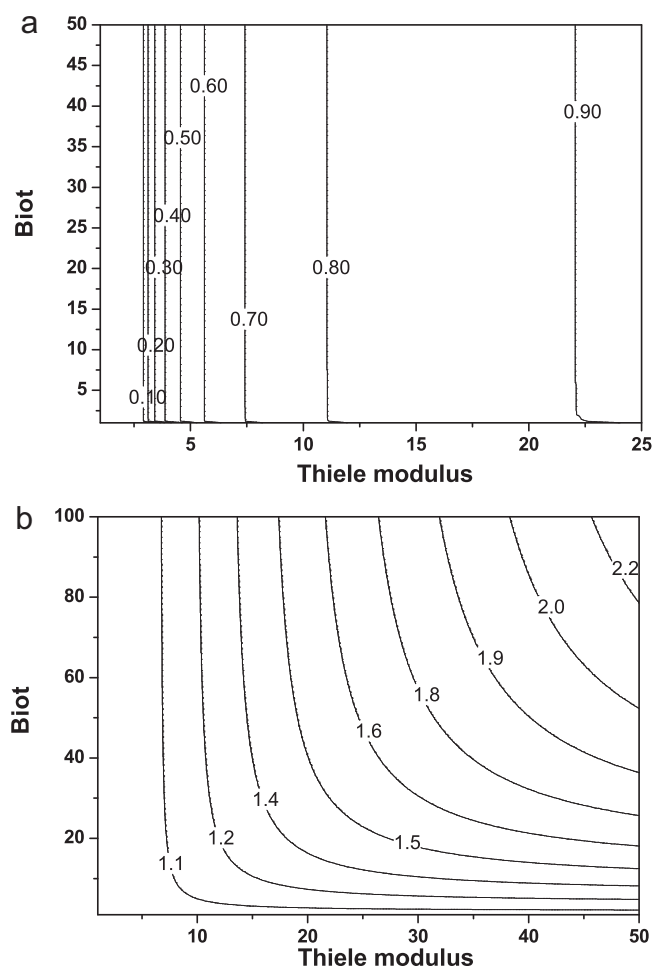


Fig. 4. The dependency of the optimal ρ value (a) and relative resolution factor, RR , (b) on Biot and Thiele modulus. $H_a = 3000$ and $H_b = 3500$.

0.1 of the adsorbent diameter. For strongly adsorbed proteins the shell thickness should be about 0.02 of the adsorbent diameter.

4.3. The optimal solid core radius – preparative chromatography

In the last section it was proven that optimal solid core radius, ρ , for which the resolution R_s reaches maximum value depends mainly on Bi , Φ , and H variables. For given criteria numbers it is very easy to find optimal ρ value by plotting Eq. (16). This section tries to answer the following question: does the value of ρ close to optimal solid core radius guarantees maximum productivity in preparative chromatography. If so, the tedious and long optimization of preparative separation could be considerably shortened.

Practically it is impossible to perform above mentioned analyzes for any possible values of criteria numbers, any isotherms and any isotherms parameters. Only the exemplary analyze was done for the Langmuir kinetic adsorption process and following criteria numbers: $Pe = 50,000$, $St = 10,000$, $Bi = 1000$, $Fi = 10$, $H_a = 4$, $H_b = 6$, $Q_s = 20$, $C_r = 1$, $y_f \leq 30$ for nonlinear adsorption kinetic. Eq. (5a) was replaced by an appropriate two component Langmuir kinetic for both species (a) and (b).

The objective function, OF, used in this work is the product of the productivity, Pr , and the recovery yield, Y :

$$OF = Pr_i Y_i = \frac{C_{fi} t_p u Y_i}{\Delta t_c} Y_i = u \frac{C_r y_{fi} \tau_p Y_i}{\Delta \tau_c} Y_i \quad (17)$$

