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Modeling and analysis of dynamic behavior of adsorption stratified column beds packed with partially fractal porous adsorbent particles

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MODELING AND ANALYSIS OF DYNAMIC BEHAVIOR OF ADSORPTION STRATIFIED COLUMN BEDS PACKED WITH PARTIALLY FRACTAL POROUS ADSORBENT PARTICLES

by

MIN LI

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This dissertation has been prepared in the styles utilized by the Journal of Separation Science and the appendices have been added for the purposes of normal dissertation writing.

ABSTRACT

In this work novel porous adsorbent media having partially fractal structures and stratified packed-beds are constructed and their dynamic performance with respect to their adsorptive capacity through the construction and solution of rigorous models is studied. The results show that conventional columns packed with partially fractal porous adsorbent particles provide larger breakthrough times and dynamic utilization of the adsorptive capacity of the column when compared with those of conventional columns employing conventional adsorbent particles which do not possess a partially fractal structure. Furthermore, stratified column beds exhibit superior species separation performance than conventional columns when they are packed with either conventional or partially fractal porous adsorbent media, and their highly desirable separation performance is increased further when the spatial ligand density distribution in the adsorbent particles is non-uniform and is described by certain functional forms. The stratified columns packed with partially fractal porous adsorbent media provide to the designer and user of chromatographic column systems, especially in preparative and process chromatography, more degrees of freedom with respect to the number of variables and parameters that could be controlled in the design, construction, and operation of efficient chromatographic adsorption separation systems. The models, porous media, and systems constructed in this work can also be extended into other relevant fields including chemical catalysis, biocatalysis, and membrane separations which employ porous media.

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1. INTRODUCTION

Affinity adsorption separation processes are considered to be highly selective separation methods in the downstream processing (bioseparation) of biologically active macromolecules in laboratory and large-scale applications. Most of the affinity adsorption separations are carried out in chromatographic columns packed with porous adsorbent particles.

Adsorbent porous media having partially fractal structures could be constructed by gluing microspheres in each recursion of the fractal particle, that is, a porous adsorbent particle of a given radius is considered to be made by smaller in radius porous adsorbent particles which themselves are made by even smaller in radius porous adsorbent particles and so on. By increasing the total number of the recursions of the fractal particle, the total intraparticle pore surface area of the partially fractal particle is significantly increased. The adsorbent media possessing partially fractal structures have high adsorptive capacities and reduced overall intraparticle mass transfer resistance when compared to conventional porous adsorbent media, because their large intraparticle pore surface areas are easily accessible due to the desirable pore-size distributions and high pore connectivities that characterize the intraparticle pore structure of partially fractal porous adsorbent media.

The stratified column beds are packed beds which are comprised of several packed-bed sections. The radii of the packed porous adsorbent particles decrease in size along the axis of bulk flow which means that the largest in size particles are packed at the inlet section of the column and the smallest in size particles are packed at the section of the column where the bulk fluid exits. This structure of a stratified packed-bed decreases both the overall external and intraparticle mass transfer resistances and, thus, increases the dynamic separation performance of the adsorbent column. Therefore, the stratified column bed systems packed with partially fractal porous adsorbent particles can provide highly effective and efficient chromatographic separations and high dynamic capacities when higher throughputs are required when compared with those obtained from conventional columns.

In this work, rigorous mathematical models are constructed and solved in order to study and analyze the dynamic adsorption performance of stratified column bed systems packed with partially fractal porous adsorbent particles for various design and operating conditions.

In the first paper of this dissertation, partially fractal porous adsorbent particles with the total number of the recursion of the fractal of the particle taken to be equal to one are constructed and employed in conventional and stratified column beds. The immobilized ligands have uniform spatial density distribution and the separation performance as well as the dynamic capacity of the column beds is determined. Furthermore, the theoretical and practical implications of the results are presented and discussed.

In the second paper of this dissertation, the adsorption performance and the dynamic capacity of stratified column beds packed with porous adsorbent particles having a partially fractal structure with the total number of the recursion of the fractal being equal to one and a non-uniform spatial ligand density distribution, are studied. Furthermore, detailed analysis and discussion of the results is presented.

In the third paper of this dissertation, a rigorous and general mathematical model which describes the dynamic behavior of the adsorption of adsorbate in single and stratified column beds packed with partially fractal porous adsorbent particles for any magnitude of the total number of the fractal is constructed and solved for the case where the total number of the fractal is equal to two. The results indicate that significantly larger separation efficiencies and dynamic adsorptive capacities are realized as the total number of the recursion of the fractal is increased.

PAPER I

ADSORPTION IN A STRATIFIED COLUMN BED PACKED WITH POROUS PARTICLES HAVING PARTIALLY FRACTAL STRUCTURES AND A DISTRIBUTION OF PARTICLE DIAMETERS

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ABSTRACT

Stratified column bed systems whose sections are formed by packing adsorbent particles with a partially fractal structure are proposed and studied. The simulation results clearly show that the breakthrough times and the shape of the breakthrough curves obtained from stratified column beds, are significantly larger and sharper, respectively, than those obtained from conventional columns. The stratified column beds provide to the designer and user of chromatographic column systems more degrees of freedom with respect to the number of parameters and variables that could be controlled in the design, construction, and operation of efficient chromatographic adsorption systems. Furthermore, the results suggest that the stratified column beds could provide a higher dynamic adsorptive capacity than conventional columns when it is required to increase the column throughput.

1. Introduction

It has been shown by Liapis [1] that chromatographic columns packed with porous adsorbent particles having a partially fractal structure exhibit a significantly higher dynamic adsorptive capacity than columns packed with porous adsorbent particles whose pores do not have a fractal structure. An important aspect in the fractal structure is the concept of self-similarity [1,2] which is related [1] to the concept of geometrical (physical) similarity, and, thus, the spherical porous adsorbent particles with a partially fractal structure and a given particle radius are considered to be made by smaller in radius spherical porous adsorbent particles which themselves are made by even smaller in radius spherical porous adsorbent particles and so on. Furthermore, Liapis and co-workers [1, 3-10] through detailed modeling and simulation approaches have shown the scientific and engineering reasons for the better performance realized in chromatographic columns packed with porous adsorbent particles having partially fractal structures.

Mathews [11] studied experimentally the effect of a distribution of adsorbent particle sizes on the breakthrough profiles from fixed-bed adsorbers and compared his experimental results with the results obtained by simulating the behavior of a stratified bed using the homogeneous solid phase adsorption model [12] which neglects mass transfer by pore diffusion and considers that intraparticle mass transfer in the porous adsorbent particles occurs only by solid phase diffusion; this model has well known serious physical limitations [13,14]. Mathews [11] constructed the stratified bed with the smaller particles at the top and the larger particles at the bottom of the bed, and found that breakthrough occurred earlier in the downflow mode while delayed breakthrough was obtained in the upflow mode, when compared to a uniform particle size bed. We can explain the experimental results of Mathews [11] by the physical mechanisms [1,15-18] which have shown that as the particle size decreases (i) the value of the film mass transfer coefficient in the hydrodynamic boundary layer (film) that surrounds the particles increases, considering, of course, that the bed porosity and the superficial velocity of the flowing fluid stream remain unchanged in the different sections of the stratified packed bed where each section is packed with a different particle size, (ii) the lengths of the intraparticle diffusional pathways of the adsorbate molecules in the porous adsorbent particles decrease, assuming, of course, that the pore size distribution and pore connectivity [1,9,10,18-22] of the pores in the smaller in size particles are similar to those characterizing the pore structure of the larger in size porous adsorbent particles, and (iii) the total surface area of the channels for bulk flow formed by the packed adsorbent particles increases per unit volume of packed bed, considering, of course, that the column diameter remains unchanged. Items (i) and (ii) lead to a smaller overall mass transfer resistance and together with item (iii) provide a larger mass transfer rate in the smaller in size porous adsorbent particles. Therefore, one could expect that, based on basic and sound mass transfer principles, in a stratified packed bed where the particle size of the adsorbent particles decreases as we move from the inlet section to the outlet section of the bed, the overall average concentration gradient for mass transfer would be larger than the overall average concentration gradient that would exist in a column packed with adsorbent particles having uniform size; the experimental results of Mathews [11] confirm this expectation. In other words, the stratified packed bed provides a sharper in shape concentration front for the adsorbate while the column packed with particles of uniform size makes the shape of the concentration front of the adsorbate to be more disperse and, thus, the dynamic separation of the adsorbate in the stratified packed bed is more efficient. It is worth mentioning at this point that the periodic countercurrent operation of packed beds [5,15] (another name used for the periodic countercurrent operation of packed beds is simulated moving beds) involves a set of columns whose total length is L and which are packed with adsorbent particles having uniform size and provides a more efficient separation than a fixed-bed of length L packed with particles of the same uniform size as in the simulated moving beds, because the dispersive concentration front of the adsorbate is in the column that is being removed and is replaced by a bed of regenerated (fresh) adsorbent particles which is placed at the section of the sequence of beds that includes the exiting flowing fluid stream from the system of beds undergoing periodic countercurrent operation. Thus, the average concentration gradient of the adsorbate in the set of beds undergoing periodic countercurrent operation is higher than that of a fixed-bed. The above discussion indicates that an appropriately constructed stratified packed bed of adsorbent particles can, as is the case with the periodic countercurrent operation of packed beds, provide more efficient separation for an adsorbate of interest than that obtained in a fixed-bed of adsorbent particles of uniform size. But it should be mentioned here that the sequence of the interacting mass transfer mechanisms, the relative importance of the mass transfer mechanisms at a given time and position in the packed bed, and the magnitudes of the mass transfer rates of the adsorbate that result from the interaction of the mass transfer mechanisms are different in a stratified packed bed than those encountered in the periodic countercurrent operation of a packed bed whose multiple sections are all packed with adsorbent particles of the same uniform size. Furthermore, Meyers and Liapis [9,10] have shown that the whole packed bed of an adsorber as well as of a catalytic chemical or biochemical reactor could be considered as a single large porous particle whose interstitial channels (pores) for bulk fluid flow could be characterized by a pore network model which interacts with the pore network model that characterizes the porous structure of the adsorbent particles, and the interaction between the pores where bulk fluid flow occurs and the pores of the adsorbent particles could be random or semi-random; of course, when the concept of self-similarity in the fractal structure is related to the concept of geometrical (physical) similarity [1] for the pores of the single large porous particle (the whole packed bed), then the single large porous particle can be considered to represent a partially fractal structure which can provide significantly larger mass transfer rates [1] for the effective separation of an adsorbate of interest than the currently used packed bed adsorption columns or adsorption monoliths. But it would be difficult from the technical point of view, to construct in practice an actual partially fractal packed bed. However, it could be possible to construct in practice an approximate partially fractal structure for a packed bed, so that one could then obtain more efficient separations than those provided from the currently employed in practice packed beds.

In this work we present an approach by which a fixed bed of adsorbent particles with an approximate partially fractal structure could be constructed and compare its dynamic adsorptive capacity with that obtained from a fixed bed of adsorbent particles having uniform size.

2. System formulation and mathematical model

A stratified packed bed of total length L is considered and is represented by the connected in a continuous sequence set of the fixed-bed sections S_i (i=1,2,3,..,N) as shown in Fig. 1 where each section has a length L_i (i=1,2,3,..,N) such that $L=\sum_{i=1}^{N} L_i$, and $C_{d,in}$ and $C_{d,out}$ represent the inlet and outlet concentrations of the adsorbate, respectively. The lengths, L_i (i=1,2,3,...,N), of the fixed-beds could be related through the expression

$$\frac{L_i}{L_{i+1}}=\alpha_i, \qquad i=1,2,3,..,N-1 \tag{1}$$

where the parameter α_i could have a constant value. In each section of length L_i (i=1,2,3,..,N), spherical porous adsorbent particles of radius $R_{p,i}$ (i=1,2,3,..,N) with a partially fractal structure are packed, and the values of the radii of the particles are related through the expression

$$\frac{R_{p,i}}{R_{p,i+1}}=\beta_i\,, \qquad i=1,2,3,..,N-1 \tag{2}$$

where the parameter β_i is greater than unity ($\beta_i>1$) for i=1,2,3,..,N-1, and, thus, $R_{p,1}>R_{p,2}>R_{p,3}>\ldots>R_{p,N-1}>R_{p,N}$. Therefore, the fixed-bed of length L in Fig. 1 is a stratified packed bed with a decreasing radius of the packed porous adsorbent particles along the axial direction of the bed, as the flowing fluid stream moves from the inlet section to the outlet section of the bed. The porosity ε_i (i=1,2,3,..,N) in each fixed-bed section of the stratified packed bed is taken to have the same value, ε, and, thus, $\varepsilon_i=\varepsilon$ (i=1,2,3,..,N). In such a stratified packed bed adsorber, the value of the film mass transfer coefficient, $K_{f,i}$, of the adsorbate solute increases as it moves from the inlet section to the outlet section of the column while the lengths of the intraparticle diffusional pathways of the adsorbate in the porous adsorbent spherical particles decrease, and the combination of these two effects would lead to an average mass transfer rate in the stratified packed bed that would be larger than the average mass transfer rate in a fixed-bed of length L packed only with adsorbent particles of radius $R_{p,1}$.

Furthermore, the spherical porous adsorbent particles packed in each section of the stratified bed have a partially fractal structure which means that a porous adsorbent particle of a given radius is considered to be made by smaller in radius porous adsorbent particles which themselves are made by even smaller in radius porous adsorbent particles and so on. Thus, we can relate [1] the radius, $R_{p,i}$, of a given spherical adsorbent particle to the radius, $R_{m,i,j+1}$, of the microspheres that make up the particle of radius $R_{p,i}$ through the expression given in Eq.(3) where it is considered that the porosity $\varepsilon_{m,i,j+1}$ of each microsphere of radius $R_{m,i,j+1}$ is equal to the porosity $\varepsilon_{p,i}$ of the adsorbent particle of radius $R_{p,i}$

$$R_{m,i,j+1}=\tau_i^j R_{p,i}, \quad i=1,2,3,\ldots,N \text{ and } j=0,1,2,3,\ldots,N' \qquad (3)$$

In Eq.(3) i denotes the adsorbent particles packed in section S_i of the stratified bed, $R_{m,i,j+1}$ represents the radius of the microspheres that make up the adsorbent particle of radius $R_{p,i}$ after j divisions, N′ denotes the total number of divisions (the total number of recursions of the fractal), and τ_i represents the ratio of the radii between smaller and larger spherical particles that make up the adsorbent particles of radius $R_{p,i}$. It is important to mention here that the term ‘microsphere’ is used in this work to provide a convenient generic name for all particles whose radii $R_{m,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,3,…,N′) are smaller than the radius $R_{p,i}$ of a given porous adsorbent particle in section S_i of the stratified bed. Of course, the porous structure of the partially fractal adsorbent particle of radius $R_{p,i}$ has been formed by gluing together the microspheres of radius $R_{m,i,j+1}$ at each division j; it is important to mention here that the gluing process of the microspheres at each level of division j has to provide a strong enough structure among the glued microspheres so that the adsorbent particles of radius $R_{p,i}$ are structurally strong and do not disintegrate by the applied pressure drop required to maintain a desirable superficial fluid velocity through the bed of the packed column. The value of τ_i in Eq. (3) is less than unity ($\tau_i < 1$) and the value of N′ is finite; it is worth noting that the term τ_i^j in Eq. (3) becomes smaller as the value of j increases. For a complete fractal $N'=\infty$, and this value of N′ is not considered here because in this case the linear dimension (size) of the smallest pores in the adsorbent particles would be equal to zero and these smallest pores would not allow the transport of water molecules and adsorbate solute [1]. Therefore, the value of N' has to be finite and have a magnitude such that all pores in the partially fractal adsorbent particles have linear dimensions (sizes) that could allow the effective transport of solvent and adsorbate solute. It should be noted here that for a given porous adsorbent particle of radius $R_{p,i}$, and a given value of τ_i , the total internal (intraparticle) wetted surface area, $A_{ws,i}$, of the particle increases as the total number of divisions, N', increases, because the number of smaller in size pores in the partially fractal adsorbent particle of radius, $R_{p,i}$, increases with increasing N'. Therefore, the partially fractal adsorbent particles of different radii packed in the stratified packed bed can provide not only a variation in the lengths of the intraparticle diffusional pathways of the adsorbate solute as it moves from the inlet section to the outlet section of the packed bed, but can also provide a varying internal adsorption surface area which can significantly affect the rate [1, 7, 20-22] at which adsorption takes place. In Fig.2, schematic representations of partially fractal adsorbent particles with $N'=1$, $N'=2$, and $N'=3$ are presented.

In the systems studied in this work, the pressures employed for maintaining the superficial velocity, V_f, of the flowing liquid stream to have the same value in every section of the stratified column bed, are such that insignificant viscous heating occurs and the liquid stream behaves everywhere in the column as an incompressible fluid. It is important to discuss at this point the fact that in a stratified packed bed where the porosity ε_i of each packed section does not vary and is equal to a constant bed porosity value ε ($\varepsilon_i=\varepsilon$, $i=1,2,3,..N$), the pressure drop, ΔP_i, required to be applied along the length L_i of each packed section of the stratified bed has to be different if the superficial velocity, $V_{f,i}$, of the flowing fluid stream is required to have the same value V_f in each section of the stratified packed bed, that is, $V_{f,i} = V_f$ for i=1,2,3,…,N. For example, if the stratified bed is comprised of two sections (i=1, 2) whose lengths are L_1 and L_2, respectively, and if $\varepsilon_1=\varepsilon_2=\varepsilon$ and $V_{f,1}=V_{f,2}=V_f$, then it can be easily shown through the use of the Blake-Kozeny equation [23] for laminar flow in packed beds that

$$\Delta P_{sb} = \frac{\Delta P_{fb}}{L}\left[L_1 + L_2\left(\frac{R_{p,1}}{R_{p,2}}\right)^2\right] \tag{4}$$

where ΔP_{sb} represents the pressure drop in the stratified bed of length L ($L=\sum_{i=1}^{2} L_i$), and the sections of the beds of length L_1 and L_2 are packed with particles of radius $R_{p,1}$ and $R_{p,2}$, respectively, with $R_{p,1}$ greater than $R_{p,2}$ ($R_{p,1} > R_{p,2}$). In Eq. (4), ΔP_{fb} represents the pressure drop across a column whose bed of length L is packed with particles whose radius is equal to $R_{p,1}$. If the stratified bed has three or more packed bed sections, one can easily obtain through the employment of the Blake-Kozeny equation the relationships between the pressure drops required in the different sections of the stratified bed so that the value of the superficial velocity of the flowing fluid stream remains unchanged in each section of the stratified bed. Thus, in the operation of a stratified bed it would be desirable to be able to control the pressure drop along the packed sections of the column. The discussion in this paragraph indicates that the values of the parameters α_i and β_i in Eqs. (1) and (2) would be in part determined from considerations of minimizing the energy required for flow along the length of the stratified bed so that the specified value of the superficial velocity of the flowing fluid stream is realized and maintained. Furthermore, the parameters τ_i and N' in Eq. (3) would be determined from considerations of maximizing both the rate of intraparticle mass transfer and the rate of adsorption of the adsorbate onto the surface of the pores of the adsorbent particles, as well as from the technological capabilities and limitations of constructing microspheres of different radii and controlled porosity and gluing them strongly together to form the porous adsorbent particles that have a partially fractal structure. Also, since (i) the length, L_i, of each section of the stratified bed affects the mean residence time of the adsorbate in each section which in turn affects the overall mass transfer rate of the solute in each section, and (ii) the magnitude of the radius, $R_{p,i}$, of the particles packed in each section of the stratified bed affects the mass transfer rate of the adsorbate in the particles packed in each section, it is important to indicate here that the values of the parameters α_i and β_i in Eqs. (1) and (2) would be in part determined from mass transfer considerations as well. Thus, the discussion and expressions presented in the above paragraphs indicate that a stratified bed whose different sections are packed with porous adsorbent particles of different radii and which have a partially fractal structure, provides to the designer and user of chromatographic media and column systems more degrees of freedom with respect to the number of parameters and variables that could be manipulated (controlled) in designing, constructing, and operating a chromatographic adsorption system that could significantly reduce the dispersion of the propagating along the column mass front of the adsorbate, and maintaining a high dynamic adsorption capacity and separation efficiency for a given throughput requirement than the currently used in practice conventional chromatographic systems.

In order to simulate the dynamic behavior of the stratified packed bed whose porous adsorbent particles have a partially fractal structure, a mathematical model that properly accounts for the mass transfer and adsorption mechanisms involved in the stratified adsorption system is needed. It is indeed fortunate for us that the mathematical model of Heeter and Liapis [5, 7] can, after the introduction of some small changes, be adapted to simulate the stratified packed bed adsorber presented in this work. Heeter and Liapis [5, 7] considered porous adsorbent particles whose partially fractal structure had a value for the number of recursions of the fractal, N′, equal to one (N′=1), and their column was packed with porous adsorbent particles of only a single size radius along the whole column length. It is tedious but rather straightforward to extend the model of Heeter and Liapis [5, 7] for the mass transfer and adsorption of adsorbate in porous adsorbent particles whose partially fractal structures have values of N′ greater than one, by simply adding to their model the differential material balance equation of the adsorbate for each additional size of microsphere considered in the partially fractal structure of the porous adsorbent particles until all sizes of microspheres that correspond up to the desired value of N′ have been considered. Furthermore, the boundary condition at the surface of the porous adsorbent particles given by Eq. (16) of Heeter and Liapis [5], should be replaced by the following expression:

$$\text{at } R=R_{p,i}, \qquad -D_{p,i}\left.\frac{\partial C_{p,i}}{\partial R}\right|_{R=R_{p,i}} = K_{f,i}\left(C_{p,i}\big|_{R=R_{p,i}} - C_{d,i}\right), \quad i=1,2,3,..,N \qquad (5)$$

In Eq. (5), $D_{p,i}$ denotes the effective pore diffusion coefficient of the adsorbate in the porous adsorbent particles of radius $R_{p,i}$, R represents the radial distance in the particle, $C_{p,i}$, denotes the concentration of the adsorbate in the pore fluid of the adsorbent particle, $C_{d,i}$ is the concentration of the adsorbate in the flowing fluid stream, $K_{f,i}$ is the film mass transfer coefficient of the adsorbate, and the subscript i indicates the section of the stratified bed. The values of $K_{f,i}$ (i=1,2,3,..,N) could, for a given stratified packed bed, be estimated from the correlations presented in References [16,17].

The differential material balance equation for the adsorbate in the flowing fluid stream which is given by Eq. (1) of Heeter and Liapis [5], has to be solved for each section of length L_i (i=1,2,3,..,N) of the stratified packed bed presented here. It is worth noting that the exiting stream from each section of length L_i where i=1,2,3,..,N-1, becomes an inlet stream to the section following the section of length L_i, and, therefore,

$$C_{d,out}\Big|_{x=L_i} = C_{d,in}\Big|_{x=L_{i+1}}, \text{ i=1, 2, 3,..,N-1} \tag{6}$$

In Eq.(6), $C_{d,out}\Big|_{x=L_i}$ and $C_{d,in}\Big|_{x=L_{i+1}}$ denote the concentration of the adsorbate in the flowing fluid stream exiting and entering specific sections of the stratified bed indicated by the lengths L_i and L_{i+1}, respectively, and the variable x represents the axial distance in the column. In this work, intraparticle fluid flow [1, 3-7, 9, 10] is not considered and it is taken that the transport of the adsorbate in the porous adsorbent particles occurs by diffusion; therefore, in the model of Heeter and Liapis [5] the value of their parameter F is taken to be equal to zero which implies that the intraparticle Peclet number becomes equal to zero and the adsorbent particles are purely diffusive.

3. Results and discussion

The stratified column beds studied in this work are packed with porous particles having partially fractal structures with the value of the total number of recursions of the fractal, N′, being equal to 1 (N′=1) for all porous adsorbent particles. All columns have the same diameter and total length, L. The values of the parameters that remain constant for the adsorption systems considered here are listed in Table 1. The parameters $k_{1,i}$, $k_{2,i}$, and

$C_{T,i}$, characterize the dynamic adsorption mechanism of the adsorbate being adsorbed onto the active sites on the surface of the pores of the particles, as is indicated in the interaction kinetics expression presented in Eq. (22) of the work of Heeter and Liapis [5]; when adsorption equilibrium occurs, $C_{T,i}$ and $K_i = k_{1,i}/k_{2,i}$ represent the parameters of the equilibrium Langmuir adsorption isotherm [5,13]. The values of the parameters in Table 1 are from adsorption systems reported in the literature [1, 3-10, 14, 21, 22, 24-27] and, for the purposes of the simulations of this study, are considered to have appropriate magnitudes since they characterize adsorption systems of practical use. Stratified column beds of two ($N = 2$, $L=\sum_{i=1}^{2} L_i$) and three ($N = 3$, $L = \sum_{i=1}^{3} L_i$) sections are investigated in this work, and, thus, the values of the parameters N, L_i, $R_{p,i}$, α_i, β_i, and τ_i (for $i = 1,2,\ldots,N$) were varied, as indicated in Table 2. Because in Table 1 $\varepsilon_i = \varepsilon = 0.35$ for $i = 1,2,\ldots,N$, it is important to note that the fraction of the volume of each section S_i of the stratified packed bed column occupied by the adsorbent particles is the same. Furthermore, since the porosities, $\varepsilon_{p,i}$ of the adsorbent particles and those of the microspheres, $\varepsilon_{m,i,j+1}$ are taken to be equal ($\varepsilon_{p,i} = 0.60$ and $\varepsilon_{m,i,j+1} = 0.60$ for $i =1,2,\ldots,N$ and $j = 0,1,2,\ldots,N'$, as shown in Table 1) and by considering that $\varepsilon_{p,i}$ and τ_i could be constant for all additional divisions, then the characteristic dimension of the pores of size $\lambda_{m,i,j+1}$ after j divisions is given by

$$\lambda_{m,i,j+1}=\tau_i^j \lambda_{p,i} \quad \text{for } i=1,2,\ldots,N \text{ and } j=0,1,2,\ldots,N' \qquad (7)$$

The volume of each of the pores of characteristic dimension $\lambda_{m,i,j+1}$ is proportional to $(\tau_i^j \lambda_{p,i})^3$, and, thus, the number of pores of characteristic size $\lambda_{m,i,j+1}$ is

$$n_{m,i,j+1}=\gamma \left(\frac{V_{p,i} \; \varepsilon_{p,i} \; (1-\varepsilon_{p,i})^j}{(\tau_i^j \lambda_{p,i})^3}\right) \quad \text{for } i = 1,2,\ldots,N \text{ and } j = 0,1,2,\ldots,N' \qquad (8)$$

In Eqs. (7)–(8), $\tau_i < 1$ (see Eq. (3)), the parameter $\lambda_{p,i}$ represents the characteristic dimension of the pores in the adsorbent particles of radius $R_{p,i}$ (i =1,2,…,N) and could be determined from an expression characterizing the packing structure [1, 28] of the microspheres of division j = 1, while $\lambda_{m,i,j+1}$ denotes the characteristic dimension of the pores in the microspheres of the adsorbent particles having radius $R_{p,i}$ (i = 1,2,…,N) after j divisions (j = 0,1,2,…,N′). In Eq. (8), γ is a proportionality constant. By considering a geometrical shape for the pores (i.e., cylindrical geometry), then an estimate for the value of the total internal wetted surface area $A_{ws,i}$ for the particles of radius $R_{p,i}$ (i = 1,2,…,N) could be obtained. The data in Table 1 indicate that, in this work, the value of the total number of recursions of the fractal N′ was taken to be equal to one (N′ = 1).

The value of the film mass transfer coefficient $K_{f,i}$ was determined from the correlation developed by Wilson and Geankoplis [16] for given values of $R_{p,i}$, $V_{f,i}$, ε_i, of the free molecular diffusion coefficient, D_{fm}, of the adsorbate and of the viscosity and density of the solution. When $\varepsilon_i = \varepsilon$ = constant and $V_{f,i} = V_f$ = constant for i = 1,2,3,…,N, it can be shown that

$$K_{f,i+1} = K_{f,i}\left[\left(\frac{R_{p,i}}{R_{p,i+1}}\right)^{0.66}\right] \text{ for i = 1,2,3,…,N-1} \tag{9}$$

where $R_{p,i} > R_{p,i+1}$ for i = 1,2,3,…,N-1. The axial dispersion coefficient D_{L_i} (i = 1,2,3,…,N) in each section of the stratified bed is taken to be approximately equal to zero because for the systems studied here the formal quantitative criterion developed by Mears [29] is satisfied and, thus, axial dispersion effects can be neglected.

The criterion that is used to compare the performance of the different stratified column beds is the breakthrough time, t_b. In this study, the breakthrough time, t_b, is defined as the time when the concentration, $C_{d,out}$, of the adsorbate in the outlet stream from the column becomes equal to 1% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column [7, 21]. In Tables 2-4 the values of the breakthrough time, t_b, are listed for the adsorption systems studied in this work as well as the times when the concentration of the adsorbate in the column outlet stream becomes equal to 5% and 10% of the inlet concentration of the adsorbate in the column.

In Table 2, simulation results are presented from a conventional column whose length is 0.5 m and where (i) in case A the column is packed with porous adsorbent particles which do not have a partially fractal structure and (ii) in case B the column is packed with porous adsorbent particles which have a partially fractal structure with the total number of recursions of the fractal being equal to one (N'=1). The results in case A show that the breakthrough time increases as the radius of the porous adsorbent particles decreases because the film mass transfer coefficient increases as the radius of the particles decreases and also the average length of the pathways for the diffusion of the adsorbate in the porous space of the adsorbent particles decreases as the particle size decreases; thus, the overall resistance to the mass transfer of the adsorbate in the particles decreases as the particle size decreases. Furthermore, as the particle size decreases the total surface area of the channels for bulk flow formed from the packed in the column particles increases [1, 16]. Therefore, the average along the column mass transfer rate of the adsorbate leaving the flowing fluid stream and arriving at the surface of the particles through the hydrodynamic boundary layer increases as the size of the particles decreases because the mass transfer rate is determined from the product of the mass flux of the adsorbate with the total surface area of the channels for bulk flow. The increase in the mass transfer rate of the adsorbate from the flowing fluid stream to the surface of the particles and the reduction in the overall resistance to mass transfer of the adsorbate in the particles which are realized as the particle size decreases, lead to larger breakthrough times, and, thus, better utilization of the adsorptive capacity of the packed column. The results for case B in Table 2 where the packed in the column particles have a partially fractal structure with N'=1, show that for a given particle size, $R_{p,1}$, the breakthrough time increases as the radius, $R_{m,1,2}$, of the microspheres (from which the particle of radius $R_{p,1}$ is made) decreases, and this is equivalent to increasing the value of the ratio $1/\tau_1$ in Table 2. The physical reasons for explaining the increases in the breakthrough time as the size of the microspheres decreases, are that (a) the length of the pathways for the diffusion of the adsorbate in the microspheres decreases and this results to a smaller resistance for mass transfer in the microspheres and a larger adsorbate concentration gradient in the fluid in the pores of the microspheres which provides a larger mass flux for the adsorbate in the microspheres, and (b) the total internal wetted surface area, $A_{ws,1}$, of the pores of the adsorbent particle increases as the size of the microspheres from which the particle is made decreases [1], and this leads to the increase of the average mass transfer rate of the adsorbate in the particle; it is important to indicate here that because the total internal wetted surface area of the pores of the adsorbent particles increases as the size of the microspheres decreases, the total amount of adsoptive active sites (e.g., immobilized ligands) in such particles could be expected to be larger than that found when the same in size adsorbent particles would have been constructed from larger in size microspheres. The results in Table 2 clearly show that the performance of the columns packed with adsorbent particles having a partially fractal structure is significantly superior (much larger breakthrough times are realized) than that obtained when the columns are packed with adsorbent particles which do not have a partially fractal structure. It is also observed from the data in Table 2 that the column performance increases as the radius $R_{p,1}$ of the packed adsorbent particles decreases and the ratio $1/\tau_1$ increases (note that the ratio $1/\tau_1$ increases as the radius of the microspheres decreases); the physical reasons for these results were discussed in detail above. In Figure 3, the breakthrough curves for the column systems of Table 2 employing adsorbent particles of radius $R_{p,1}=50\times10^{-6}$ m are presented. The data on Figure 3 clearly show that the breakthrough curves of the columns packed with adsorbent particles having a partially fractal structure are significantly sharper than the breakthrough curve obtained from the column packed with adsorbent particles which do not have a partially fractal structure, and, furthermore, the degree of sharpness increases significantly as the value of $1/\tau_1$ increases from 3 to 10. When the value of $1/\tau_1$ is increased from 10 to 20, the increases in the breakthrough time (see Table 2) and sharpness of the breakthrough curve are not as large as are in the case where $1/\tau_1$ is increased from 3 to 10; this is also the trend for the systems of case B in Table 2 whose values of $R_{p,1}$ are 75×10^{-6} m, and 25×10^{-6} m, respectively. This trend implies that, for the operating conditions and parameter values employed in the column systems of case B in Table 2, (i) the increase in the total internal wetted surface area, $A_{ws,1}$, of the pores of the adsorbent particles and (ii) the shorter in length diffusion pathways that are realized when the radius, $R_{m,1,2}$, of the microsphere is decreased, lead to a larger mass transfer rate for the adsorbate and the relative increase in the magnitude of the mass transfer rate is becoming smaller as the value of the radius, $R_{m,1,2}$, of the microsphere is further reduced.

In Tables 3 and 4 simulation results obtained from stratified column beds packed with porous adsorbent particles having a partially fractal structure are presented, when the columns involve two and three sections, respectively; in all cases, the total length, L, of each stratified column bed is 0.5 m. For the stratified beds, the values of the parameters $R_{p,1}$, α_i, β_i and $1/\tau_i$ are varied in order to ascertain their effects on the breakthrough time; it is important to indicate here that the values of α_i, β_i, and $1/\tau_i$ have the same magnitude in every section of the stratified packed beds considered in Tables 3 (i=1, 2) and 4 (i=1, 2, 3). The results show that the value of the radius, $R_{p,1}$, of the adsorbent particles packed in the first section of the stratified bed has a very important effect on the column performance, indicating that the breakthrough time increases very significantly when the value of $R_{p,1}$ is decreased due to the physical reasons discussed above, as well as due to the fact that as the value of $R_{p,1}$ is decreased in section one of the stratified bed, the subsequent sections of the bed are formed by packing particles having radii smaller than $R_{p,1}$ since in the stratified bed it is required to have $R_{p,1}>R_{p,2}>R_{p,3}$, and, thus, if the selected value of $R_{p,1}$ is small, then the smaller radii of the particles packed in the subsequent sections of the stratified bed will maintain an overall large mass transfer rate for the adsorbate and this leads to shorter breakthrough times; indeed this is the case, as the results in Tables 3 and 4 indicate. As the number, N, of the sections in the stratified bed is increased, then for a selected value of $R_{p,1}$ and when the values of the parameters α_i, β_i, and $1/\tau_i$ are kept constant, the breakthrough time of the stratified bed with three sections is significantly larger than that of a stratified bed employing two sections because the third section of the stratified bed with three sections is made from packed particles whose radius is smaller than the radius of the particles packed in the second section of the stratified bed having two sections, and this leads to a higher total mass transfer rate in the stratified bed comprised of three sections.

By examining the results in Tables 3 and 4, one can observe that apart from the very significant effect that the values of $R_{p,1}$ and N have on the breakthrough time, t_b, as discussed above, the values of β_i and $1/\tau_i$ also have a very important effect on the value of the breakthrough time. As the values of β_i and $1/\tau_i$ increase, when the values of $R_{p,1}$, N, and α_i are kept constant, it is observed that there is a significant increase in the breakthrough time. The effect of $1/\tau_i$ on the breakthrough time is larger when the magnitude of $1/\tau_i$ is increased from 3 to 10 while the relative influence of $1/\tau_i$ on the breakthrough time is smaller when the value of $1/\tau_i$ is increased from 10 to 20; this indicates that for the systems examined in this work, the relative increase in the mass transfer rate of the adsorbate is becoming smaller as the value of the radius of the microsphere, $R_{m,1,2}$, is further reduced. The effect of decreasing the value of α_i from 1.5 to 1.0 is to increase the breakthrough time, as expected, but the increase in the magnitude of the breakthrough time obtained from (a) a decrease in the value of $R_{p,1}$ and (b) increases in the values of N, β_i, and $1/\tau_i$, is significantly more substantial than that obtained from reducing the value of α_i. Furthermore, by comparing the results on Table 2 with those on Tables 3 and 4 it is clearly observed that the stratified column beds provide significantly larger breakthrough times than those obtained from conventional column beds.

In Figure 4 the breakthrough curves for the column systems of Tables 3 and 4 with $R_{p,1}=50\times10^{-6}$ m, $\alpha_i=1.5$, $\beta_i=1.5$ and when the values of $1/\tau_i$ are equal to 3, 10, and 20, are plotted for a stratified column bed comprised of two (N=2)) or three (N=3) sections;

in all cases, the total length, L, of the stratified column bed is 0.5 m. The results in Figure 4 clearly show that when the values of the parameters α_i, β_i, and $1/\tau_i$ have the same magnitude in each section of the stratified column bed, then the breakthrough times and the sharpness of the breakthrough curves increase as the number, N, of the sections in the stratified column bed increases. It can also be observed that breakthrough curves 3 and 4 obtained from a stratified column bed with N=2 and whose values for the parameter $1/\tau_i$ are equal to 10 and 20, respectively, provide a larger breakthrough time than that obtained from a stratified column bed with N=3 and $1/\tau_i=3$; this result strongly indicates the significant increase that can be realized in the mass transfer rate of the adsorbate by employing microspheres with lower values of $R_{m,1,2}$ which make the value of $1/\tau_i$ to become larger. Of course, when in the stratified column bed with N=3 the values of $1/\tau_i$ are equal to 10 and 20, respectively, then breakthrough curves 5 and 6 show that the breakthrough times obtained from these systems are larger and the shape of the curves is sharper than those obtained from breakthrough curves 3 and 4.

4. Conclusions and remarks

It was first shown in this work that conventional columns packed with porous adsorbent particles having a partially fractal structure provide larger breakthrough times and utilization of the adsorptive capacity of the column when compared with the performance obtained from conventional columns employing porous adsorbent particles which do not have a partially fractal structure. The physical mechanisms responsible for the occurrence of this difference in performance were also presented and discussed. Then stratified column bed systems whose sections are formed by packing adsorbent particles with a partially fractal structure were proposed and studied. The simulation results clearly showed that (1) the breakthrough times and (2) the shape of the breakthrough curves obtained from stratified column beds, are significantly larger and sharper, respectively, than those obtained from conventional columns, and, furthermore, the superior performance provided by the stratified column beds can be improved by increasing the values of the parameters N, β_i, and $1/\tau_i$, and decreasing the value of the parameter α_i, as discussed above. The stratified column beds provide to the designer and user of chromatographic media and column systems more degrees of freedom with respect to the number of parameters and variables that could be controlled in the design, construction, and operation of efficient chromatographic adsorption systems.

The results from the stratified column beds suggest that such column systems could provide a higher dynamic adsorptive capacity than conventional columns when it is required to increase the column throughput (increase the superficial velocity of the flowing fluid stream). Furthermore, the concepts which are relevant to stratified beds and porous media having a partially fractal structure could also prove useful in the design, construction, and operation of packed beds involving chemical and biochemical catalysis, as well as in fluidized and expanded beds.

5. Nomenclature

$A_{ws,i}$	total internal wetted surface area of particles of radius $R_{p,i}$ (i=1,2,3,…,N), m^2
$C_{d,i}$	concentration of adsorbate in the flowing fluid stream in section i (i=1,2,3,…,N), kg/m^3
$C_{d,in}$	inlet concentration of adsorbate in the column, kg/m^3
$C_{d,in}\big\|_{x=L_{i+1}}$	inlet concentration of adsorbate in section L_{i+1} of the column (i=1,2,3,…,N-1), kg/m^3
$C_{d,out}$	outlet concentration of adsorbate from the column, kg/m^3
$C_{d,out}\big\|_{x=L_i}$	outlet concentration of adsorbate from section L_i of the column (i=1,2,3,…,N), kg/m^3
$C_{p,i}$	concentration of adsorbate in the pore fluid of particles of radius $R_{p,i}$ (i=1,2,3,…,N), kg/m^3
$C_{T,i}$	maximum equilibrium concentration of adsorbate in the adsorbed phase of the adsorbent particles of radius $R_{p,i}$ (i=1,2,3,…,N), kg/m^3 of adsorbent particle
D_{fm}	free molecular diffusion coefficient of adsorbate, m^2/s
D_{L_i}	axial dispersion coefficient of adsorbate in section S_i (i=1,2,3,…,N) of stratified bed, m^2/s
$D_{p,i}$	effective pore diffusion coefficient of adsorbate in the pore fluid of particles of radius $R_{p,i}$ (i=1,2,3,…,N), m^2/s
$D_{p,m,i,j+1}$	effective pore diffusion coefficient of adsorbate in the pore fluid of the microspheres of radius $R_{m,i,j+1}$ where i=1,2,3,…,N and j=0,1,2,3,…,N′, m^2/s
$k_{1,i}$	adsorption rate constant in the adsorbent particles of section S_i (i=1,2,3,…,N), $m^3/(kg\ s)$
$k_{2,i}$	desorption rate constant in the adsorbent particles of section S_i (i=1,2,3,…,N), s^{-1}

K_i	equilibrium adsorption constant of adsorbate in the particles of section S_i ($K_i=k_{1,i}/k_{2,i}$ for i=1,2,3,…,N), m^3/kg
$K_{f,i}$	film mass transfer coefficient of adsorbate in section S_i (i=1,2,3,…,N), m/s
L	total column length, m
L_i	length of section S_i of stratified bed (i=1,2,3,…,N), m
$n_{m,i,j+1}$	number of pores of characteristic size $\lambda_{m,i,j+1}$
N	total number of sections of stratified bed
N′	total number of recursions of the fractal (total number of divisions)
R	radial distance in adsorbent particle, m
$R_{p,i}$	radius of adsorbent particles in section S_i (i=1,2,3,…,N), m
$R_{m,i,j+1}$	radius of the microspheres in the particles of radius $R_{p,i}$ (i=1,2,3,…,N) after j divisions (j=0,1,2,…,N′), m
S_i	section i of stratified bed (i=1,2,3,…,N)
t	time, s
T	temperature, K
t_b	breakthrough time, s
V_f	superficial velocity of fluid in a column, m/s
$V_{f,i}$	superficial velocity of fluid in section S_i (i=1,2,3,…,N) of stratified column bed, m/s
$V_{p,i}$	volume of the particle of radius $R_{p,i}$ (i=1,2,3,…,N), m^3
x	axial distance, m

Greek letters

α_i	parameter defined by Eq. (1), i=1,2,3,…,N
β_i	parameter defined by Eq. (2), i=1,2,3,…,N
γ	proportionality constant in Eq. (8)

ΔP_{fb}	pressure drop in a column of length L packed with particles of radius $R_{p,1}$, kg m^{-1} s^{-2}
ΔP_i	pressure drop along the length L_i of section S_i (i=1,2,3,…,N), kg m^{-1} s^{-2}
ΔP_{sb}	pressure drop in a stratified bed of length L comprised of two sections such that $L=\sum_{i=1}^{2} L_i$, kg m^{-1} s^{-2}
ε_i	bed porosity in section S_i (i=1,2,3,…,N) of stratified bed
$\varepsilon_{p,i}$	porosity in particles of radius $R_{p,i}$ (i=1,2,3,…,N)
$\varepsilon_{m,i,j+1}$	porosity in the microspheres of radius $R_{m,i,j+1}$ where i=1,2,3,…,N and j=0,1,2,3,…,N′
$\lambda_{m,i,j+1}$	linear characteristic dimension of pores in the microspheres of particles of radius $R_{p,i}$ (i=1,2,3,…,N) after j divisions (j=0,1,2,…,N′), m
$\lambda_{p,i}$	linear characteristic dimension of pores in particles of radius $R_{p,i}$ (i=1,2,3,…,N), m
μ	viscosity of solution, kg m^{-1} s^{-1}
ρ	density of solution, kg/m^3
τ_i	parameter defined by Eq. (3), i=1,2,3,…,N

Subscripts

i	denotes the section number in a stratified bed, i=1,2,3,…,N
j	denotes the division (recursion) number of the fractal, j=0,1,2,…,N′

6. References

[1] Liapis, A. I., *Math. Model. Sci. Comput*. 1993, *1*, 397-414.