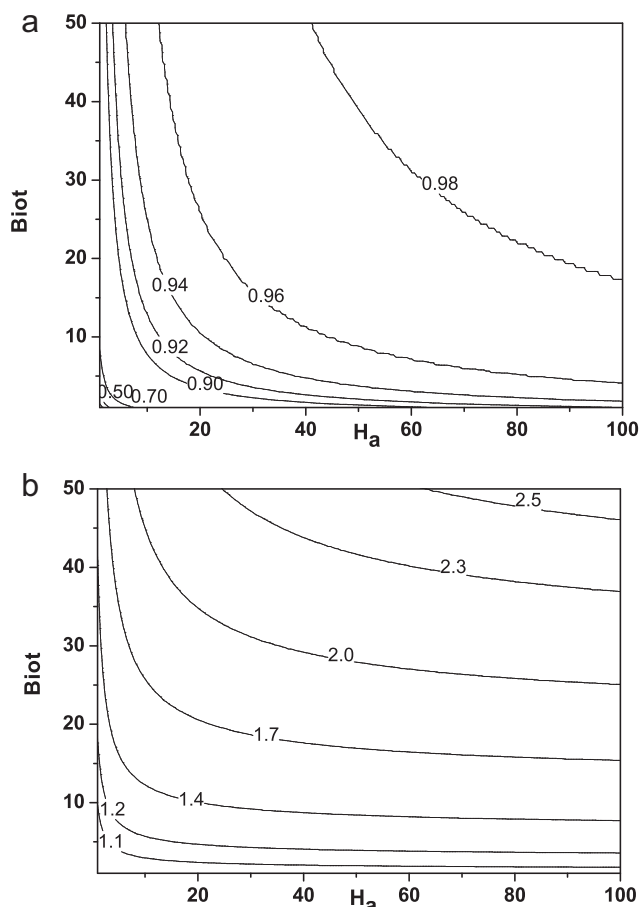


Fig. 5. The dependency of the optimal ρ value (a) and relative resolution factor, RR , (b) on Biot and Henry constants H_a and $H_b = 1.2 \cdot H_a$. The calculation performed for instantaneous adsorption process ($\Phi = \infty$).

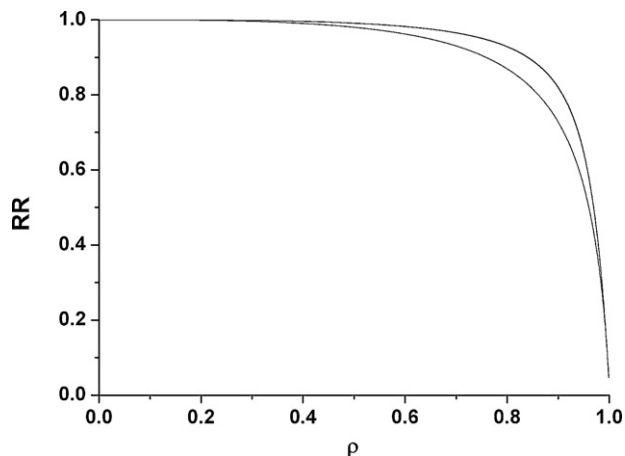


Fig. 6. Relative resolution versus dimensionless solid core radius. $Pe = 50,000$, $St = 10,000$, $Bi = 0.1$, $\Phi = 1$, bottom line, $\Phi \geq 10$ upper line, $H_a = 3$, $H_b = 3.5$.

where Pr_i is the mass of the key product i collected during the cycle time Δt_c , Y_i is the yield defined as the fraction of the component that is recovered in the purified fraction product, and Δt_c is the duration of a production cycle, between two successive injections. Constructed in this way, the OF function assures high values of the productivity and the yield, enabling a reasonable cost of purification of the final product.

The optimization of the product $Pr \cdot Y$ with GR model is very long. The computation can be much shorter using ED model or LKM.

The LKM consist of Eq. (9) and Eq. (5a) assuming the Langmuir kinetic model. In Eq. (5) the y_p should be replaced by y . For very low concentration the Eq. (5a) simplifies to model (5b). The ED model consist of Eq. (9) and Langmuir isotherm or linear isotherm.

The solution of GR model and LKM ((Eq. (9)) and (Eq. (5b))) are identical (see Fig. 7 – Gaussian band profile) when the effective dispersion coefficient is calculated from Eq. (18):

$$D_a = \frac{D_L \varepsilon_e}{\varepsilon_t} + \left(\frac{k_1}{1+k_1} \right)^2 \frac{u^2 R_e}{\varepsilon_t \varepsilon_e F^2} \times \left[\frac{R_e}{5D_{eff}} \frac{1+2Q+3Q^2-Q^3-5Q^4}{(1+Q+Q^2)} + \frac{1}{k_{ext}} \right] \quad (18)$$

The solution of the GR model and the Ed model ((Eq. (9)) and linear isotherm) are also identical (see Fig. 7 Gaussian band profile) when the effective dispersion coefficient is calculated from Eq. (18a):

$$D_a = \frac{D_L \varepsilon_e}{\varepsilon_t} + \left(\frac{k_1}{1+k_1} \right)^2 \frac{u^2 R_e}{\varepsilon_t \varepsilon_e F^2} \left[\frac{R_e}{5D_{eff}} \frac{1+2Q+3Q^2-Q^3-5Q^4}{(1+Q+Q^2)} + \frac{1}{k_{ext}} + \frac{1}{(1-\varepsilon_p)(1-\rho^3)} \left(\frac{k_p}{1+k_p} \right)^2 \frac{1}{k'_{ads}} \right] \quad (18a)$$

The Eqs. (18) and (18a) can be developed after the application of the same mathematical manipulation as discussed in [24] for totally porous adsorbent.