[2] Avnir, D. (Editor), *The Fractal Approach to Heterogeneous Chemistry*, John Wiley and Sons, New York 1989.

[3] Liapis, A. I., Xu, Y., Crosser, O.K., Tongta, A., *J. Chromatogr. A* 1995, *702*, 45-57.

[4] Xu, Y., Liapis, A. I., *J. Chromatogr. A* 1996, *724*, 13-25.

[5] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A* 1995, *711*, 3-21.

[6] Heeter, G. A., Liapis, A. I. *J. Chromatogr. A* 1996, *734*, 105-123.

[7] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A* 1996, *743*, 3-14.

[8] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A* 1997, *760*, 55-69.

[9] Meyers, J. J., Liapis, A. I., *J. Chromatogr. A* 1998, *827*, 197-213.

[10] Meyers, J. J., Liapis, A. I., *J. Chromatogr. A* 1999, *852*, 3-23.

[11] Mathews, A. P., *Fundamentals of Adsorption*, Liapis, A.I. (Editor), Engineering Foundation, New York 1987, pp. 345-354.

[12] Rosen, J. B., *J. Phys. Chem*. 1952, *20*, 387-393.

[13] Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, John Wiley and Sons, New York 1984.

[14] Do, D. D., *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press, London, United Kingdom, 1998.

[15] Liapis, A. I., Rippin, D. W. T., *AIChE J*. 1979, *25*, 455-460.

[16] Wilson, E. J., Geankolpis, C. J., *Ind. Eng. Chem. Fund*. 1966, *5*, 9-17.

[17] Foo, S. C, Rice, R. G., *AIChE J*. 1975, *21*, 1149-1156.

[18] Riccardi, E., Wang, J.-C., Liapis, A. I., *J. Phys. Chem. B* 2008, *112*, 7478-7488.

[19] Riccardi, E., Wang, J.-C., Liapis, A. I., *J. Phys. Chem. B* 2009, *113*, 2317-2327.

[20] Riccardi, E., Wang, J.-C., Liapis, A. I., *J. Chem. Phys*. 2010, *133*, 084904-1-084904-12.

[21] Liapis, A. I., Riccardi, E., Wang, J.-C., J. Sep. Sci 2010, 33, 2749-2756.

[22] Wang, J.-C., Liapis, A. I., Chemie Ingenieur Technik 2011, 83, 152-165.

[23] Bird, R. B., Stewart, W. E., Lightfoot, E.N., Transport Phenomena, 2nd Edition, Wiley and Sons, New York, 2002.

[24] Arnold, F. H., Blanch, H. W., Wilke, C. R., *Chem. Eng. J.* 1985, *30*, B9-B24.

[25] Arnold, F. H., Blanch, H. W., Wilke, C. R., *Chem. Eng. J.* 1985, *30*, B25-B36.

[26] Riccardi, E., Liapis, A. I., *J. Sep. Sci.* 2009, *32*, 4059-4068.

[27] Unger, K. K., Ditz, R., Machtejevas, E., Skudas, R., *Angew. Chem. Int. Ed.* 2010, *49*, 2300-2312.

[28] Liapis, A. I., Bruttini, R., *Int. J. Heat Mass Transf*. 2009, *52*, 100-111.

[29] Mears, D. E., *Ind. Eng. Chem. Fundamentals* 1976, *15*, 20-31.

Table 1. Common values of the parameters used in the adsorption systems of this study. The adsorbate (solute) considered in this work is BSA.

$C_{d,in} = 0.10$ kg/m^3, $C_{T,i} = 78.3$ kg/m^3 particle for $i = 1,2,3,\ldots,N$

$D_{fm} = 6.70\times10^{-12}$ m^2/s, $D_{L_i} \cong 0$ m^2/s for $i = 1,2,3,\ldots,N$

$D_{p,i} = 2.50\times10^{-12}$ m^2/s for $i = 1,2,3,\ldots,N$

$D_{p,m,i,j+1} = 2.50\times10^{-12}$ m^2/s for $i = 1,2,3,\ldots,N$ and $j = 0,1,2,\ldots,N'$

$k_{1,i} = 1.05$ m^3 kg^{-1} s^{-1} for $i = 1,2,3,\ldots,N$

$k_{2,i} = 0.131$ s^{-1} for $i = 1,2,3,\ldots,N$

$K_i = k_{1,i}/k_{2,i} = 8.016$ m^3 kg^{-1} for $i = 1,2,3,\ldots,N$

$L = 0.50$ m

$N' = 1$

$T = 296.15$ K

$V_{f,i} = 2.778\times10^{-3}$ m s^{-1} for $i = 1,2,3,\ldots,N$

$\varepsilon_i = 0.35$ for $i = 1,2,3,\ldots,N$

$\varepsilon_{p,i} = 0.60$ for $i=1,2,3,\ldots,N$

$\varepsilon_{m,i,j+1} = 0.60$ for $i = 1,2,3,\ldots,N$ and $j = 0,1,2,\ldots,N'$

$\mu = 0.894\times10^{-3}$ kg m^{-1} s^{-1}

$\rho = 997$ kg/m^3

Table 2. Number of minutes needed for the outlet concentration, $C_{d,out}$, of the adsorbate from a conventional column bed to be equal to 1% (breakthrough time, t_b), 5%, and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the conventional column bed, for different values of $R_{p,1}$. Case A denotes that the column bed is formed by packing porous adsorbent particles which do not have a partially fractal structure. Case B denotes that the column bed is formed by packing porous adsorbent particles having a partially fractal structure with N'=1 and the parameter $1/\tau_1$ is given different values. In all cases, L=0.5 m and V_f=2.778x10^{-3} ms^{-1}.

Case	L (m)	$R_{p,1}$ (m)	$R_{m,1,2}$ (m)	$1/\tau_1$	Time, t (min)		
					1%	5%	10%
A	0.5	75×10^{-6}			1.10	1.26	2.30
A	0.5	50×10^{-6}			2.12	5.73	11.91
A	0.5	25×10^{-6}			42.90	113.54	189.17
B	0.5	75×10^{-6}	25×10^{-6}	3	1.53	4.45	9.94
B	0.5	75×10^{-6}	7.50×10^{-6}	10	6.79	28.63	61.43
B	0.5	75×10^{-6}	3.75×10^{-6}	20	17.76	56.51	94.71
B	0.5	50×10^{-6}	16.67×10^{-6}	3	9.71	36.38	76.91
B	0.5	50×10^{-6}	5.00×10^{-6}	10	57.16	141.30	213.90
B	0.5	50×10^{-6}	2.50×10^{-6}	20	86.81	166.01	231.28
B	0.5	25×10^{-6}	8.33×10^{-6}	3	215.34	406.34	538.32
B	0.5	25×10^{-6}	2.50×10^{-6}	10	356.46	520.20	627.54
B	0.5	25×10^{-6}	1.25×10^{-6}	20	372.42	529.80	634.14

Table 3. Number of minutes needed for the outlet concentration, $C_{d,out,}$, of the adsorbate from a stratified column bed comprised of two sections (N=2) and packed with particles having a partially fractal structure to be equal to 1% (breakthrough time, t_b), 5%, and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the stratified column bed, for different values of L_1, $R_{p,1}$, α_i, β_i, and $1/\tau_i$ where i=1, 2. In all cases, L = 0.5 m, N′ = 1, and $V_{f,i} = V_f = 2.778\times10^{-3}$ m s^{-1} for i=1, 2.

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	Time, t (min)		
						1%	5%	10%
2	0.30	75×10^{-6}	1.5	1.5	3	3.28	11.96	27.28
2	0.30	50×10^{-6}	1.5	1.5	3	26.62	87.45	163.10
2	0.30	25×10^{-6}	1.5	1.5	3	343.85	546.11	669.61
2	0.25	75×10^{-6}	1.0	1.5	3	3.96	14.84	33.52
2	0.25	50×10^{-6}	1.0	1.5	3	32.68	103.53	187.61
2	0.25	25×10^{-6}	1.0	1.5	3	375.50	577.76	697.99
2	0.30	75×10^{-6}	1.5	1.5	10	20.20	68.05	121.11
2	0.30	50×10^{-6}	1.5	1.5	10	111.90	220.52	305.62
2	0.30	25×10^{-6}	1.5	1.5	10	473.45	643.03	744.41
2	0.25	75×10^{-6}	1.0	1.5	10	25.04	79.63	136.58
2	0.25	50×10^{-6}	1.0	1.5	10	126.59	240.46	328.37
2	0.25	25×10^{-6}	1.0	1.5	10	501.91	670.88	769.52
2	0.30	75×10^{-6}	1.5	1.5	20	42.08	98.44	147.32
2	0.30	50×10^{-6}	1.5	1.5	20	139.20	239.09	318.07
2	0.30	25×10^{-6}	1.5	1.5	20	486.09	650.81	749.99
2	0.25	75×10^{-6}	1.0	1.5	20	49.09	109.38	160.91
2	0.25	50×10^{-6}	1.0	1.5	20	152.99	257.85	339.98
2	0.25	25×10^{-6}	1.0	1.5	20	513.94	678.36	774.91
2	0.30	75×10^{-6}	1.5	3.0	3	33.44	98.60	169.27
2	0.30	50×10^{-6}	1.5	3.0	3	160.21	300.59	401.13
2	0.30	25×10^{-6}	1.5	3.0	3	580.15	736.22	818.15
2	0.25	75×10^{-6}	1.0	3.0	3	52.97	142.03	228.29
2	0.25	50×10^{-6}	1.0	3.0	3	216.11	372.50	476.95
2	0.25	25×10^{-6}	1.0	3.0	3	663.25	806.74	877.40
2	0.30	75×10^{-6}	1.5	3.0	10	111.73	208.95	285.50
2	0.30	50×10^{-6}	1.5	3.0	10	278.10	415.84	506.36
2	0.30	25×10^{-6}	1.5	3.0	10	685.93	816.36	881.60
2	0.25	75×10^{-6}	1.0	3.0	10	146.69	259.67	343.19
2	0.25	50×10^{-6}	1.0	3.0	10	337.57	482.54	573.74
2	0.25	25×10^{-6}	1.0	3.0	10	760.22	877.31	932.39
2	0.30	75×10^{-6}	1.5	3.0	20	136.00	229.29	301.12
2	0.30	50×10^{-6}	1.5	3.0	20	297.26	428.62	515.86
2	0.30	25×10^{-6}	1.5	3.0	20	696.18	822.94	886.42
2	0.25	75×10^{-6}	1.0	3.0	20	172.00	277.38	356.38
2	0.25	50×10^{-6}	1.0	3.0	20	354.47	493.74	582.13
2	0.25	25×10^{-6}	1.0	3.0	20	769.13	882.98	936.55

Table 4. Number of minutes needed for the outlet concentration, $C_{d,out,}$, of the adsorbate from a stratified column bed comprised of three sections (N=3) and packed with particles having a partially fractal structure to be equal to 1% (breakthrough time, t_b), 5%, and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the stratified column bed, for different values of L_1, $R_{p,1}$, α_i, β_i, and $1/\tau_i$ where i=1, 2, 3. In all cases, L = 0.5 m, N′ = 1, and $V_{f,i} = V_f = 2.778\times10^{-3}$ m s^{-1} for i=1, 2, 3.

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	Time, t (min)		
						1%	5%	10%
3	0.237	75×10^{-6}	1.5	1.5	3	8.35	30.99	65.45
3	0.237	50×10^{-6}	1.5	1.5	3	63.18	168.67	271.03
3	0.237	25×10^{-6}	1.5	1.5	3	461.52	654.63	763.15
3	0.1667	75×10^{-6}	1.0	1.5	3	14.66	51.87	103.29
3	0.1667	50×10^{-6}	1.0	1.5	3	99.01	234.14	349.52
3	0.1667	25×10^{-6}	1.0	1.5	3	546.88	731.20	828.39
3	0.237	75×10^{-6}	1.5	1.5	10	48.18	121.55	187.31
3	0.237	50×10^{-6}	1.5	1.5	10	176.58	303.67	397.33
3	0.237	25×10^{-6}	1.5	1.5	10	579.31	741.09	829.88
3	0.1667	75×10^{-6}	1.0	1.5	10	73.78	162.86	236.79
3	0.1667	50×10^{-6}	1.0	1.5	10	226.31	365.47	464.45
3	0.1667	25×10^{-6}	1.0	1.5	10	655.90	808.89	887.46
3	0.237	75×10^{-6}	1.5	1.5	20	75.06	147.32	206.98
3	0.237	50×10^{-6}	1.5	1.5	20	199.86	318.47	407.43
3	0.237	25×10^{-6}	1.5	1.5	20	590.40	748.20	835.20
3	0.1667	75×10^{-6}	1.0	1.5	20	101.53	85.26	252.87
3	0.1667	50×10^{-6}	1.0	1.5	20	246.83	378.12	473.15
3	0.1667	25×10^{-6}	1.0	1.5	20	665.62	815.10	891.98
3	0.237	75×10^{-6}	1.5	3.0	3	280.03	400.85	475.58
3	0.237	50×10^{-6}	1.5	3.0	3	421.49	542.00	610.92
3	0.237	25×10^{-6}	1.5	3.0	3	794.38	903.98	950.37
3	0.1667	75×10^{-6}	1.0	3.0	3	421.91	551.96	624.18
3	0.1667	50×10^{-6}	1.0	3.0	3	603.65	716.59	772.23
3	0.1667	25×10^{-6}	1.0	3.0	3	970.51	1034.89	1050.85
3	0.237	75×10^{-6}	1.5	3.0	10	331.64	442.80	509.08
3	0.237	50×10^{-6}	1.5	3.0	10	523.01	635.66	696.27
3	0.237	25×10^{-6}	1.5	3.0	10	883.20	971.40	1003.20
3	0.1667	75×10^{-6}	1.0	3.0	10	487.51	601.94	663.25
3	0.1667	50×10^{-6}	1.0	3.0	10	696.86	795.17	840.51
3	0.1667	25×10^{-6}	1.0	3.0	10	1039.76	1071.06	1077.01
3	0.237	75×10^{-6}	1.5	3.0	20	350.31	457.72	521.37
3	0.237	50×10^{-6}	1.5	3.0	20	537.95	646.29	704.53
3	0.237	25×10^{-6}	1.5	3.0	20	926.67	982.23	1008.76
3	0.1667	75×10^{-6}	1.0	3.0	20	502.42	613.18	672.37
3	0.1667	50×10^{-6}	1.0	3.0	20	708.23	803.02	846.62
3	0.1667	25×10^{-6}	1.0	3.0	20	1056.23	1075.59	1080.42

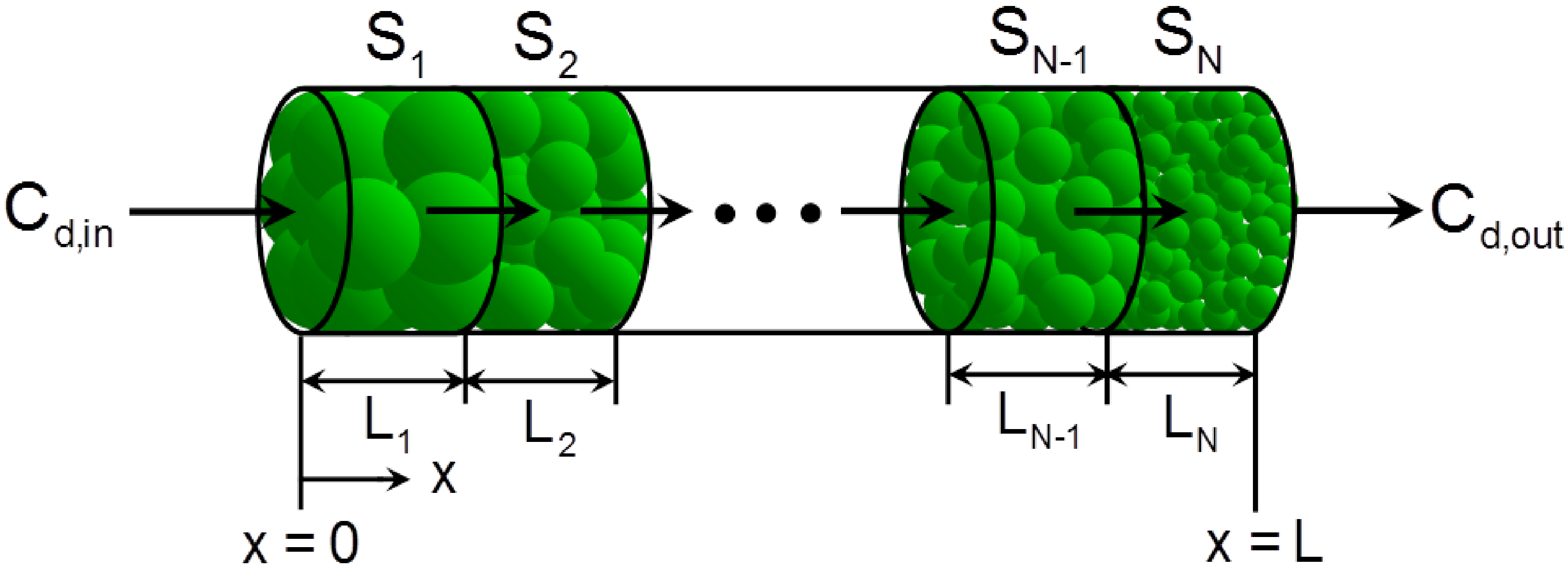

Figure 1. Schematic representation of a stratified column bed of N sections. Each section S_i (i=1,2,3,..,N) has a length L_i (i=1,2,3,..,N) so that $L=\sum_{i=1}^{N} L_i$, and each section is packed with porous adsorbent particles of radius $R_{p,i}$ (i=1,2,3,..,N) such that $R_{p,i} > R_{p,i+1}$ (i=1,2,3,..,N-1).

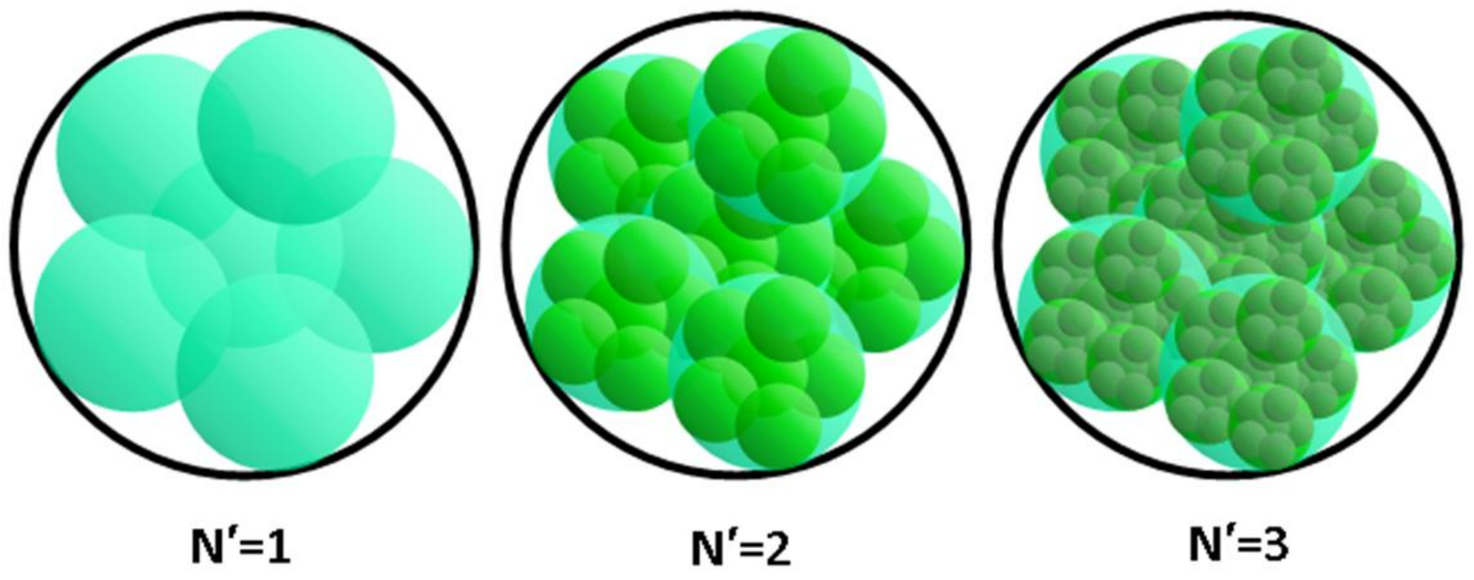

Figure 2. Schematic representation of partially fractal porous adsorbent particles with the total number N′ of recursions of the fractal being equal to (a) one (N′=1), (b) two (N′=2), and (c) three (N′=3)

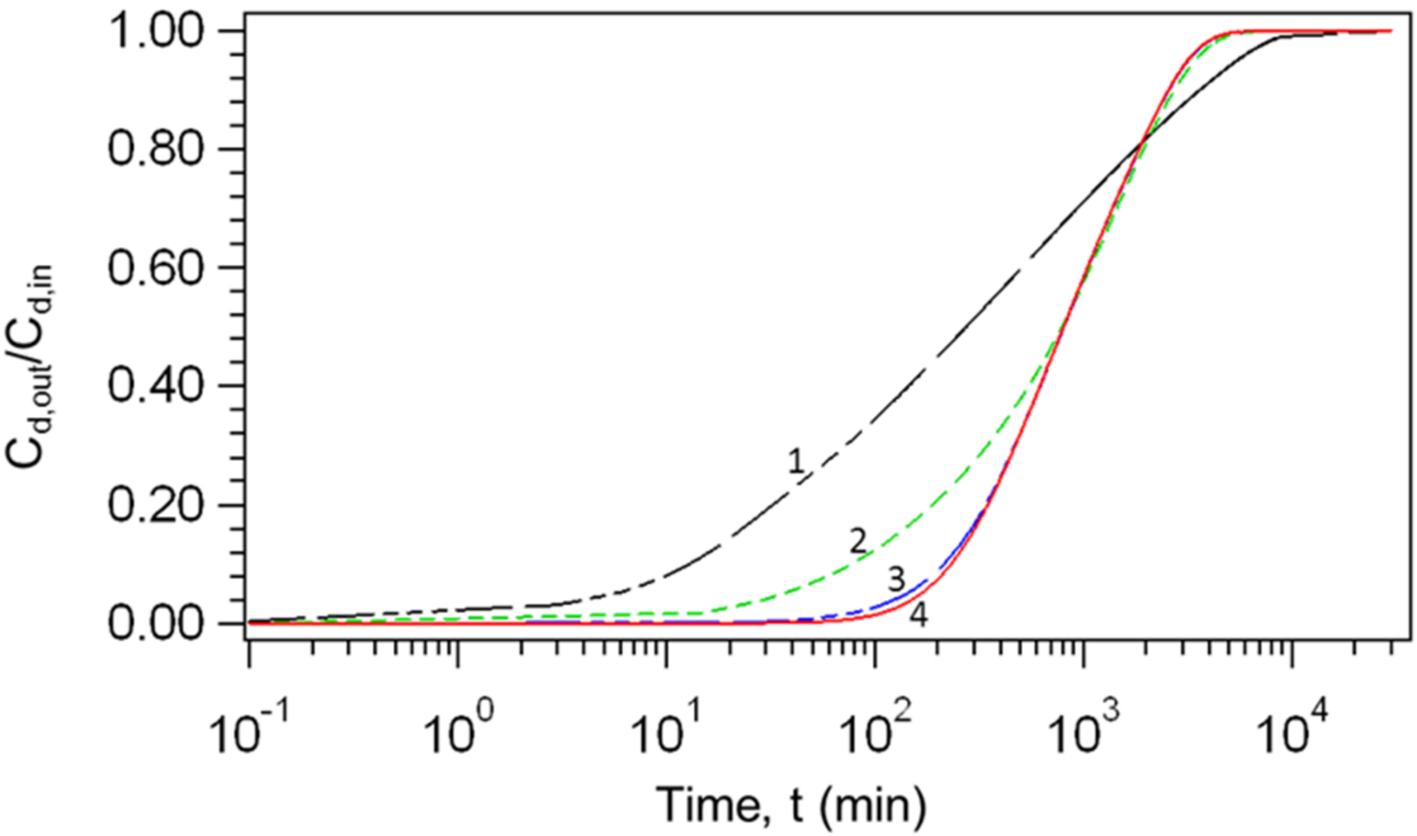

Figure 3. Breakthrough curves from conventional columns of total length L = 0.5 m and when $R_{p,1}$ is equal to 50×10^{-6} m.

Curve 1: Adsorbent particles without a partially fractal structure;

Curve 2: Adsorbent particles with $1/\tau_1 = 3$;

Curve 3: Adsorbent particles with $1/\tau_1 = 10$; Curve 4: Adsorbent particles with $1/\tau_1 = 20$.

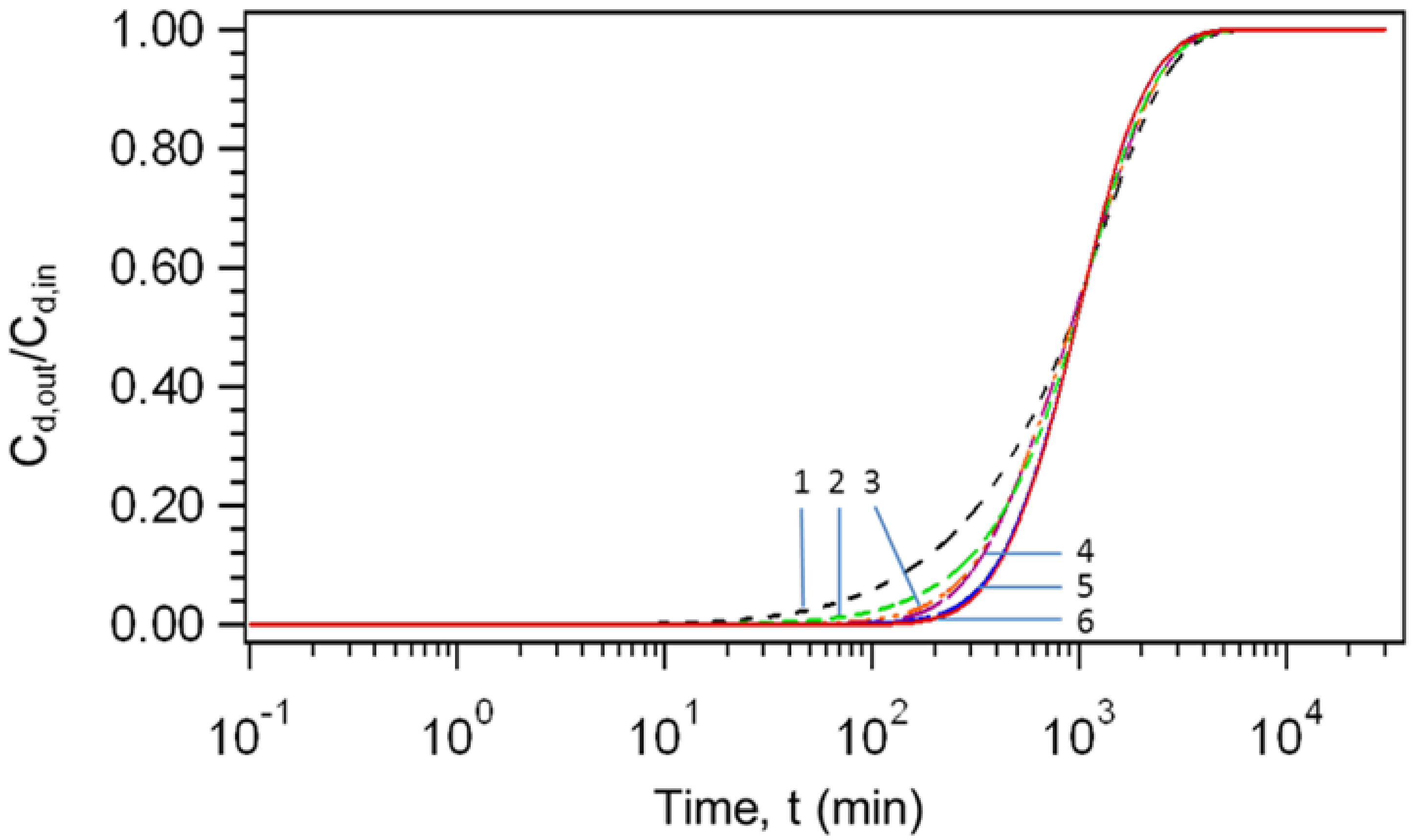

Figure 4. Breakthrough curves from stratified column beds of total length L = 0.5 m and when $R_{p,1}$ is equal to 50×10^{-6} m, $\alpha_i = 1.5$ and $\beta_i = 1.5$.

Curve 1: N = 2 and $1/\tau_i = 3$; Curve 2: N = 3 and $1/\tau_i = 3$; Curve 3: N = 2 and $1/\tau_i = 10$;

Curve 4: N = 2 and $1/\tau_i = 20$; Curve 5: N = 3 and $1/\tau_i = 10$; Curve 6: N = 3 and $1/\tau_i = 20$.

PAPER II

THE DYNAMIC BEHAVIOR OF A STRATIFIED COLUMN BED PACKED WITH POROUS ADSORBENT PARTICLES HAVING PARTIALLY FRACTAL STRUCTURES AND A NON-UNOFORM LIGAND DENSITY DISTRIBUTION

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ABSTRACT

The dynamic behavior of adsorption in a single column and in stratified column beds packed with porous adsorbent particles having partially fractal structures is studied when all columns have the same total length and the spatial ligand density distribution in the porous microspheres from which the porous adsorbent particles are made, is either uniform or non-uniform and such that the concentration of the immobilized ligands (active sites) increases monotonically from the center of the microspheres to their outer surface. The total number of immobilized ligands in the porous adsorbent particles has the same value whether the spatial ligand density distribution is uniform or non-uniform. The results in this study clearly show that for a given value of the superficial velocity of the flowing fluid stream in the column (for a given value of throughput) the breakthrough time is significantly increased when the radius of the microspheres is decreased, the total number of sections of the stratified column bed is increased, and the spatial ligand density distribution employed in the microspheres is non-uniform. Furthermore, when the superficial velocity of the flowing fluid stream in the column is increased (throughput is increased) the effect that (i) the reduction in the radius of the microspheres and (ii) the increase in the number of sections of the stratified column bed have on providing robust and effective dynamic adsorptive capacity and smaller reductions on the breakthrough time is substantially larger than that realized through the use of the non-uniform ligand density distribution. Similar trends are also observed in the dynamic behavior of adsorption in the systems studied here when the value of the concentration of the adsorbate in the flowing fluid stream entering the column (inlet concentration) has such a

high magnitude that the value of the equilibrium concentration of the adsorbate in the adsorbed phase determined from the equilibrium Langmuir isotherm that would correspond to the inlet concentration of the adsorbate in the flowing fluid stream is, for all practical purposes, at its saturation limit.

1. Introduction

It has been shown by Liapis et al. [1] that in conventional columns packed with porous adsorbent particles having non-fractal [1-3] structures, the dynamic adsorption performance depends very significantly on the spatial density distribution of the immobilized ligands. Furthermore, Liapis et al. [1] showed that the column systems whose porous adsorbent particles have a non-uniform spatial ligand density distribution and such that the concentration of the immobilized ligands increases monotonically from the center of the particle to the outer particle surface, exhibit (i) larger breakthrough times, (ii) steeper breakthrough curves, and (iii) higher dynamic utilization of the adsorptive capacity of the column as the superficial velocity of the flowing fluid stream in the column increases (throughput increase) than those obtained from column systems using adsorbent particles in which the spatial distribution of the immobilized ligands is uniform. In all cases [1] the total number of immobilized ligands in the particles has the same number whether the spatial density distribution of the immobilized ligands is uniform or non-uniform. Liapis et al. [1] explained qualitatively and quantitatively the physical mechanisms responsible for the above stated results and also indicated that the importance of this type of monotonically increasing ligand density distribution is significantly enhanced when (a) the size of the particle radius is increased, and (b) continuous counter-current and periodic counter-current (simulated moving beds) operations are employed. Also, Li and Liapis [2] have recently shown that for porous adsorbent particles having a uniform spatial density distribution of immobilized ligands (1) the dynamic adsorption performance of conventional columns packed with porous adsorbent particles having partially fractal [2,3] structures is significantly better than that of conventional columns packed with porous adsorbent particles having non-fractal [1-3] structures, and (2) the dynamic adsorption performance of stratified column beds packed with porous adsorbent particles having partially fractal structures is substantially higher than that of conventional columns packed with porous adsorbent particles having partially fractal structures. The trend of the results in items (1) and (2) above was also obtained [4] when the value of the inlet concentration of the fluid stream entering the column was increased to a magnitude such that the value of the corresponding concentration of the adsorbate in the adsorbed phase that was determined from the Langmuir equilibrium isotherm at the inlet concentration of the adsorbate in the flowing fluid stream had attained, for all practical purposes, its maximum value (saturation limit). Li and Liapis [2] explained qualitatively and quantitatively the physical mechanisms which together with (α) the structural advantages provided by the porous particles having a partially fractal structure provide the superior dynamic adsorption performance obtained by the systems discussed in item (1) above, and (β) the structural advantages provided by the stratified column beds lead to the higher dynamic adsorption performance obtained by the systems discussed in item (2) above.

In this work, the dynamic adsorption performance of stratified column beds packed with porous adsorbent particles having a partially fractal structure and a non-uniform spatial ligand density distribution, is studied.

2. System formulation and mathematical model

The system formulation and mathematical model constructed and employed by Li and Liapis [1] for the study of the dynamic adsorption performance of stratified beds packed with porous adsorbent particles having partially fractal structures, is also used in this work after the introduction of certain modifications discussed in this section due to the form of the non-uniform ligand density distribution function employed in this study. Li and Liapis [2] considered in their study that the spatial density distribution of the immobilized ligands in the porous microspheres of radius $R_{m,i,j+1}$ (i = 1,2,3,..,N; j=1,2,..,N′) from which the partially fractal porous adsorbent particles of radius $R_{p,i}$ (i =1,2,3,..,N) are formed, is uniform. This means that in Eq. (22) in the work of Heeter and Liapis [5] whose expression for use in a stratified bed of N sections takes the form [2, 4]

$$\frac{\partial C_{sm,i}}{\partial t} = k_{1,i} C_{pm,i} (C_{T,i} - C_{sm,i}) - k_{2,i} C_{sm,i} \qquad \text{for i=1,2,3,..,N} \qquad (1)$$

the value of the parameter $C_{T,i}$ has the same constant magnitude at every radial position, r ($0 \leq r \leq R_{m,i,j+1}$), in the microspheres. The parameter $C_{T,i}$ denotes the local maximum [2] equilibrium concentration of adsorbate in the adsorbed phase and, therefore, in the case of a monovalent adsorbate adsorbing onto a monovalent ligand [1,2,5-10] the value of $C_{T,i}$ could also be considered to represent the local maximum concentration of the immobilized ligands. Thus, when the spatial distribution of immobilized ligands is uniform then the value of $C_{T,i}$ is the same at every radial position, r, in the microspheres. When the condition of equilibrium adsorption is attained, then the accumulation term $\partial C_{sm,i} / \partial t$ in Eq.(1) becomes equal to zero and the Langmuir equilibrium adsorption isotherm is obtained [5, 11].

But for the adsorption systems studied in this work, the spatial density distribution of the immobilized ligands in the microspheres forming the partially fractal porous adsorbent particles of radius $R_{p,i}$ is considered to be non-uniform and this requires that the value of the parameter $C_{T,i}$ in Eq. (1) has to vary with the radial position, r, in the microspheres. There are different functional forms for the variation of $C_{T,i}$ with respect to the radial variable, r, that could be considered [1]. For the systems studied in this work, the selected functional form for $C_{T,i}$ is as follows:

$$C_{T,i} = C_{T,\max,i}\left(\frac{r}{R_{m,i,j+1}}\right)^4 \qquad \text{for } 0 \le r \le R_{m,i,j+1} \text{ and } i=1,2,3,..,N \text{ and } j=1,2,..,N' \qquad (2)$$

In Eq. (2) $C_{T,\max,i}$ denotes the value of the maximum concentration of immobilized ligands in the porous adsorbent microspheres of radius $R_{m,i,j+1}$, i represents the section number in a stratified bed, j denotes the division (recursion) number of the fractal, N is the total number of sections in a stratified bed, and N′ represents the total number of recursions of the fractal [2]. In the work of Li and Liapis [2] as well as in this study, the value of N′ is taken to be equal to one (N′ = 1). The expression in Eq. (2) clearly indicates that the value of $C_{T,i}$ increases monotonically as the value of r increases and acquires its highest value at the surface of the microsphere where r = $R_{m,i,j+1}$. The selection of the functional form of $C_{T,i}$ given by Eq. (2) was based on the findings of Liapis et al. [1] who showed that in conventional columns packed with porous adsorbent particles having non-fractal [1-3] structures, the highest dynamic adsorption performance was obtained from the system whose spatial density distribution of the immobilized ligands was non-uniform and such that the concentration of the immobilized ligands increased monotonically from the center of the particle to the outer particle surface, as is the case from Eq. (1) for the values of $C_{T,i}$ in the microspheres of radius $R_{m,i,j+1}$ which form the partially fractal porous adsorbent particles. It is very important to indicate here that if the partially fractal porous adsorbent particles are constructed by the procedure discussed in Li and Liapis [2] and if the ligand had been already immobilized in the microspheres of the smallest practical size whose radius would be $R_{m,i,N'+1}$ and for the system considered in this work with $N'=1$, this means that the radius of our smallest microspheres would be $R_{m,i,2}$ and the partially fractal porous adsorbent particles of radius $R_{p,i}$ would be formed by gluing together [2] the microsphers of radius $R_{m,i,2}$. Thus, if the ligand density distribution in the microspheres of radius $R_{m,i,2}$ is given by Eq. (2), then the concentration of the ligand on the surface of the pores of the porous adsorbent particles of radius $R_{p,i}$ whose total number of recursions of the fractal [2,3], N', is equal to one ($N'=1$), would be equal to the value of $C_{T,max,i}$ in Eq. (2). In this work, it is considered that the partially fractal porous adsorbent particles with $N' = 1$ and radius $R_{p,i}$ are formed by gluing together the porous microspheres of radius $R_{m,i,2}$ in which the ligand has been immobilized and its spatial non-uniform density distribution function is given by the following expression:

$$C_{T,i} = C_{T,max,i}\left(\frac{r}{R_{m,i,2}}\right)^4 \qquad \text{for } 0 \le r \le R_{m,i,2} \text{ and } i=1,2,3,..,N \tag{2a}$$

Of course, if the partially fractal porous particles of radius $R_{p,i}$ (i=1,2,3,..,N) are formed from the gluing of microspheres of recursion number j (where j = 1,2,..,N′) and radius $R_{m,i,j+1}$ when no ligands have been immobilized in the microspheres in an *a priori* manner, and then the immobilization process of the ligands is allowed to occur in the pore structure of the partially fractal porous particles of radius $R_{p,i}$, it should become apparent to the reader that the spatial ligand density distribution function could attain functional forms other than those given in Eqs. (2) and (2a). Therefore, the approach that would be employed in practice [2] for the construction of the partially fractal porous adsorbent particles of radius $R_{p,i}$ plays a very important role in determining the mathematical forms of the spatial ligand density distribution functions in the microspheres of radii $R_{m,i,j+1}$ (i=1,2,..,N and j = 1,2,..,N′) and along the radial direction R of the partially fractal porous adsorbent particles of radius $R_{p,i}$ (i =1,2,3,..,N), for a total number N′ of recursions of the fractal. It is important to note here that from the above discussion it becomes apparent that a very large number of different mathematical forms of the spatial density distribution functions of the immobilized ligands could be constructed by considering the immobilization process of the ligands to occur in microspheres of different radii sizes $R_{m,i,j+1}$ which would correspond to a division (recursion) number j of the fractal that could take values from j=1 to j=N'. Furthermore, it could be possible to pack different sections of the stratified packed bed with porous adsorbent particles having partially fractal structures and different functional forms for the spatial density distribution of the immobilized ligands, so that the dynamic performance of the adsorption process in a stratified bed could be maximized. These interesting possibilities increase significantly the number of design and operational variables (and, thus, the number of degrees of freedom with respect to the variables that could be selected) that one could exploit in order to design, construct, and operate optimally adsorption systems.

In this work, as was stated above, the functional form of the $C_{T,i}$ employed in our simulations is given by Eq. (2a). But in order to properly compare the dynamic adsorption performance obtained from stratified beds packed with partially fractal particles of radius $R_{p,i}$ in whose microspheres the non-uniform spatial ligand density distribution is given by Eq. (2a) with the dynamic adsorption performance obtained from stratified beds packed with partially fractal particles of radius $R_{p,i}$ in whose microspheres the spatial distribution of the immobilized ligands is uniform and such that $C_{T,i}$ in Eq. (1) is given by Eq. (3)

$$C_{T,i} = C_{T,i,U} = \text{ constant} \qquad \text{for } 0 \le r \le R_{m,i,2} \text{ and } i = 1,2,3,..,N \tag{3}$$

one has to require that in both cases the total number of immobilized ligands in any given section i (i =1,2,3,..,N) of the stratified beds has to be the same, and, therefore, the value of $C_{T,max,i}$ in Eq. (2a) has to be determined through its relation to the value of $C_{T,i,U}$ in Eq. (3); the symbol $C_{T,i,U}$ in Eq. (3) denotes the local maximum concentration of immobilized ligands when their spatial density distribution is uniform and, thus, the value of $C_{T,i,U}$ is the same and equal to a constant value for all radial positions r in the microspheres. It is relatively easy to show [4] that when $C_{T,max,i}$ in Eq. (2a) is related to $C_{T,i,U}$ in Eq. (3) through the expression

$$C_{T,max,i} = (\frac{7}{3})C_{T,i,U} \qquad \text{for } i = 1,2,3,..,N \qquad (4)$$

then the total number of immobilized ligands in each section i of the stratified beds of the two cases to be compared, as discussed above, is the same.