In dimensionless form Eqs. (18) and (18a) reads:

$$\frac{1}{Pe_a} = \frac{1}{Pe} \frac{\varepsilon_e}{\varepsilon_t} + \frac{\varepsilon_e}{\varepsilon_t F'} \left(\frac{k_1}{1+k_1} \right)^2 \times \left[\frac{1}{St} + \frac{Bi}{5St} \left(\frac{1+2\rho+3\rho^2-\rho^3-5\rho^4}{(1+\rho+\rho^2)^2} \right) \right] \quad (19)$$

$$\frac{1}{Pe_a} = \frac{1}{Pe} \frac{\varepsilon_e}{\varepsilon_t} + \frac{\varepsilon_e}{\varepsilon_t F'} \left(\frac{k_1}{1+k_1} \right)^2 \left[\frac{1}{St} + \frac{Bi}{5St} \left(\frac{1+2\rho+3\rho^2-\rho^3-5\rho^4}{(1+\rho+\rho^2)^2} \right) + \frac{1}{(1-\varepsilon_p)(1-\rho^3)} \left(\frac{k_p}{1+k_p} \right)^2 \frac{3Bi}{St\Phi^2} \right] \quad (19a)$$

It should be noted that the term with adsorption kinetic rate was omitted in Eqs. (18) and (19), because dispersion due to slow kinetic is taken into account by Eq. (5b).

In the case of the nonlinear kinetic model (Eq. (5a)) or the nonlinear isotherm model the Henry constant in Eqs. (12a) should be replaced by a local isotherm slope [24]. The comparison of the peak profiles calculated with GR (solid line), LKM (dotted line) for Langmuir adsorption-desorption kinetic and ED model (dashed line) for the Langmuir isotherm are presented in Fig. 7. For the nonlinear kinetic the band profiles obtained with the GR model or LKM are slightly different, however the beginning and the end of these peaks are at the same time. The solution with the ED model approximates the peak calculated with the GR model considerably poorer, however, also in this case, the beginning and the end of these peaks overlap each other. The CPU time needed for solution of the ED model is much shorter than the time needed to solve the LKM, so the initial step of optimization should be done with the ED model.

In the following the optimal solid core radius, for which the objective function reaches maximum, was estimated using the LKM model. In the calculations it was assumed that $u = 1$ cm/min and the product purity equals 0.01. The optimized parameters were: inlet

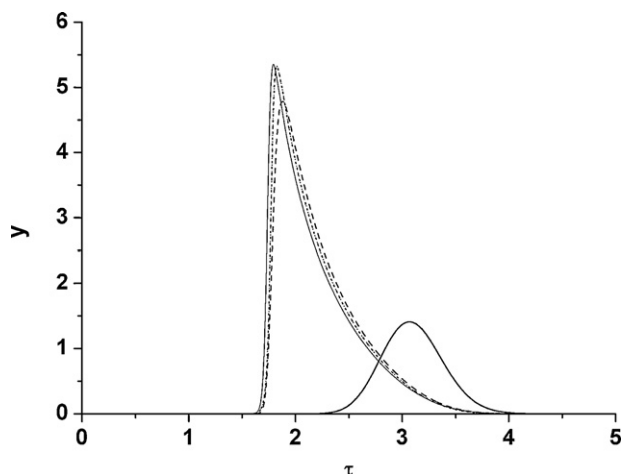


Fig. 7. Comparison of the peak profiles calculated with GR (solid line), LMK (dotted line) and ED model (dashed line) for linear (Gaussian peak) and Langmuir adsorption-desorption kinetic (or Langmuir isotherm for ED model). Calculations were done for: $Pe = 50,000$, $St = 10,000$, $Bi = 1000$, $Fi = 10$, $\rho = 0.8$, $H = 4$, $Q_s = 20$, $C_r = 1$ and $y_f = 30$.

species concentration, the same for both components, injection time and solid core radius.

For the optimization the hybrid of simulated annealing and the simplex algorithm was applied [25,26].

For the given above model parameters and the linear adsorption kinetic, the optimal values of dimensionless solid core radius and maximum value of relative resolutions was $\rho = 0.802$, $RR = 1.27$.