3. Results and discussion

The stratified column beds studied in this work are packed with porous adsorbent particles having partially fractal structures with the value of the total number, N′, of recursions of the fractal being equal to 1 (N′ = 1) for all porous adsorbent particles. All columns have the same diameter and total length L. The values of the parameters that remain constant for the adsorption systems considered here are listed in Table 1. The parameters $k_{1,i}$ and $k_{2,i}$ characterize the dynamic adsorption mechanism (see Eq. (1)) of the adsorbate being adsorbed onto the immobilized ligands (active sites) on the surface of the pores of the particles. When the spatial ligand density distribution in the microspheres is uniform, the value of $C_{T,i,U}$ for the systems studied in this work is taken to be equal [2] to 78.3 kg/m^3 particle for i = 1,2,3,..,N. For the systems whose spatial ligand density distribution is non-uniform and is given by Eq. (2a), the value of $C_{T,max,i}$ is determined from Eq. (4) and the value of $C_{T,max,i}$ for the systems studied here is equal to 182.7 kg/m^3 particle for i = 1,2,3,..,N. It is worth mentioning again at this point that the total number of immobilized ligands in a given section i (i = 1,2,3,..,N) of the stratified beds has the same value whether the spatial ligand density distribution in the microspheres is uniform or non-uniform. The values of the parameters in Table 1 are from adsorption systems reported in the literature [2] and, for the purposes of the simulations of this study, are considered to have appropriate magnitudes since they characterize adsorption systems of practical use. Stratified column beds of two (N = 2, $L=\sum_{i=1}^{2}L_i$) and three (N = 3, $L=\sum_{i=1}^{3}L_i$) sections are investigated in this work, and their results are also compared with those obtained when the whole column has only one section (N = 1) of length L and is packed with porous adsorbent particles having a partially fractal structure. The value of the radius $R_{p,1}$ of the porous adsorbent particles having a partially fractal structure and being packed in the column having only one section (N = 1) and length L, and also in the first section (i = 1) of the stratified column beds having either two (N = 2) or three (N = 3) sections and a total length L, is taken [2] to be equal to 50×10^{-6} m. Furthermore, the values of α_i ($\alpha_i=L_i/L_{i+1}$ for i = 1,2,3,..,N-1) and β_i ($\beta_i=R_{p,i}/R_{p,i+1}$ for i = 1,2,3,..,N-1) for the stratified column bed systems studied here are taken [2] to be equal to 1.5 and 1.5 for i = 1,2,3,..,N-1, respectively. Therefore, from the values of α_i and the total length L of the column the length L_i of each section i of a stratified column bed can be determined while from the values of $R_{p,1}$ and β_i the radius $R_{p,i}$ of the porous adsorbent particles having a partially fractal structure and are packed in each section i of a stratified column bed can be determined. We can relate [2, 3] the radius $R_{p,i}$ of the porous adsorbent particles to the radius $R_{m,i,j+1}$ of the microspheres that make up the particle of radius $R_{p,i}$ through the expression [2] given in Eq. (5)

$$R_{m,i,j+1}=\tau_i^j R_{p,i} \qquad \text{for } i=1,2,3,..,N \text{ and } j=1,2,3,..,N' \tag{5}$$

where it is considered that the porosity $\varepsilon_{m,i,j+1}$ of each microsphere of radius $R_{m,i,j+1}$ is equal to the porosity $\varepsilon_{p,i}$ of the adsorbent particle of radius $R_{p,i}$. The term τ_i^j in Eq. (5)

represents at the j division (recursion) of the fractal the ratio of the radius $R_{m,i,j+1}$ of the microspheres to the radius $R_{p,i}$ of the porous adsorbent particles which are formed from the gluing of the microspheres of radius $R_{m,i,j+1}$; it is worth mentioning here that the value of τ_i is smaller than one (τ_i <1) and, therefore, as the value of the recursion of the fractal, j (j=1,2,3,..,N'), increases the value of the term τ_i^j in Eq. (5) becomes even smaller. For the systems studied here where the value of N′ is equal to one and, thus, j = 1 = N′, Eq. (5) becomes

$$R_{m,i,2}=\tau_i R_{p,i} \qquad \text{for } i=1,2,3,..,N \tag{5a}$$

Thus, if the values of $R_{p,i}$ and τ_i are known, then the value of $R_{m,i,2}$ is determined from Eq. (5a). The term $1/\tau_i$ represents the ratio of $R_{p,i}/R_{m,i,2}$ and this means that $1/\tau_i$ has values greater than one ($(1/\tau_i)>1$) because the value of τ_i is smaller [2] than one (τ_i <1) since the value of $R_{p,i}$ is greater than the value of $R_{m,i,j+1}$, and, thus, as the value of $1/\tau_i$ increases the ratio of $R_{p,i}/R_{m,i,2}$ increases. Therefore, for a given size of the radius, $R_{p,i}$, of the particles in section i of a stratified column bed, the value of the radius, $R_{m,i,2}$, of the microspheres from which the particles of radius $R_{p,i}$ are formed, is decreasing as the value of the term $1/\tau_i$ is increasing. The value of the superficial velocity, $V_{f,i}$, of the flowing fluid stream in each section i of the stratified column bed is taken to be constant and equal [2] to the superficial velocity, V_f, of the fluid in the column that has only one section (N=1) and the same total length, L, as the stratified column beds; this implies that $V_{f,i} = V_f$ for i = 1,2,3,..,N for the adsorption systems studied in this work.

The criterion that is used to compare the performance of the different adsorption column systems is the breakthrough time, t_b. In this study, as was also the case in Li and Liapis [2], the breakthrough time, t_b, is defined as the time when the concentration, $C_{d,out}$, of the adsorbate in the outlet stream from the column becomes equal to 1% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column. In Tables 2 and 3 the values of the breakthrough time, t_b, are reported for the adsorption systems studied in this work as well as the times when the concentration of the adsorbate in the column outlet stream becomes equal to 5% and 10% of the inlet concentration of the adsorbate in the column.

The simulation results in Table 2 clearly show that for given values of N and $1/\tau_i$, the effect of increasing the superficial velocity (increasing the throughput) results, as expected, to a decrease in the value of the breakthrough time, t_b, but the decrease in the value of t_b is smaller in the systems employing the spatial non-uniform ligand density distribution function given in Eq. (2a). This occurs because the non-uniform ligand density distribution in the microspheres provides a higher average adsorption rate [1] in the adsorbent particles than that obtained when the ligand density distribution function in the microspheres of the adsorbent particles is uniform. Thus, the effect of the increase of the magnitude of the superficial velocity, $V_{f,i}$, on the dynamic adsorptive capacity of the column is smaller in the column beds with adsorbent particles in whose microspheres the spatial ligand density distribution function is non-uniform and has the form given in Eq. (2a). Also, for given values of N and $V_{f,i}$, the breakthrough time, t_b, increases significantly as the value of $1/\tau_i$ increases and this is the case for both ligand density distributions. Furthermore, the effect that the increased values of $1/\tau_i$ have on providing smaller reductions on the breakthrough time, t_b, as the value of $V_{f,i}$ increases, is substantially larger than the effect that the spatial non-uniform ligand density distribution has on the breakthrough time, t_b, for the same increase in the value of $V_{f,i}$. Of course, increased values of $1/\tau_i$ mean that the radius, $R_{m,i,2}$, of the microspheres is decreased, and the physical reasons for explaining the increases in the breakthrough time, t_b, as the radius (size) of the microspheres decreases, are that (a) the length of the pathways for the diffusion of the adsorbate in the microspheres decreases [2] and this results to a smaller resistance for mass transfer in the microspheres and a larger adsorbate concentration gradient in the fluid in the pores of the microspheres which provides a larger mass flux for the adsorbate in the microspheres, and (b) the total internal wetted surface area, $A_{ws,i}$, of the pores of the adsorbent particle increases as the size of the microspheres from which the adsorbent particle is made decreases [2, 3], and this leads to the increase of the average mass transfer rate of the adsorbate in the particle. Furthermore, the results indicate that when the value of $1/\tau_i$ is increased from 10 to 20, the relative increases, for given values of N and $V_{f,i}$, in the breakthrough time, t_b, are not as large as are in the case where $1/\tau_i$ is increased from 3 to 10. This implies that, for the operating conditions and parameter values employed in the systems studied in this work, (i) the increase in the total internal wetted surface area, $A_{ws,i}$, of the pores of the adsorbent particles and (ii) the shorter in lengh diffusion pathways that are realized when the radius $R_{m,i,2}$ of the microspheres is decreased, lead to a larger mass transfer rate for the adsorbate and the relative increase in the magnitude of the mass transfer rate is becoming smaller as the value of the radius, $R_{m,i,2}$, of the microspheres is further reduced. Also, for given values of $1/\tau_i$ and $V_{f,i}$ the results in Table 2 show that as the number N of the sections in the column is increased the breakthrough time, t_b, becomes larger because, for example, the third section of the stratified bed with three sections is made from packed adsorbent particles whose radius is smaller than the radius of the adsorbent particles packed in the second section of the stratified bed having two sections, and this leads to a higher total mass transfer rate [2] in the stratified bed comprised of three sections. From the simulation results listed in Table 2 and the above discussion, one could ascertain that for the adsorption systems studied in this work, the breakthrough time, t_b, increases and a higher dynamic adsorption capacity is realized as the values of $1/\tau_i$ and N increase and the spatial ligand density distribution in the microspheres is non-uniform and is given by the expression in Eq. (2a). With respect to the degree of influence of $1/\tau_i$, N, and of the non-uniform ligand density distribution (Eq. (2a)) on t_b and the dynamic adsorptive capacity, one could observe from the results in Table 2 that increases in the value of $1/\tau_i$ have the largest effect on increasing the value of t_b and the dynamic adsorptive capacity, followed by increases in the value of N, and then followed by the desirable (positive) effects that the non-uniform ligand density distribution has on the values of t_b and on the dynamic adsorptive capacity.

In Table 3 the simulation results for the column bed systems studied in Table 2 but with an inlet adsorbate concentration, $C_{d,in}$, whose magnitude is fifteen times larger than the magnitude of $C_{d,in}$ employed in the systems whose results are given in Table 2, are reported. The effect of this high inlet concentration, $C_{d,in}$, of 1.5 kg/m^3 is examined because at this high inlet concentration the equilibrium Langmuir isotherm obtained by setting the term $\partial C_{sm,i} / \partial t = 0$ in Eq. (1) and also by using Eq. (3) representing the uniform ligand density distribution for the value of $C_{T,i}$ in Eq. (1), provides such a value for the equilibrium concentration, $C_{sm,eq,i}$, of the adsorbate in the adsorbed phase that, for all practical purposes, is at its maximum value (saturation limit). It can be observed that the trends in the results reported in Table 3 as the values of $1/\tau_i$, N, and $V_{f,i}$ are increased and the spatial ligand density distribution function is changed from being uniform (Eq. (3)) to non-uniform (Eq. (2a)), are similar to those observed in Table 2 and discussed above. While the magnitude of the increases in the values of the breakthrough time, t_b, and of the dynamic adsorptive capacity as the values of $1/\tau_i$ and N increase and the spatial ligand density distribution changes from uniform to non-uniform with its functional form provided by Eq.(2a), is slightly smaller for the systems whose inlet adsorbate concentration has a magnitude fifteen times larger than that in the systems considered in Table 2, the influence of $1/\tau_i$, N, and of the non-uniform ligand density distribution on the values of t_b and on the dynamic adsorptive capacity of the column beds is very significant. Again, the increases in the value of $1/\tau_i$ provide the largest increases in the values of t_b and of the dynamic adsorptive capacity, followed by increases in the number, N, of the sections of the stratified column bed, and then followed by the desirable effects that the non-uniform ligand density distribution has on the values of t_b and on the dynamic adsorptive capacity.

4. Conclusions and remarks

The results in this study clearly showed that for a given value of the superficial velocity, $V_{f,i}$, of the flowing fluid stream in the column (for a given value of throughput in the column) the breakthrough time, t_b, is significantly increased when (a) the radius, $R_{m,i,2}$, of the microspheres is decreased, which implies that the value of the parameter $1/\tau_i$ is increased, (b) the total number, N, of the sections of the stratified column bed is increased, and (c) the spatial ligand density distribution employed in the microspheres of the adsorbent particles is non-uniform and its functional form is given by Eq. (2a). Furthermore, when the superficial velocity, $V_{f,i}$, of the flowing fluid stream in the column is increased (throughput is increased) the effect that (1) the reduction in the value of the radius, $R_{m,i,2}$, of the microspheres which implies an increase in the value of the parameter $1/\tau_i$, and (2) the increase in the total number, N, of the sections of the stratified column bed have on providing robust and effective dynamic adsorptive capacity and smaller reductions on the breakthrough time, t_b, is significantly larger than that realized through the use of the non-uniform ligand density distribution. Similar trends in the dynamic behavior of adsorption were observed in the systems studied in this work when the value of the concentration, $C_{d,in}$, of the adsorbate in the fluid stream entering the column had such a high magnitude that the equilibrium concentration, $C_{sm,eq,i}$, of the adsorbate in the adsorbed phase determined from the equilibrium Langmuir isotherm that would correspond to the value of the inlet concentration, $C_{d,in}$, was, for all practical purposes, at its maximum value (saturation limit).

In all cases, the increases in the value of the parameter $1/\tau_i$ provided the largest increases in the value of t_b and of the dynamic adsorptive capacity, followed by increases in the total number, N, of the sections of the stratified column bed, and then followed by the desirable (positive) effects that the non-uniform ligand density distribution had on the value of t_b and on the dynamic adsorptive capacity.

5. Nomenclature

$A_{ws,i}$	total internal wetted surface area of particles of radius $R_{p,i}$ (i=1,2,3,…,N), m^2
$C_{d,in}$	inlet concentration of adsorbate in the column, kg/m^3
$C_{d,out}$	outlet concentration of adsorbate from the column, kg/m^3
$C_{sm,eq,i}$	equilibrium concentration of adsorbate in the adsorbed phase of the microspheres of the adsorbent particles in section i (i=1,2,3,…,N) of the stratified column bed determined from the Langmuir equilibrium adsorption isotherm, kg/m^3 of adsorbent particle
$C_{sm,i}$	concentration of the adsorbate in the adsorbed phase of the microspheres of the adsorbent particles in section i (i=1,2,3,…,N) of the stratified column bed, kg/m^3 of adsorbent particle
$C_{T,i}$	local maximum equilibrium concentration of adsorbate in the adsorbed phase of the microspheres, kg/m^3 of adsorbent particle
$C_{T,i,U}$	maximum equilibrium concentration of adsorbate in the adsorbed phase of the microspheres when the spatial ligand density distribution is uniform (Eq. (3)), kg/m^3 of adsorbent particle
$C_{T,max,i}$	maximum equilibrium concentration of adsorbate in the adsorbed phase of the microspheres when the spatial ligand density distribution is non-uniform (Eqs. (2a) and (4)), kg/m^3 of adsorbent particle
D_{fm}	free molecular diffusion coefficient of adsorbate, m^2/s
D_{L_i}	axial dispersion coefficient of adsorbate in section i (i=1,2,3,…,N) of stratified column bed, m^2/s
$D_{p,i}$	effective pore diffusion coefficient of adsorbate in the pore fluid of particles of radius $R_{p,i}$ where i=1,2,3,…,N, m^2/s
$D_{p,m,i,j+1}$	effective pore diffusion coefficient of adsorbate in the pore fluid of the microspheres of radius $R_{m,i,j+1}$ where i=1,2,3,…,N and j=1,2,3,…,N′, m^2/s
$k_{1,i}$	adsorption rate constant in the adsorbent particles of section i (i=1,2,3,…,N) of stratified column bed, $m^3/(kg\ s)$
$k_{2,i}$	desorption rate constant in the adsorbent particles of section i (i=1,2,3,…,N) of stratified column bed, s^{-1}

L	total column length, m
L_i	length of section i (i=1,2,3,…,N) of stratified column bed, m
N	total number of sections of stratified column bed
N'	total number of recursions of the fractal (total number of divisions)
r	radial distance in the microspheres of radius $R_{m,i,j+1}$, m
$R_{p,i}$	radius of adsorbent particles in section i (i=1,2,3,…,N) of stratified column bed, m
$R_{m,i,j+1}$	radius of the microspheres in the particles of radius $R_{p,i}$ (i=1,2,3,…,N) after j divisions (j=1,2,…,N′), m
t	time, s
T	temperature, K
t_b	breakthrough time, s
V_f	superficial velocity of fluid in a column, m/s
$V_{f,i}$	superficial velocity of fluid in section i (i=1,2,3,…,N) of stratified column bed, m/s

Greek letters

α_i	L_i/L_{i+1} for i = 1,2,3,..,N-1
β_i	$R_{p,i}/R_{p,i+1}$ for i = 1,2,3,..,N-1
ε_i	bed porosity in section i (i=1,2,3,…,N) of stratified column bed
$\varepsilon_{p,i}$	porosity in particles of radius $R_{p,i}$ where i=1,2,3,…,N
$\varepsilon_{m,i,j+1}$	porosity in the microspheres of radius $R_{m,i,j+1}$ where i=1,2,3,…,N and j=1,2,3,…,N′
μ	viscosity of solution, kg m^{-1} s^{-1}
ρ	density of solution, kg/m^3

τ_i	parameter defined by Eq. (5) where i=1,2,3,…,N

Subscripts

i	denotes the section number in a stratified column bed, i=1,2,3,…,N
j	denotes the division (recursion) number of the fractal, j = 1,2,…,N′

6. References

[1] Liapis, A. I., Riccardi, E., Wang J.-C., *J. Sep. Sci*. 2010, *33*, 2749-2756.

[2] Li, M., Liapis, A. I., *J. Sep. Sci*. 2012, *35*, 947-956.

[3] Liapis, A. I., *Math. Model. Sci. Comput* 1993, *1*, 397-414.

[4] Li, M., *Ph.D. Dissertation* 2012, Department of Chemical and Biological Engineering, Missouri University of Science and Technology, Rolla, Missouri, U. S. A.

[5] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A* 1995, *711*, 3-21.

[6] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A* 1996, *743*, 3-14.

[7] Arve, B. H., Liapis, A. I., *AIChE J*. 1987, *33*, 179-193.

[8] Arve, B. H., Liapis, A. I., *Biotechnol. Bioeng*. 1988, *32*, 616-627.

[9] Riccardi, E., Liapis, A. I., *J. Sep. Sci*. 2009, *32*, 4059-4068.

[10] Unger, K. K., Liapis, A. I., *J. Sep. Sci*. 2012, *35*, 1201-1212.

[11] Do, D. D., *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press, London, United Kingdom 1998.

Table 1. Common values of the parameters used in the adsorption systems of this study. The adsorbate (solute) considered in this work is BSA [2].

$C_{T,i,U}$ = 78.3 kg/m^3 particle for i =1,2,3,..,N

$C_{T,\max,i} = (\frac{7}{3})C_{T,i,U}$ = 182.7 kg/m^3 particle for i = 1,2,3,..,N

$D_{fm} = 6.70\times10^{-12}$ m^2/s

$D_{L_i} \cong 0$ m^2/s for i = 1,2,3,…,N

$D_{p,i} = 2.50\times10^{-12}$ m^2/s for i = 1,2,3,..,N

$D_{p,m,i,j+1} = 2.50\times10^{-12}$ m^2/s for i = 1,2,3,…,N and j = 1,2,…,N′

$k_{1,i}$ = 1.05 m^3/(kg s) for i = 1,2,3,…,N

$k_{2,i}$ = 0.131 s^{-1} for i = 1,2,3,…,N

L = 0.50 m

N′ = 1

$R_{p,1} = 50\times10^{-6}$ m

T = 296.15 K

$\alpha_i = 1.5$ for i = 1,2,3,…,N

$\beta_i = 1.5$ for i = 1,2,3,…,N

$\varepsilon_i = 0.35$ for i = 1,2,3,…,N

$\varepsilon_{p,i} = 0.60$ for i =1,2,3,…,N

$\varepsilon_{m,i,j+1} = 0.60$ for i = 1,2,3,…,N and j = 1,2,…,N′

$\mu = 0.894\times10^{-3}$ kg/(m s)

$\rho = 997$ kg/m^3

Table 2. Number of minutes needed for the outlet concentration, $C_{d,out}$, of the adsorbate from a column bed comprised of one section (N = 1), two sections (N = 2), and three sections (N = 3) and packed with particles having a partially fractal structure to be equal to 1% (breakthrough time, t_b), 5%, and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column for various values of $1/\tau_i$ and $V_{f,i}$ (i=1,2,3,…,N). In all cases, $C_{d,in} = 0.1$ kg/m^3, L=0.5 m, and the values of the parameters $1/\tau_i$ and $V_{f,i}$ were kept with the same magnitude in each section i (i=1,2,3,…,N) of a stratified column bed, as well as in the column having only one section (N=1).

			Uniform ligand density distribution, Eq. (3)			Non-Uniform ligand density distribution, Eq. (2a)		
N	$1/\tau_i$	$V_{f,i}$ (m/s)	Time t (min)			Time t (min)		
			1%	5%	10%	1%	5%	10%
1	3	2.778×10^{-3}	9.71	36.38	76.90	19.93	71.76	139.97
1	3	5.556×10^{-3}	0.94	3.06	7.01	1.58	6.17	14.54
1	3	8.334×10^{-3}	0.37	0.79	1.66	0.44	1.47	3.32
1	10	2.778×10^{-3}	57.15	141.19	213.64	79.94	161.39	228.27
1	10	5.556×10^{-3}	5.09	19.96	40.09	9.66	31.51	53.23
1	10	8.334×10^{-3}	1.09	4.75	11.06	2.06	8.91	18.65
1	20	2.778×10^{-3}	86.79	166.01	231.28	95.35	171.24	234.55
1	20	5.556×10^{-3}	12.73	35.36	56.22	17.86	40.04	59.51
1	20	8.334×10^{-3}	2.97	11.47	21.55	5.17	15.35	24.93
2	3	2.778×10^{-3}	26.62	87.45	163.10	53.01	151.85	247.98
2	3	5.556×10^{-3}	2.21	8.39	18.74	4.40	17.24	36.99
2	3	8.334×10^{-3}	0.58	1.95	4.47	0.98	3.95	9.25
2	10	2.778×10^{-3}	111.90	220.52	305.61	133.60	235.75	315.92
2	10	5.556×10^{-3}	14.35	43.49	72.84	23.45	55.37	82.67
2	10	8.334×10^{-3}	3.27	12.75	25.49	6.21	20.13	34.10
2	20	2.778×10^{-3}	139.20	239.09	318.08	145.86	242.86	320.45
2	20	5.556×10^{-3}	27.13	58.31	84.68	32.07	61.70	86.87
2	20	8.334×10^{-3}	8.18	22.70	36.14	11.51	25.85	38.38
3	3	2.778×10^{-3}	63.21	168.74	271.13	111.75	244.94	350.91
3	3	5.556×10^{-3}	5.83	21.05	42.83	11.97	40.17	73.96
3	3	8.334×10^{-3}	1.34	5.13	11.43	2.71	10.53	22.48
3	10	2.778×10^{-3}	176.61	303.72	397.37	195.35	315.84	405.68
3	10	5.556×10^{-3}	31.47	72.68	107.85	42.20	82.55	115.21
3	10	8.334×10^{-3}	8.78	26.39	44.33	14.25	34.03	51.23
3	20	2.778×10^{-3}	199.90	318.50	407.47	205.19	321.49	409.43
3	20	5.556×10^{-3}	45.53	84.81	116.71	49.73	87.38	118.35
3	20	8.334×10^{-3}	16.58	36.09	52.71	19.86	38.52	54.32

Table 3. Number of minutes needed for the outlet concentration, $C_{d,out}$, of the adsorbate from a column bed comprised of one section (N = 1), two sections (N = 2), and three sections (N = 3) and packed with particles having a partially fractal structure to be equal to 1% (breakthrough time, t_b), 5%, and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column for various values of $1/\tau_i$ and $V_{f,i}$ (i=1,2,3,…,N). In all cases, $C_{d,in}$ = 1.5 kg/m^3, L=0.5 m, and the values of the parameters $1/\tau_i$ and $V_{f,i}$ were kept with the same magnitude in each section i (i=1,2,3,…,N) of a stratified column bed, as well as in the column having only one section (N=1).

N	$1/\tau_i$	$V_{f,i}$ (m/s)	Uniform ligand density distribution, Eq. (3)			Non-Uniform ligand density distribution, Eq.		
			Time t (min)			Time t (min)		
			1%	5%	10%	1%	5%	10%
1	3	2.778×10^{-3}	5.81	15.80	27.72	11.18	29.06	45.62
1	3	5.556×10^{-3}	0.77	1.68	3.04	1.14	3.03	5.78
1	3	8.334×10^{-3}	0.37	0.56	0.89	0.39	0.85	1.51
1	10	2.778×10^{-3}	26.72	46.71	59.62	33.80	51.35	62.09
1	10	5.556×10^{-3}	3.03	8.34	13.38	5.23	11.50	16.05
1	10	8.334×10^{-3}	0.77	2.27	4.27	1.31	3.86	6.33
1	20	2.778×10^{-3}	36.07	52.39	62.45	39.00	53.51	62.74
1	20	5.556×10^{-3}	6.41	12.45	16.61	8.14	13.61	17.18
1	20	8.334×10^{-3}	1.78	4.61	6.92	2.72	5.59	7.61
2	3	2.778×10^{-3}	14.76	35.78	55.32	28.02	56.81	74.81
2	3	5.556×10^{-3}	1.48	3.97	7.30	2.68	7.65	13.63
2	3	8.334×10^{-3}	0.49	1.08	1.96	0.74	1.94	3.73
2	10	2.778×10^{-3}	49.59	70.49	82.38	55.47	72.99	83.31
2	10	5.556×10^{-3}	7.82	16.61	22.48	11.55	19.18	23.86
2	10	8.334×10^{-3}	3.27	12.75	25.49	3.51	7.82	10.67
2	20	2.778×10^{-3}	56.97	73.48	83.45	58.76	73.98	83.59
2	20	5.556×10^{-3}	12.75	19.72	24.08	14.23	20.32	24.27
2	20	8.334×10^{-3}	4.37	8.38	10.95	5.58	9.01	11.21
3	3	2.778×10^{-3}	33.64	65.95	87.12	56.27	85.54	99.78
3	3	5.556×10^{-3}	3.47	9.23	15.69	6.77	16.87	25.73
3	3	8.334×10^{-3}	0.91	2.45	4.51	1.65	4.73	8.43
3	10	2.778×10^{-3}	74.88	93.68	103.75	78.76	95.00	104.26
3	10	5.556×10^{-3}	16.12	25.89	31.39	19.58	27.37	32.02
3	10	8.334×10^{-3}	4.91	10.60	14.29	7.45	12.26	15.09
3	20	2.778×10^{-3}	79.66	95.26	104.36	80.69	95.54	104.46
3	20	5.556×10^{-3}	20.42	27.66	32.12	21.39	27.96	32.23
3	20	8.334×10^{-3}	8.22	12.57	15.22	9.14	12.91	15.34

PAPER III

ADSORPTION IN COLUMNS PACKED WITH POROUS ADSORBENT PARTICLES HAVING PARTIALLY FRACTAL STRUCTURES

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ABSTRACT

A mathematical model is constructed and solved that could describe the dynamic behavior of the adsorption of a solute of interest in single and stratified columns packed with partially fractal porous adsorbent particles. The results show that a stratified column bed whose length is the same as that of a single column bed, provides larger breakthrough times and a higher dynamic utilization of the adsorptive capacity of the particles than those obtained from the single column bed, and the superior performance of the stratified bed becomes especially more important when the superficial velocity of the flowing fluid stream in the column is increased to accommodate increases in the system throughput. This occurs because the stratified column bed provides larger average external and intraparticle mass transfer and adsorption rates per unit length of packed column. It is also shown that increases in the total number of recursions of the fractal and the ratio of the radii between larger and smaller microspheres that make up the partially fractal particles, increase the intraparticle mass transfer and adsorption rates and lead to larger breakthrough times and dynamic utilization of the adsorptive capacity of the particles. The results of this work indicate that highly efficient adsorption separations could be realized through the use of a stratified column comprised from a practically reasonable number of sections packed with partially fractal porous adsorbent particles having reasonably large (i) total number of recursions of the fractal and (ii) ratio of the radii between larger and smaller microspheres from which the partially fractal particles are made from. It is important to mention here that the physical concepts and modeling approaches presented in this work could be, after a few modifications of the model,

applied in studying the dynamic behavior of chemical catalysis and biocatalysis in reactor beds packed with partially fractal porous catalyst particles.

1. Introduction

It has been shown by Li and Liapis [1, 2] that adsorption columns packed with porous adsorbent particles having a partially fractal structure with the value of the total number of the fractal, N′, being equal to 1 (N′ = 1) provide larger breakthrough times and dynamic utilization of the adsorptive capacity of the column when compared with the performance obtained from adsorption columns employing porous adsorbent particles which do not have a partially fractal structure. This finding has been shown [1, 2] to occur in separation systems employing either conventional [1-4] or stratified [1, 2, 5] adsorption columns. Furthermore, Li and Liapis [1, 2] have shown that stratified adsorption columns provide larger breakthrough times and dynamic utilization of the adsorptive capacity of the packed adsorbent particles than conventional adsorption columns when the bed porosity and total length of the stratified adsorption column are equal to those of the conventional adsorption column. Certain key scientific and engineering science mass transfer and adsorption mechanisms responsible for the occurrence of better separation performance when (i) porous adsorbent particles having partially fractal structures are employed in the packed beds of columns and (ii) stratified adsorption columns are used, are presented and discussed in the works of Li and Liapis [1,2]. It is also important to mention here that the partially fractal porous particles can provide higher values for the three-dimensional pore connectivity of the pores [6-14] than the pore connectivity values obtained in conventional porous particles, and this makes the effective pore diffusional velocities of the adsorbate in partially fractal porous particles to be larger than those in conventional porous particles and, thus, the effective mass fluxes and concentration gradients of the adsorbate in partially fractal porous particles are larger [1,2,11-14] than in conventional porous particles.

The theoretical approach and the results of Li and Liapis [1,2] have very important implications with respect to (a) the design and construction of porous adsorbent media and (b) the design and operation of column packed beds, so that high mass transfer and adsorption rates as well as high dynamic adsorptive capacities can be realized for the effective separation of the species of interest from mixtures. These required necessities are even of higher importance in the case of adsorption separations involving large bioactive molecules which have low in magnitude molecular diffusion coefficients in porous adsorbent media and, therefore, have low diffusional velocity values in such media. In this work, a mathematical model is presented that could describe the dynamic behavior of the mass transfer and adsorption of a solute in columns packed with porous adsorbent particles having a partially fractal structure with the value of the total number of the fractal, N', being greater than or equal to one ($N' \geq 1$), and then this model is used to study and compare the dynamic behavior of column adsorption systems packed with partially fractal porous adsorbent particles having values for N' equal to 1 and 2.

2. Mathematical model

The adsorption columns considered in this work are packed with spherical porous adsorbent particles which have a partially fractal structure [1, 2, 6]. This means that a porous adsorbent particle of a given radius is considered to be made by smaller in radius porous adsorbent particles which themselves are made by even smaller in radius porous particles and so on. Thus, we can relate the radius, $R_{p,i}$, of a given spherical adsorbent particle to the radius $R_{m,i,j+1}$ of the microspheres that make up the particle of radius $R_{p,i}$ through the expression given in Eq. (1) where it is considered that the porosity $\varepsilon_{p,i,j+1}$ of each microsphere of radius $R_{m,i,j+1}$ is equal to the porosity $\varepsilon_{p,i}$ of the adsorbent particle of radius $R_{p,i}$:

$$R_{m,i,j+1} = \tau_i^j R_{p,i}\,,\ i = 1,2,3,..,N \text{ and } j = 0,1,2,3,..,N' \qquad (1)$$

In Eq. (1), i denotes the adsorbent particles packed in section S_i of a stratified column bed [1, 2], as shown in Fig.1, $R_{m,i,j+1}$ represents the radius of the microspheres that make up the adsorbent particle of radius $R_{p,i}$ after j divisions, N′ denotes the total number of divisions (the total number of recursions of the fractal), and τ_i represents the ratio of the radii between smaller and larger spherical particles that make up the adsorbent particles of radius $R_{p,i}$. It is important to mention here that, as was also indicated in the previous works of Li and Liapis [1, 2], the porosity $\varepsilon_{p,i,j+1}$ does not represent a porosity of agglomeration of porous media, but it simply denotes the porosity of the microspheres of radius $R_{m,i,j+1}$. Furthermore, in constructing the (porous) structure of the partially fractal porous adsorbent particles, it is considered that $\varepsilon_{p,i} = \varepsilon_{p,i,1} = \varepsilon_{p,i,2} = \varepsilon_{p,i,3} = \ldots = \varepsilon_{p,i,N'+1}$ where $\varepsilon_{p,i}$ is the porosity of the particles of radius $R_{p,i}$ and $\varepsilon_{p,i}$ is equal to $\varepsilon_{p,i,1}$ because the particles having a value of the recursion j being equal to zero (j=0) correspond to the particles having radius $R_{p,i,1}$, as is clearly indicated by Eq. (1) above where $R_{p,i} = R_{p,i,1}$ when j=0. In Figs. 1(a) and 1(b), schematic representations of partially fractal adsorbent particles with N′=1 and N′=2 are presented, respectively. The value of τ_i in Eq. (1) is less than unity ($\tau_i < 1$) and the value of N′ is finite [1, 2, 6]. It is important to note here that for a given porous adsorbent particle of radius $R_{p,i}$ and a given value of τ_i, the total intraparticle (internal) pore surface area, $A_{ws,i}$, of the particle increases as the total number of divisions, N′, increases, because the number of smaller in size pores in the partially fractal adsorbent particle of radius, $R_{p,i}$, increases with increasing N′ [1,2,6]. Thus, the partially fractal adsorbent particles of different radii packed in a stratified packed bed can provide not only a variation in the lengths of the intraparticle diffusional pathways of the adsorbate solute as it moves from the inlet section to the outlet section of the packed bed, but can also provide a varying internal adsorption surface area which can significantly affect the rate [1-3,6,7,8,15] at which adsorption takes place. If, as an approximation, the geometry of the pores of the partially fractal particles is considered to be cylindrical, it can then be shown [16] that in particles of radius $R_{p,i}$ with N′= 1, the surface areas of the pores in (i) the microspheres of radius $R_{m,i,2}$ of the particle, and (ii) the pores of the particle of radius $R_{p,i}$ formed from the gluing of the microspheres of radius $R_{m,i,2}$, could be estimated from Eqs. (2) and (3), respectively,

$$A_{pores,i,2} = \frac{2V_{p,i}(1-\varepsilon_{p,i})^2}{\delta R_{m,i,2}\tau_i}, \quad i = 1,2,3,..,N \tag{2}$$

$$A_{pores,i,1} = \frac{2V_{p,i}(1-\varepsilon_{p,i})}{\delta R_{p,i}\tau_i}, \quad i = 1,2,3,..,N \tag{3}$$

In Eqs. (2) and (3), $V_{p,i}$ denotes the volume of the particle of radius $R_{p,i}$ and $\varepsilon_{p,i}$ represents the particle porosity. When particles of radius $R_{p,i}$ with N′=2 are considered, then the surface areas of the pores in (a) the microspheres of radius $R_{m,i,3}$, (b) the microspheres of radius $R_{m,i,2}$ formed from the gluing of the microspheres of radius $R_{m,i,3}$, and (c) the pores of the particle of radius $R_{p,i}$ formed from the gluing of the microspheres of radius $R_{m,i,2}$, could be estimated [16] from Eqs.(4), (2) and (3), respectively,

$$A_{pores,i,3}=\frac{2V_{p,i}(1\text{-}\varepsilon_{p,i})^3}{\delta R_{m,i,3}\tau_i},\ i = 1,2,3,..,N \tag{4}$$

The parameter δ in Eqs.(2) - (4) is a proportionality constant that characterizes the packing structure of microspheres of recursion j into a sphere of recursion j-1. Also, it is worth mentioning here that in Eq. (1) when the adsorbent particle is a conventional adsorbent particle that does not have a partially fractal structure, then j=0 and Eq. (1) gives

$$R_{m,i,1} = R_{p,i} \tag{5}$$

which denotes that the conventional [1-3] porous particle of radius $R_{p,i}$ is made from a single porous particle of radius $R_{m,i,1}$ whose magnitude is equal to the value of $R_{p,i}$.

Eqs. (2) and (3) indicate that for a partially fractal particle with N'=1, the relationship between $A_{pores,i,2}$ and $A_{pores,i,1}$ could be determined by

$$A_{pores,i,2} = (1\text{-}\varepsilon_{p,i})(\frac{1}{\tau_i})A_{pores,i,1} \tag{6}$$

By considering Eqs. (2), (4), and (6) it can be shown that for a partially fractal particle with N'=2, the relationship among $A_{pores,i,3}$, $A_{pores,i,2}$, and $A_{pores,i,1}$ is as follows:

$$A_{pores,i,3} = (1\text{-}\varepsilon_{p,i})(\frac{1}{\tau_i})A_{pores,i,2}= (1\text{-}\varepsilon_{p,i})^2(\frac{1}{\tau_i})^2A_{pores,i,1} \tag{7}$$

From Eqs. (6) and (7), it can be deduced that the surface area, $A_{pores,i,j+1}$, of the pores of a given recursion j of a partially fractal porous particle of radius $R_{p,i}$ could be determined from the following expression:

$$A_{pores,i,j+1} = (1\text{-}\varepsilon_{p,i})^j(\frac{1}{\tau_i})^jA_{pores,i,1} \quad \text{for i =1,2,..,N and j=0,1,2,..,N'} \tag{8}$$

For physically plausible values of $\varepsilon_{p,i}$ [1-6] and $1/\tau_i$ [1, 2], Eqs. (6)-(8) indicate that one could expect $A_{pores,i,N'+1} > A_{pores,i,N'} > \ldots > A_{pores,i,3} > A_{pores,i,2} > A_{pores,i,1}$. These results clearly indicate that as the value of the total number, N', of the recursion of the fractal increases, the total intraparticle (internal) pore surface area, $A_{ws,i}$, of the particle of radius $R_{p,i}$ increases. This would suggest that for a given partially fractal particle of radius $R_{p,i}$, the total amount of ligand molecules (adsorption sites) that could be immobilized on its total intraparticle pore surface area, $A_{ws,i}$, (the value of $A_{ws,i}$ could be estimated by adding the values of $A_{pores,i,j+1}$ for j=0,1,2,..,N′, that is $A_{ws,i} = \sum_{j=0}^{N'} A_{pores,i,j+1}$) increases as the total number, N′, of the recursion of the fractal increases.

One could now suggest that the immobilization of adsorption sites (ligands) on the intraparticle pore surface area of partially fractal particles could be realized by at least two different approaches. In approach (A), the partially fractal particle with recursion number N′ of the fractal is constructed from base matrices and then the ligand is introduced to the partially fractal particles so that adsorption sites could be attached (immobilized) on the pore surfaces of the spherical particles of recursion number j = 0,1,2,..,N′. In approach (B), adsorption sites (ligands) are immobilized only on the pore surfaces of the microspheres of recursion number N′ and then these smallest microspheres are glued to form porous spheres of recursion numbers N′-1, N′-2, N′-3,.., 2,1, and 0. Thus, in approach (B) the surfaces of the pores in the microspheres of recursion numbers N′-1, N′-2, N′-3, ..,1 and 0, do not have immobilized ligands (adsorption sites). It is apparent that the partially fractal adsorbent particles formed by approach (A) would have a higher adsorptive capacity than the partially fractal adsorbent particles formed by approach (B), and, therefore, approach (A) would represent the more desirable method for forming partially fractal adsorbent particles. We presented approach (B) only for the reason that there could be cases where the construction of perfusive [6, 9] particles may consider the formation of partially fractal adsorbent particles with a low value for the recursion number, N′, of the fractal so that the pores of the particle where ligand molecules have not been immobilized are mainly used for intraparticle convective flow [6, 9].

A stratified packed bed of total length L, as shown in Fig.1(c), is considered and is represented by the connected in a continuous sequence set of the fixed-bed sections S_i (i=1,2,3,..,N) where each section has a length L_i (i=1,2,3,..,N) such that $L=\sum_{i=1}^{N} L_i$, and $C_{d,in}$ and $C_{d,out}$ represent the inlet and outlet concentrations of the adsorbate, respectively. The lengths, L_i, of the fixed-beds could be related through the expression

$$\frac{L_i}{L_{i+1}} = \alpha_i,\ i = 1,2,3,..,N-1 \tag{9}$$

where the parameter α_i could have a constant value. In each section of length L_i, spherical porous adsorbent particles of radius $R_{p,i}$ with a partially fractal structure are packed, and the values of the radii of the particles are related through the expression

$$\frac{R_{p,i}}{R_{p,i+1}} = \beta_i,\ \ i = 1,2,3,..,N-1 \tag{10}$$

where the parameter β_i is greater than unity ($\beta_i > 1$) for i=1,2,3,..,N-1, and, thus, $R_{p,1}>R_{p,2}>R_{p,3}>\ldots>R_{p,N-1}>R_{p,N}$ [1,2]. The porosity ε_i in each fixed-bed section of the stratified packed bed is taken to have the same value ε, and, thus, $\varepsilon_i = \varepsilon$ (i=1,2,3,..,N); this requirement implies that the fraction of the volume of each section S_i (i=1,2,..,N) occupied by the solid phase of the partially fractal porous adsorbent particles is the same in each section of the stratified packed bed. Thus, the fraction of the volume of the whole column of length L occupied by the solid phase of the partially fractal porous adsorbent particles is the same in a conventional column or in a stratified column, but the total pore surface area associated with the particles packed in the stratified column is larger than that of the conventional column because of the requirement imposed by Eq. (10). In such a stratified packed bed adsorber, the value of the film mass transfer coefficient, $K_{f,i}$, of the adsorbate solute increases [1] as it moves from the inlet section to the outlet section of the column while the lengths of the intraparticle diffusional pathways of the adsorbate in the spherical porous adsorbent particles decrease and the total intraparticle suface area could increase, and the combination of these three effects would lead to an average mass transfer rate per unit length in the stratified column that would be larger than the average mass transfer rate per unit length in a fixed-bed of length L packed only with adsorbent particles of radius $R_{p,1}$; this latter fixed-bed would result from the system where N=1 and this means that the fixed-bed column has only one section, S_1, whose length is L. For the stratified bed in Fig. 1, the exiting stream from each section of length L_i becomes an inlet stream in the section following the section of length L_i.