In the case of preparative chromatography the optimal core radius, ρ_{prep} , and the value of objective function were:

for first component: $OF = 3.74 \times 10^{-4}$, $\tau_p = 0.00675$, $y_f = 24.1$, $\rho = 0.788$
 $OF = 3.72 \times 10^{-4}$, $\tau_p = 0.00553$, $y_f = 29.8$, assuming
 $\rho = 0.802$

for second component: $OF = 6.52 \times 10^{-3}$, $\tau_p = 0.0124$, $y_f = 30.0$, $\rho = 0.827$
 $OF = 6.35 \times 10^{-3}$, $\tau_p = 0.0138$, $y_f = 29.9$, assuming
 $\rho = 0.802$

Very similar ρ_{prep} values were obtained for $Q_s = 4$.

As can be seen the optimal core radius in the preparative chromatography depends on the analyzed component and differs from the core radius assuring maximum resolution, ρ_{res} . For the first component $\rho_{prep} < \rho_{res}$ and for the second $\rho_{prep} > \rho_{res}$.

However, it should be noted that the maximum values for objective function differ only slightly from these values obtained assuming $\rho = \rho_{res}$.

5. Conclusions

In the work the analysis of the chromatographic column efficiency packed with the superficially porous particles and their separation power in analytical and preparative conditions was presented. The analysis of the column efficiency was based on the HETP model. The calculation encompassed a very high and low external and internal mass transfer resistances, low and large axial dispersion, very slow and fast adsorption kinetic rate. It was found that for low Henry constant and any adsorption kinetic rate or for the Thiele modulus greater than about 20, the shell thickness should be as low as possible. For Henry constant greater than about 50 and Φ lower than 2, the column effectiveness reaches maximum value for totally porous adsorbent particle. These conclusion is true for any practically achieved St , Bi and Pe numbers.

From analysis of the separation power of column packed with shell particles follows that the resolution is increasing when Biot number, Thiele modulus and Henry constants for both components are increasing (keeping ratio of Henry constants unchanged). The optimal solid core radius increases when adsorption rate increases.

This value slightly depends on the external mass transfer resistances.

The highest relative resolution is achieved for instantaneous adsorption-desorption process, as should be expected. The resolution is increasing when the Henry constant and the core radius are increasing. However, for the Biot number and the Henry constant less than about 5 the benefit of the application of the shell adsorbent becomes negligible. For very low Biot number the resolution obtained on shell adsorbent is lesser than on totally porous adsorbent.

The obtained results can help in preparing shell adsorbent for specific analytical separation.

The calculation of the optimal solid core radius for optimization of preparative separation, for finite adsorption rate, requires large numbers of solutions of mass transport equation. The time of the calculation can be considerably shortened when instead of the GR model the ED model or the LKM is used. The solution of the LKM or the ED model is equivalent to solution of the GR model when apparent dispersion is calculated from Eq. (18) or (18a), respectively. However, the solution of ED model for nonlinear chromatography is less accurate in comparison with the solution of LKM.

Nomenclature

Bi	Biot number
C, C_p	concentration in mobile phase or in the stagnant fluid phase contained in the pores
C_r	reference concentration
D_{eff}	effective particle diffusivity
D_a	apparent dispersion coefficient
D_L	axial dispersion coefficients
F'	phase ratio
H	Henry constant
HETP	height equivalent to theoretical plates
k_{ads}, k_{des}	adsorption and desorption rate constant
$k_{ads}' = k_{ads} \cdot q_s$	apparent adsorption rate constant
k_{ext}	External mass transfer coefficient
L	column length
Pe, Pe_a	Peclet number or apparent Peclet number
q	concentration in stationary phase
q_s	saturation capacity
Q	dimensionless concentration in stationary phase
Q_s	dimensionless saturation capacity
r	radial coordinate
R	resolution factor
RR	relative resolution factor
R_i	radius of inert solid core
R_e	particle radius
St	Stanton number
t	time
u	superficial velocity
V_m	partial molar volume
x	dimensionless axial coordinate
y, y_p	dimensionless concentration in mobile or in the stagnant fluid phase in the pores
z	axial coordinate

Greek symbol

ε_e	external porosity
ε_t	total column porosity
ε_p	particle porosity
Φ	Thiele modulus
μ_1	first absolute moment
μ_2'	second central moment ratio of the radius of the inner solid core, R_i , to the radius of the particle, R_e

τ dimensionless time
 τ_p dimensionless time during the constant concentration is fed into column

Subscripts

f inlet value
 0 initial value

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