Adsorption of adsorbate is considered to take place from a flowing liquid in the fixed-beds of adsorbent particles in sections S_i (i=1,2,..,N) under isothermal conditions, and the concentration gradients in the radial direction of the bed are considered to be not significant [1-4]. A differential mass balance for the adsorbate in the fluid stream flowing through a section S_i packed with spherical adsorbent particles gives

$$\frac{\partial C_{d,i}}{\partial t} - D_{L_i}\frac{\partial^2 C_{d,i}}{\partial x^2} + \frac{V_{f,i}}{\varepsilon_i}\left(\frac{\partial C_{d,i}}{\partial x}\right) = \left(\frac{1-\varepsilon_i}{\varepsilon_i}\right)\left(\frac{3}{R_{p,i}}\right)K_{f,i}\left(C_{p,i}\Big|_{R=R_{p,i}} - C_{d,i}\right),\ i=1,2,..,N \quad (11)$$

In Eq. (11), the superficial velocity, $V_{f,i}$, of the fluid stream is taken to be independent of the space variable x because the liquid solutions encountered in most separations involving biomolecules are very dilute and the main component of the solution is the carrier (solvent) fluid. An expression for estimating the value of the axial dispersion coefficient of the adsorbate, D_{L_i} , was presented by Arnold et al. [17, 18], but in most practical systems the axial dispersion is so low that by setting its value equal to zero the error introduced in the prediction of the behavior of an adsorption system is not significant [17, 18]. When D_{L_i} =0 for i =1,2,..,N, Eq. (11) takes the form

$$\frac{\partial C_{d,i}}{\partial t}+\frac{V_{f,i}}{\varepsilon_i}\left(\frac{\partial C_{d,i}}{\partial x}\right)=\left(\frac{1-\varepsilon_i}{\varepsilon_i}\right)\left(\frac{3}{R_{p,i}}\right)K_{f,i}\left(C_{p,i}\Big|_{R=R_{p,i}}-C_{d,i}\right),\ \text{i=1,2,3,..,N} \qquad (11a)$$

The initial and boundary conditions of Eq. (11a) are as follows:

$$\text{at } t = 0,\quad C_{d,i} = 0 \text{ for } 0 \le x \le L=\sum_{i=1}^{N} L_i,\quad \text{i=1,2,3,..,N} \qquad (12)$$

$$\text{at } x = 0,\ C_{d,1} = C_{d,in},\ t > 0 \qquad (13)$$

$$\text{at } x = L_i,\ C_{d,out}\Big|_{x=L_i} = C_{d,in}\Big|_{x=L_{i+1}},\ t > 0,\ \text{i=1,2,3,..,N-1} \qquad (14)$$

$$\text{at } x = L,\ \left.\frac{\partial C_{d,N}}{\partial x}\right|_{x\,=\,L} = 0,\ t > 0 \qquad (15)$$

In Eq. (15), the value of L is equal to $\sum_{i=1}^{N} L_i$, as discussed above.

In this study, only one-site adsorbate-ligand complexes [15, 19] are considered to be formed from the interaction between the adsorbate molecules and the immobilized ligands; for adsorbate-ligand complexes involving more than one ligand (multi-site adsorbate-ligand complexes), one could consult the studies in References [19, 20]. The interaction between unbound adsorbate, $A_{ads,i,j+1}$, and vacant immobilized ligand, $L_{lig,i,j+1}$, is considered to be of the form

$$A_{ads,i,j+1} + L_{lig,i,j+1} \underset{k_{2,i,j+1}}{\overset{k_{1,i,j+1}}{\rightleftarrows}} A_{ads,i,j+1}L_{lig,i,j+1} \tag{16}$$

where $A_{ads,i,j+1}L_{lig,i,j+1}$ represents the one-site adsorbate-ligand complex. The differential mass balance equation for the adsorbate in the fluid in the pores of the particles of radius $R_{p,i}$ and $R_{m,i,j+1}$ is given by

$$\varepsilon_{p,i,j+1}\frac{\partial C_{p,i,j+1}}{\partial t} + (1-\varepsilon_{p,i,j+1})\frac{\partial \overline{C}_{ps,i,j+1}}{\partial t} + \frac{\partial C_{s,i,j+1}}{\partial t} = \varepsilon_{p,i,j+1}D_{p,i,j+1}\left[(\frac{2}{R_{i,j+1}})\frac{\partial C_{p,i,j+1}}{\partial R_{i,j+1}} + \frac{\partial^2 C_{p,i,j+1}}{\partial R^2_{i,j+1}}\right]$$

$$\text{for i=1,2,3,..,N and j =0,1,2,..,N'-1} \tag{17}$$

The accumulation term, $\partial C_{s,i,j+1}/\partial t$, in Eq. (17) of the adsorbate in the adsorbed phase is determined from the adsorption model in expression (16) and has the form

$$\frac{\partial C_{s,i,j+1}}{\partial t} = k_{1,i,j+1}C_{p,i,j+1}(C_{T,i,j+1}-C_{s,i,j+1})-k_{2,i,j+1}C_{s,i,j+1} \quad \text{for i=1,2,..,N and j=0,1,2,..,N'-1} \tag{18}$$

The differential mass balance equation for the adsorbate in the fluid in the pores of the smallest in the particle microspheres of radius $R_{m,i,N'+1}$ is given by Eq. (19)

$$\varepsilon_{p,i,N'+1}\frac{\partial C_{p,i,N'+1}}{\partial t} + \frac{\partial C_{s,i,N'+1}}{\partial t} = \varepsilon_{p,i,N'+1}D_{p,i,N'+1}\left[(\frac{2}{R_{i,N'+1}})\frac{\partial C_{p,i,N'+1}}{\partial R_{i,N'+1}} + \frac{\partial^2 C_{p,i,N'+1}}{\partial R^2_{i,N'+1}}\right] \quad \text{for i=1,2,3,..,N} \tag{19}$$

where

$$\frac{\partial C_{s,i,N'+1}}{\partial t} = k_{1,i,N'+1}C_{p,i,N'+1}(C_{T,i,N'+1}-C_{s,i,N'+1})-k_{2,i,N'+1}C_{s,i,N'+1} \quad \text{for i=1,2,..,N} \tag{20}$$

It is worth mentioning here that if the dynamic adsorption mechanism is described by an expression other than the second-order mechanism employed in Eqs. (18) and (20), then the right-hand-side expressions in Eqs. (18) and (20) should be replaced by the appropriate model expression of the prevailing adsorption mechanism. The term $\partial \overline{C}_{ps,i,j+1}/\partial t$ for i=1,2,..,N and j =0,1,2,..,N′-1 in Eq. (17), represents the accumulation of adsorbate in the pore fluid and adsorbed phase of the microspheres of radius $R_{m,i,j+2}$ with j in $R_{m,i,j+2}$ having values of j =0,1,2,3,..,N′-1. The expression for this accumulation term is

$$\frac{\partial \overline{C}_{ps,i,j+1}}{\partial t} = \left(\frac{3}{R_{m,i,j+2}^{\ \ 3}}\right)\frac{\partial}{\partial t}\left[\int_0^{R_{m,i,j+2}} \varepsilon_{p,i,j+2} C_{p,i,j+2} R_{i,j+2}^2 \, dR_{i,j+2} + \int_0^{R_{m,i,j+2}} (1-\varepsilon_{p,i,j+2})\overline{C}_{ps,i,j+2} R_{i,j+2}^2 dR_{i,j+2} + \int_0^{R_{m,i,j+2}} C_{s,i,j+2} R_{i,j+2}^2 dR_{i,j+2}\right] \quad \text{for i=1,2,..,N and j = 0,1,2,3,..,N'-1} \tag{21}$$

The initial and boundary conditions in Eqs.(17)-(20) are as follows:

$$\text{at } t = 0,\ C_{p,i,j+1} = 0, \quad \text{for } 0 \le R_{i,j+1} \le R_{m,i,j+1},\ \text{i=1,2,3,..,N and j=0,1,2,..,N'-1} \tag{22}$$

$$\text{at } t = 0,\ C_{s,i,j+1} = 0, \quad \text{for } 0 \le R_{i,j+1} \le R_{m,i,j+1},\ \text{i=1,2,3,..,N and j=0,1,2,..,N'-1} \tag{23}$$

$$\text{at } t = 0,\ C_{p,i,N'+1} = 0, \quad \text{for } 0 \le R_{i,N'+1} \le R_{m,i,N'+1},\ \text{i = 1,2,3,..,N} \tag{24}$$

$$\text{at } t = 0,\ C_{s,i,N'+1} = 0, \quad \text{for } 0 \le R_{i,N'+1} \le R_{m,i,N'+1},\ \text{i = 1,2,..,N} \tag{25}$$

$$\text{at } R_{i,j+1} = 0,\ \frac{\partial C_{p,i,j+1}}{\partial R_{i,j+1}} = 0 \qquad \text{for t>0, i=1,2,3,..,N and j =0,1,2,..,N'-1} \tag{26}$$

$$\text{at } R_{i,N'+1} = 0,\ \frac{\partial C_{p,i,N'+1}}{\partial R_{i,N'+1}} = 0 \qquad \text{for t>0, i=1,2,3,..,N} \tag{27}$$

$$\text{at } R_{i,1} = R_{m,i,1} = R_{p,i},\ -D_{p,i,1}\left.\frac{\partial C_{p,i,1}}{\partial R_{i,1}}\right|_{R_{i,1}=R_{p,i}} = K_{f,i}\left(C_{p,i,1}\Big|_{R_{i,1}=R_{p,i}} - C_{d,i}\right) \quad \text{for t>0 and i=1,2,3,..,N} \tag{28}$$

$$\text{at } R_{i,j+1} = R_{m,i,j+1},\ C_{p,i,j+1} = C_{p,i,j}(t,R_{i,j}) \qquad \text{for t>0, i=1,2,..,N and j=1,2,..,N'-1} \tag{29}$$

$$\text{at } R_{i,N'+1} = R_{m,i,N'+1},\ C_{p,i,N'+1} = C_{p.i,N'}(t,R_{i,N'}) \ \text{for t>0, i=1,2,3,..,N} \tag{30}$$

The terms $C_{T,i,j+1}$ and $C_{T,i,N'+1}$ in Eqs. (18) and (20) represent the maximum concentration of adsorbate in the adsorbed phase on the surface of the pores in the spherical particles of radii $R_{m,i,j+1}$(i=1,2,3,..,N and j=0,1,2,..,N′-1) and $R_{m,i,N'+1}$ (i=1,2,3,..,N), respectively; it is worth noting again here for clarity that $R_{m,i,1} = R_{p,i}$ (i=1,2,3,..,N). If the accumulation terms in Eqs.(18) and (20) are set equal to zero, this could imply that the adsorption step occurs in effect infinitely fast and adsorption equilibrium takes place and follows the Langmuir equilibrium adsorption isotherm [1-4]. It is instructive to mention here that one could attempt to relate to a first degree of approximation the values of $C_{T,i,j+1}$ and $C_{T,i,N'+1}$ to the values of the surface areas $A_{pores,i,j+1}$ and $A_{pores,i,N'+1}$ of the pores in the spherical particles of radii $R_{m,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,..,N′-1) and $R_{m,i,N'+1}$ (see, for example, Eqs.(6) - (8) above for the relation between different surface areas of pores in different spherical particles). Therefore, by considering that the amount of ligand that could be immobilized on a surface could increase as the area of the surface increases, one could then expect that it could be physically plausible that the maximum concentration of adsorbate in the adsorbed phase would depend on the surface area on which the ligands have been immobilized and, thus, the values of $C_{T,i,j+1}$ (i=1,2,3,…,N and j=0,1,2,..,N′-1) and $C_{T,i,N'+1}$ could be expected to increase as the amount of immobilized ligands (adsorption sites) increases (see expression (16) above) due to increased pore surface areas. Thus, it could be reasonable to expect that the inequality $C_{T,i,N'+1}>C_{T,i,N'}>\ldots>C_{T,i,2}>C_{T,i,1}$ could be realized due to the increased pore surface area obtained as the total number, N′, of the recursions of the fractal increases and leads to pore surface areas which follow the inequality $A_{pores,i,N'+1}>A_{pores,i,N'}>\ldots>A_{pores,i,2}>A_{pores,i,1}$ for i = 1,2,3,..,N. Furthermore, Eqs. (17) and (21) indicate that the rate of adsorbate uptake becomes higher as the total number, N′, of the recursion of the fractal increases. In effect one could suggest that the ″swallowing″ rate of the adsorbate by the partially fractal porous adsorbent particles increases as the value of N′ increases.

Eqs.(11)-(30) represent a mathematical model that could be used to study the dynamic behavior of adsorption in columns packed with porous adsorbent particles having partially fractal structures and where there are ligand molecules immobilized on the surface of the pores in the particles of each division (recursion) number j = 0,1,2,3,..,N′, and this implies that the immobilization of the ligands in the adsorbent particles took place by approach (A) discussed above. If the immobilization of the ligands occurs by approach (B) where ligands are immobilized only on the pore surfaces of the smallest microspheres of radius $R_{m,i,N'+1}$, then the terms $\partial C_{s,i,j+1}/\partial t$ and $C_{s,i,j+2}$ in Eqs.(17) – (18) and Eq. (21), respectively, are set equal to zero for j=0,1,2,3,..,N′-1. It should be noted here that while the variables and parameters employed in Eqs. (1) - (30) above have been appropriately defined in the text, the reader will find a complete nomenclature for all variables and parameters as well as their units in the material of this paper submitted as supporting information.

It is also worth mentioning here that if in the larger in diameter pores of the partially fractal particles convective fluid flow could take place under the applied pressure drop regime employed in the packed bed sections of the column, then in certain pores of the particles of radii $R_{m,i,j+1}$ the adsorbate molecules could be transported by both intraparticle convective flow and pore diffusional mass transfer mechanisms and this could correspond to what is termed as intraparticle mass transfer by perfusion [6,10,21]. In such partially fractal particles there could be regions of pore space where mass transfer of adsorbate occurs by perfusion while in other regions of pore space the sizes of the pore diameters are such that intraparticle convective fluid flow cannot occur and mass transfer of adsorbate takes place only by pore diffusion. If intraparticle convective fluid flow could occur in certain porous particles of radius $R_{m,i,j+1}$, then a convective mass transfer term could be added [6,10] in Eqs. (17) and (19) and the intraparticle velocity field could be determined from the expressions in Reference [10]. The intraparticle fluid velocity increases the rate of transport of adsorbate in the pore space of the adsorbent particles because the magnitude of the intraparticle convective velocity of the adsorbate could be significantly larger than the magnitude of the intraparticle diffusional velocity of the adsorbate [6, 9-14] and, thus, the adsorbate in the pore fluid could move faster to pore regions where unoccupied ligands exist and, therefore, adsorption could occur, and this reduces the dispersion of the mass wave of the adsorbate in the pores of the particles because the overall intraparticle mass transfer resistance has been reduced due to intraparticle fluid convection. But it is worth noting here that as the size of the diameter of the intraparticle pores increases in order for convective fluid flow to be able to occur, the surface area of the intraparticle pores decreases and this would imply that lower amounts of ligands (adsorption sites) could be immobilized and, thus, the overall adsorptive capacity of the conventional or of the partially fractal adsorbent particles could be reduced. Furthermore, Heeter and Liapis [13] have shown that the performance of adsorption separation systems with purely diffusive particles could be better than the performance of adsorption separation systems with perfusive particles, if purely diffusive particles could be made that have higher values of $C_{T,i,j+1}$ ($i=1,2,3,\ldots,N$ and $j=0,1,2,3,\ldots,N'$) , as could be the case with adsorbent particles having partially fractal structures, than otherwise comparable perfusive particles. The positive and negative effects of perfusive adsorbent particles with respect to separation performance are discussed in References [6, 9-14]. The possible quantitative effects of (i) intraparticle convective flow [10, 11-14, 21] in certain pore space regions of the partially fractal particles and (ii) electrophoretic mass transfer (migration) due to the interactions of charged species in the pore fluid and charged ligands immobilized on the pore surfaces [7-9, 22, 23], could be the subject of a future study. In this work, we consider that intraparticle mass transfer of adsorbate in the pore fluid of the particles of diameter $R_{m,i,j+1}$ occurs only by pore diffusion for all values of i=1,2,3,…,N and j=0,1,2,3,…,N', and, therefore, the adsorbent particles with partially fractal structures employed in this study are purely diffusive particles.

The partial differential equations of the mathematical model presented above were solved numerically by the method of orthogonal collocation [24, 25] and the resulting ordinary differential equations were integrated by Gear’s method [25].

3. Results and Discussion

The dynamic behavior of adsorption in a single column (N=1) as well as in a stratified column of two beds (N=2) is studied in this work, and the columns are packed with porous adsorbent particles having partially fractal structures with the value of the total number, N', of recursions of the fractal being equal to 1 or 2 (N'=1 or N'=2) for all porous adsorbent particles. All columns have the same diameter and total length L. The values of the parameters that remain constant for the adsorption systems considered here are listed in Table 1. The magnitude of the effective pore diffusion coefficient, $D_{p,i,j+1}$, is about 36.07% of the magnitude of the free molecular diffusion coefficient, D_{fm}, due to (a) the restrictions imposed on the movement of the adsorbate molecules in the pores of the adsorbent medium, and (b) the tortuous in length pathways the adsorbate molecules have to travel during their transport through porous media. The effects of items (a) and (b) on the values of $D_{p,i,j+1}$ depend on [7,8,14] the dynamic evolution of the pore size and pore connectivity distributions of the pores in the porous medium [7,8] before and during adsorption. It should be mentioned here that in Table 1 the effective pore diffusion coefficient, $D_{p,i,j+1}$, of lysozyme is taken to have the same value for the systems studied in this work where i=1, 2 and j=0, 1, 2 and, therefore, the largest values of N and N' are equal to 2 and 2, respectively (see Table 1). It happens to be the case for the systems studied here that the radius of the smallest pores which are located in the microspheres of radius $R_{m,2,3}$, is still large enough in magnitude [1, 6, 16] that monolayer adsorption of lysozyme on the surface of the smallest in radius pores would not make the magnitude of the effective pore diffusion coefficient $D_{p,2,3}$ of lysozyme in the smallest pores to be significantly lower than the magnitude of the effective pore diffusion coefficient $D_{p,1,1}$ of lysozyme in the pores having the largest radius and which are located in the particles of radius $R_{m,1,1}$ when also monolayer adsorption of lysozyme occurs on the surface of the largest in radius pores. Of course, the mathematical model presented here can employ different values of the effective pore diffusion coefficient $D_{p,i,j+1}$ of an adsorbate of interest at different values of i=1,2,3,…,N and j=0,1,2,3,…,N'. The values of the parameters $C_{d,in}$, $k_{1,i,j+1}$, $k_{2,i,j+1}$, L, T, ε_i, $\varepsilon_{p,i}$, $\varepsilon_{p,i,j+1}$, μ, and ρ in Table 1 are from adsorption systems reported in the literature [1-4,17-19,26] and, for the purposes of the simulations of this study, are considered to have appropriate magnitudes since they characterize adsorption systems of practical use. The film mass transfer coefficient, $K_{f,i}$, was determined from the correlation developed by Wilson and Geankoplis [27] for given values of $R_{p,i}$, $V_{f,i}$, ε_i, D_{fm}, μ and ρ. When ε_i = constant and $V_{f,i}$ =constant for i=1,2,..,N, it can be shown [1] that

$$K_{f,i+1} = K_{f,i}[(\frac{R_{p,i}}{R_{p,i+1}})^{0.66}] \quad \text{for } i = 1,2,..,N-1 \tag{31}$$

where $R_{p,i}>R_{p,i+1}$ for i =1,2,..,N-1. The expression in Eq. (31) indicates that $K_{f,i+1}$ is greater than $K_{f,i}$ for i=1,2,3,…,N-1. A stratified column of two packed beds of total length L (N=2, $L=\sum_{i=1}^{2} L_i$) is investigated in this work and its results are compared with those obtained when the whole column has only one section (N=1) of length L. The value of the radius $R_{p,1}$ of the porous adsorbent particles being packed in the column having only one section (N=1) and length L, and also in the first section (i=1) of the stratified column having two (N=2) sections is taken to be equal to 50×10^{-6} m. Furthermore, the values of α_i and β_i for the stratified column bed system studied here are taken [1, 2] to be equal to 1.5 and 1.5, respectively. Therefore, from the value of α_i and the total length L of the column, the length L_i of each section i of the stratified column bed can be determined (see Eq. (9)) while from the values of $R_{p,1}$ and β_i the radius $R_{p,i}$ of the porous adsorbent particles packed in each section i of the stratified column bed can be calculated (see Eq. (10)). The value of the superficial velocity, $V_{f,i}$, of the flowing fluid stream in each section i of the stratified column bed is taken to be constant and equal to the superficial velocity, V_f, of the fluid in the column that has only one section (N=1) and the same total length, L, as the stratified column bed; this implies that $V_{f,i}=V_f$ for i=1,2,..,N for the adsorption systems studied in this work.

The values of the parameters $C_{T,i,j+1}$ (i=1,2 and j=0,1,2) are presented in Table 2. The proportionality constant, δ, in Eq. (3) is taken [28] to be equal, as an approximation of first degree, to 1/3 and then by knowing the values of $R_{p,i}$, τ_i, $V_{p,i}$, and $\varepsilon_{p,i,}$ the pore surface area $A_{pores,i,1}$ (i=1,2) can be estimated from Eq. (3). Then by calculating the total amount of particles of radius $R_{p,i}$ packed in a given section S_i of the column, accounting for the projected surface area of an adsorbed lysozyme molecule onto the surface of the pores, and considering that the surface area $A_{pores,i,1}$ is covered by a monolayer of adsorbed lysozyme, the value of $C_{T,i,1}$ (i=1,2) can be estimated [16] and is reported in Table 2. As the value of the division (recursion) number, j, of the fractal increases, Eqs. (6) and (7) clearly indicate that the value of $A_{pore,i,2}$ is higher than the value of $A_{pores,i,1}$ and also the value of $A_{pores,i,3}$ is larger than the value of $A_{pores,i,2}$ ($A_{pores,i,3}>A_{pores,i,2}>A_{pores,i,1}$ for i=1,2). This would indicate that the value of $C_{T,i,2}$ can be larger than the value of $C_{T,i,1}$ and, furthermore, the value of $C_{T,i,3}$ can be larger than the value of $C_{T,i,2}$ ($C_{T,i,3}>C_{T,i,2}>C_{T,i,1}$ for i =1,2). By considering values of particle parameters employed in practice and assuming monolayer coverage of the pore surfaces $A_{pores,i,j+1}$ (i=1,2 and j=0,1,2), estimates of the values of $C_{T,i,j+1}$ could be obtained which suggest that the ratio $C_{T,i,j+1}/C_{T,i,j}$ (i=1,2 and j=1,2) can be significantly larger than unity. To be on the conservative side of estimated values for $C_{T,i,2}$ and $C_{T,i,3}$, we have taken that the ratios $C_{T,i,3}/C_{T,i,2}$ and $C_{T,i,2}/C_{T,i,1}$ are equal to 1.5, respectively. Therefore, the values of $C_{T,i,2}$ and $C_{T,i,3}$ in Table 2 are taken to be 50% larger than the corresponding values of $C_{T,i,1}$ and $C_{T,i,2}$, respectively, for a given value of i (i=1,2). We have used conservative values for

$C_{T,i,2}$ and $C_{T,i,3}$ because our interest here is to show the significant benefits that could be realized with respect to the dynamic adsorption of an adsorbate in columns employing partially fractal particles and, of course, the dynamic results with respect to adsorption efficiency would even be much better if higher ratios for the values of $C_{T,i,j+1}/C_{T,i,j}$ (i=1,2 and j=1,2) would be employed.

The column systems studied in this work are packed with partially fractal particles which are constructed from base matrices and then the ligand was introduced to the partially fractal particles so that adsorption sites could be immobilized (attached) on the pore surfaces of the spherical particles of recursion number j=0, 1, 2 (approach (A)); as was indicated above and on Table 1, the recursion number N' of the fractal has values of 1 and 2 in this study. The criterion that is used to compare the performance of the different adsorption column systems is the breakthrough time, t_b, [1-4, 15, 29]. The breakthrough time, t_b, is defined as the time when the concentration, $C_{d,out}$, of the adsorbate in the outlet stream from the column becomes equal to 1% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column. In Tables 3 and 4 the values of the breakthrough time, t_b, are reported for a single adsorption column (N=1) and a stratified column comprised of two sections (N=2), respectively, as well as the times when the concentration of the adsorbate in the column outlet stream becomes equal to 5% and 10% of the inlet concentration of the adsorbate in the column.

The simulation results in Tables 3 and 4 clearly show that for given values of $V_{f,i}$, and $1/\tau_i$ (i =1,2), the breakthrough time, t_b, increases as the values of N and N' increase. When the value of the total recursion number, N', of the fractal is increased from 1 to 2, the adsorptive capacity of the particles increases, as the data for $C_{T,i,j+1}$ (i=1,2 and j=0,1,2) in Table 2 indicate, and this leads to a larger amount of adsorbate being adsorbed onto the partially fractal particles and this can provide a reduction to the overall intraparticle mass transfer resistance due to the fact that the higher adsorptive capacity leads to a larger gradient in the concentration of the adsorbate in the pore fluid of the microspheres from which the partially fractal particles are made from, and this latter effect increases the intraparticle mass transfer rate. When the total number, N, of the sections of a stratified column bed is increased from 1 to 2, the film mass transfer coefficient, $K_{f,2}$, in the second section of the stratified column has a magnitude (see Eq. (31)) significantly larger than the magnitude of the film mass transfer coefficient, $K_{f,1}$, in the first section of the stratified bed and this can increase the speed of the mass of adsorbate that is being transferred from the bulk flowing fluid phase to the surface of the particles; but most importantly the adsorbate can attain large intraparticle mass transfer rates due to the fact that the partially fractal particles of the second section of the stratified column are smaller in diameter than the particles packed in the first section of the stratified column and for the same value of $1/\tau_i$ (i=1,2) in both sections of the stratified column, the adsorptive capacity per partially fractal particle is significantly larger in the particles packed in the second section of the stratified column, as the data on Table 2 clearly show. Thus,when the value of N is increased from 1 to 2, both (i) the external mass transfer rate of the adsorbate from the flowing fluid stream to the surface of the particles packed in the second section of the stratified coclumn can increase, and (ii) the intraparticle mass transfer rate of the adsorbate can increase due to the larger adsorptive capacity of the partially fractal particles packed in the second section of the stratified column which leads to a larger gradient in the concentration of the adsorbate in the pore fluid of the microspheres from which the partially fractal particles are made from. Furthermore, the results in Tables 3 and 4 indicate that for given values of N, N′, and $1/\tau_i$ (i=1, 2), the effect of increasing the superficial velocity (increasing the system throughput), $V_{f,i}$ (i=1,2), leads, as expected, to a decrease in the value of the breakthrough time, t_b, due to the decreased residence times of the adsorbate molecules in the packed column beds. But the value of t_b obtained for a given value of the superficial velocity, $V_{f,i}$ (i=1,2) , has a larger magnitude for larger values of N, N′, and $1/\tau_i$ (i=1,2). For the systems studied in this work, it is observed that for a given value of $V_{f,i}$ (i=1,2) the largest value of t_b is obtained when N=2, N′=2, and $1/\tau_i = 30$ (i=1,2) and these represent the largest numbers of N, N′, and $1/\tau_i$ (i=1,2) employed in this work. If the value of $V_{f,i}=2.778\times10^{-3}$ m/s is taken to represent the base value of the superficial velocity in this study, then the data on Tables 3 and 4 indicate that we have examined the effect that increasing values of $V_{f,i}$ have on the breakthrough time, t_b, by considering increments of 100% and 200% on the base value of $V_{f,i}$. If one determines the processed amount of adsorbate up to time t_b in the stratified column bed with N=2, N′=2, and $1/\tau_i = 30$ (i=1,2) by multiplying the inlet concentration of the adsorbate with the result obtained from the product of the volumetric flow rate with the breakthrough time, one would find that the processed amounts of adsorbate are reduced by 36.33% and 54.21% when the value of $V_{f,i}$ is increased by 100% and 200% above the base value of $V_{f,i}$, respectively; these reductions are significantly smaller than those that could occur when conventional columns packed with conventional porous adsorbent particles were employed and the base value of the superficial velocity had been increased by 100% and 200% [1-4, 15, 29]. Of course, if less conservative values for the parameter $C_{T,i,j+1}$ (i=1,2 and j=0,1,2) had been used in our simulations, then larger breakthrough times, t_b, would have been obtained and the magnitude of the effect that increasing values of the superficial velocity, $V_{f,i}$ (i=1,2), has on the breakthrough time, t_b, and the processed amount of adsorbate up to time t_b, would have been smaller.

Furthermore, the results in Tables 3 and 4 indicate that for given values of N, N′, and $V_{f,i}$ (i=1,2), the breakthrough time, t_b, increases significantly in magnitude as the value of $1/\tau_i$ (i=1,2) increases. Increased values of $1/\tau_i$ mean that the radii $R_{m,i,2}$ and $R_{m,i,3}$ of the microspheres are decreased, and the physical reasons for explaining the increases in the breakthrough time, t_b, are that (a) the length of the pathways for the diffusion of the adsorbate in the microspheres decreases [1,2] and this results to a smaller resistance for mass transfer in the microspheres and a larger adsorbate concentration gradient in the fluid of the micropores, which provides a larger mass flux for the adsorbate in the microspheres, and (b) the total internal surface area, $A_{ws,i}$ (i=1,2), of the pores of the adsorbent particle increases as the size of the microspheres from which the adsorbent particle is made decreases (see Eqs. (6) and (7)) because the number of smaller in size pores in the partially fractal adsorbent particle of radius $R_{p,i}$ increases with increasing values of $1/\tau_i$ (see Eq. (9) in Reference [1]), and this leads to larger adsorptive capacities, as the data for $C_{T,i,j+1}$ (i=1,2 and j=0,1,2) in Table 2 indicate, which result to a larger amount of adsorbate being adsorbed and this implies that the average mass transfer rate of the adsorbate in the partially fractal particle of radius $R_{p,i}$ increases. From the discussion above as well as in the previous paragraphs, it becomes apparent that increases in the values of N′ and $1/\tau_i$ act in a synergistic way to reduce the overall intraparticle mass transfer resistance by increasing the adsorptive capacity of the microspheres and also by providing a larger concentration gradient for the adsorbate molecules in the pore fluid which leads to a larger mass flux of the adsorbate in the microspheres of the partially fractal particle. In Fig. 2 the breakthrough curves for the adsorption systems with $1/\tau_i = 30$ (i=1, 2) and when N=1, 2 and N′=1, 2 are presented. As we discussed in the above paragraphs the physical reasons and mechanisms to explain the results on Tables 3 and 4, the breakthrough curves in Fig. 2 show with clarity that for a given $1/\tau_i$ (i=1,2) the breakthrough time, t_b, and the efficacy of the dynamic adsorption of the adsorbate in a column increase as the values of both parameters N and N′ increase; the largest value of t_b and highest dynamic adsorption efficiency for the adsorption systems whose breakthrough curves are shown in Fig. 2, are obtained when N=2 and N′=2. It is important to mention here that the relative importance of the parameters N and N′ on influencing the value of the breakthrough time, t_b, and the efficacy of the dynamic adsorption of the adsorbate in a column, will depend on the value of $1/\tau_i$ (i=1,2,..,N) as well as the values of the other parameters of the system that influence the dynamic behavior of the external and intraparticle mass transfer mechanisms. But the data in Tables 3 and 4 and in Fig. 2 indicate that in practice it would be desirable to use a stratified column (N≥2) whose beds are packed with partially fractal particles having technologically feasible and economically permissible high values of N′ and $1/\tau_i$ (i=1,2,..,N). Finally, it is worth mentioning that the results obtained when one uses values for the inlet concentration, $C_{d,in}$, of the adsorbate in the column that are much larger than 25.10×10^{-3} kg/m^3, follow the trends observed in the results of Tables 3 and 4 and Fig. 2.

It is worth mentioning here that not all types of materials could possess a corpuscular structure being constructed by assemblies of nano and micro particles, as it could be the case of cross-linked polymeric materials. Thus, if the research and development group of an organization cannot construct, due to technical, material, and economic limitations, actual partially fractal porous particles, then it might be possible to construct through a sequence of cross-linking operations a kind of quasi-partially fractal porous particle as depicted in the figures provided in the supporting information of this work. Of course, such quasi-partially fractal porous particles would be approximate equivalents of actual partially fractal porous particles if the physical properties with regard to local and global particle porosity, pore size and pore connectivity distributions, and diffusional path lengths associated with the actual partially fractal porous particles are closely satisfied by the pore structure of the quasi-partially fractal porous particles.

4. Conclusions and remarks

In this work a mathematical model is presented that could describe the dynamic behavior of adsorption in a single column as well as in a stratified column packed with partially fractal porous adsorbent particles. The model accounts for the mechanisms of the external mass transfer of the adsorbate through the hydrodynamic boundary layer that surrounds the spherical particles, intraparticle diffusion of adsorbate in the pore fluid of the microspheres of radius $R_{m,i,j+1}$ ($i=1,2,..,N$ and $j=0,1,2,..,N'$) from which the partially fractal particles of radius $R_{p,i}$ ($i=1,2,..,N$) are made from, and dynamic adsorption of the adsorbate onto the immobilized active sites (ligands) on the pore surfaces of the microspheres of radius $R_{m,i,j+1}$. The partial differential equations of the model were solved numerically and results were presented for the adsorption of lysozyme in a single column ($N=1$) and in a stratified column of two sections ($N=2$) packed with partially fractal porous adsorbent particles. Both the single column and the stratified column had the same total length L.

It was shown that as the values of (a) the total number, N', of recursions of the fractal and (b) $1/\tau_i$ (i=1,2,3,..,N) which represents the ratio of the radii between larger and smaller microspheres that make up the partially fractal particles of radius $R_{p,i}$ (i=1,2,3..,N), increase, then the values of the surface areas, $A_{pores,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,3,..,N′), of the pores in the microspheres of radius $R_{m,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,3,..,N′) increase which results to an increase in the value of the total intraparticle (internal) pore surface area, $A_{ws,i}$ (i=1,2,3,..,N), of the partially fractal particles of radius $R_{p,i}$ (i=1,2,3,..,N). This leads to the immobilization of a larger number of ligands (ative sites) on these larger internal pore surface areas which implies that the values of the maximum concentration of the adsorbate, $C_{T,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,3,..,N′), in the adsorbed phase could be increased as the values of N' and $1/\tau_i$ (i=1,2,3,..,N) increase. Thus, the dynamic (see Eqs. (18) and (20)) and the equilibrium adsorptive capacities of the partially fractal particles can be significantly larger than those obtained from conventional porous adsorbent particles. Furthermore, increases in the value of $1/\tau_i$ (i=1,2,3,..,N) lead to smaller in length pathways of diffusion through the microspheres of radius $R_{m,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,3,..,N′) and this results to increased values in the concentration gradient of the adsorbate in the microspheres which in turn provide higher intraparticle diffusional mass fluxes of the adsorbate in the microspheres of the partially fractal particles. This positive mass transfer effect resulting from increases in the value of $1/\tau_i$ (i=1,2,3,..,N) together with the fact that larger values of N' and $1/\tau_i$ can lead to larger values of $C_{T,i,j+1}$ which could provide a larger driving force for adsorption (see Eqs. (18) and (20)), indicate that increases in the values of N' and $1/\tau_i$ can lead to increases in the intraparticle mass transfer and adsorption rates of the adsorbate molecules. When the number of the sections, N, of the stratified column increases, the average external mass transfer rate of the adsorbate through the hydrodynamic boundary layer per unit column length is increased. Furthermore, increasing values of N could (i) decrease the average length of the pathways for intraparticle diffusion and this could increase the average concentration gradient of the adsorbate in the microspheres forming the partially fractal particles, and (ii) increase the average intraparticle pore surface area per unit length of the stratified column bed which can lead to higher $C_{T,i,j+1}$ (i=1,2,3,..,N and j=0,1,2,3,..,N′) values that can provide higher dynamic and equilibrium adsorption capacities. Thus, increases in the value of N could increase both the external and internal mass transfer rates as well as the adsorption rate of the adsorbate.

The results and analysis presented in this work clearly show that as the values of N, N′, and $1/\tau_i$ (i=1,2,3,..,N) increase, both the breakthrough time, t_b, and the dynamic utilization of the adsorptive capacity of the partially fractal particles increase. This is what would be desired to occur in adsorption separations in practice.

It is important to mention here that for the physical reasons and process benefits presented and discussed in this work, it could be possible that significant increases in mass transfer and reaction rates could be realized if in packed bed chemical and biochemical reactors the porous catalyst particles (both in chemical catalysis and biocatalysis) could be replaced by partially fractal porous catalyst particles which would be preferably packed in stratified column beds. The physical mechanisms of mass transfer in chemical catalysis and biocatalysis reactors are similar to the ones considered in this work while the adsorption mechanism of this work would be replaced by a chemical reaction or a biochemical reaction mechanism.

5. Nomenclature

$A_{ads,i,j+1}$	Adsorbate molecule in the pore fluid of particles of radius $R_{m,i,j+1}$ where i=1,2,…,N and j=0,1,2,…N'
$A_{ads,i,j+1}L_{lig,i,j+1}$	Adsorbed adsorbate onto immobilized ligand on the surface of the pores of particles of radius $R_{m,i,j+1}$ where i=1,2,..,N and j=0,1,2,..,N′
$A_{pores,i,1}$	Surface area of the pores in the particles of radius $R_{p,i}$ where i=1,2,..,N, m^2
$A_{pores,i,2}$	Surface area of the pores in the particles of radius $R_{m,i,2}$ where i=1,2,..,N, m^2
$A_{pores,i,3}$	Surface area of the pores in the particles of radius $R_{m,i,3}$ where i=1,2,..,N, m^2
$A_{ws,i}$	Total (intraparicle) surface area of the pores in the particles of radius $R_{p,i}$ $\left(A_{ws,i}=\sum_{j=0}^{N'}A_{pores,i,j+1}\right)$ where i=1,2,3,..,N, m^2
$C_{d,i}$	Concentration of adsorbate in the flowing bulk fluid in section S_i (i=1,2,..,N) of the stratified column, kg/m^3 of bulk fluid
$C_{d,in}$	Inlet concentration of adsorbate in the flowing bulk fluid of the column, kg/m^3 of bulk fluid
$C_{d,in}\big\|_{x=L_{i+1}}$	Inlet concentration of adsorbate in the flowing bulk fluid in section S_{i+1} (i=1,2,..,N-1) of the stratified column, kg/m^3 of bulk fluid
$C_{d,out}$	Concentration of adsorbate in the flowing bulk fluid exiting the column, kg/m^3 of bulk fluid
$C_{d,out}\big\|_{x=L_i}$	Concentration of adsorbate in the flowing bulk fluid exiting section S_i (i=1,2,..,N) of the stratified column, kg/m^3 of bulk fluid
$C_{p,i,j+1}$	Concentration of adsorbate in the pore fluid of particle of radius $R_{m,i,j+1}$ where i=1,2,..,N and j=0,1,2..,N′-1, kg/m^3 of the pore fluid in the particle of radius $R_{m,i,j+1}$

$C_{p,i,N'+1}$	Concentration of adsorbate in the pore fluid of particle of radius $R_{m,i,N'+1}$ (i=1,2,..,N), kg/m^3 of the pore fluid in the particle of radius $R_{m,i,N'+1}$
$\overline{C}_{ps,i,j+1}$	Average concentration of adsorbate in the pore fluid and adsorbed phase of particle of radius $R_{m,i,j+2}$ where i=1,2,..,N and j=0,1,2..,N′-1, kg/m^3 of particle of radius $R_{m,i,j+2}$
$C_{s,i,j+1}$	Concentration of adsorbate in the adsorbed phase of particle of radius $R_{m,i,j+1}$ where i =1,2,..,N and j=0,1,2..,N′-1, kg/m^3 of particle of radius $R_{m,i,j+1}$
$C_{s,i,N'+1}$	Concentration of adsorbate in the adsorbed phase of particle of radius $R_{m,i,N'+1}$ where i=1,2,..,N, kg/m^3 of particle of radius $R_{m,i,j+1}$
$C_{T,i,j+1}$	Maximum equilibrium concentration of adsorbate in the adsorbed phase of particle of radius $R_{m,i,j+1}$ where i=1,2,…,N and j=0,1,2,…,N'-1, kg/m^3 of particle of radius $R_{m,i,j+1}$
$C_{T,i,N'+1}$	Maximum equilibrium concentration of adsorbate in the adsorbed phase of particle of radius $R_{m,i,N'+1}$ where i=1,2,…,N, kg/m^3 of particle of radius $R_{m,i,N'+1}$
D_{fm}	Free molecular diffusion coefficient of adsorbate, m^2/s
$D_{p,i,j+1}$	Effective pore diffusion coefficient of adsorbate in the pores of particle of radius $R_{m,i,j+1}$ where i =1,2,..,N and j=0,1,2..,N′-1, m^2/s
$D_{p,i,N'+1}$	Effective pore diffusion coefficient of adsorbate in the pores of particle $R_{m,i,N'+1}$ where i =1,2,..,N, m^2/s
$k_{1,i,j+1}$	Adsorption rate constant in particle of radius $R_{m,i,j+1}$ where i =1,2,..,N and j=0,1,2..,N′, m^3/(kg s)
$k_{2,i,j+1}$	Desorption rate constant in particle of radius $R_{m,i,j+1}$ where i =1,2,..,N and j=0,1,2..,N′, 1/s
$K_{f,i}$	Film mass transfer coefficient of adsorbate in section S_i (i =1,2,..,N) of column, m/s
L	Total column length, m
L_i	Length of section S_i (i =1,2,..,N) of stratified column, m

$L_{lig,i,j+1}$	Immobilized ligand (adsorption site) on the surface of the pores of particle of radius $R_{m,i,j+1}$ where i =1,2,..,N and j=0,1,2..,N′
N	Total number of sections of stratified bed
N'	Total number of recursions of the fractal (total number of divisions)
$R_{i,j+1}$	Radial coordinate in particle of radius $R_{m,i,j+1}$ where i =1,2,..,N and j=0,1,2..,N′-1, m
$R_{i,N'+1}$	Radial coordinate in particle of radius $R_{m,i,N'+1}$ where i=1,2,…,N, m
$R_{p,i}$	Radius of adsorbent particles in section S_i (i =1,2,..,N) of stratified column, m
$R_{m,i,j+1}$	Radii of particles from which the particle of radius $R_{p,i}$ is made from and where i=1,2,…,N and j=0,1,2,…N'-1, m
$R_{m,i,N'+1}$	Radius of the smallest porous microspheres in the particles of radius $R_{p,i}$ where i=1,2,…,N, m
S_i	Section i of stratified column (i = 1,2,..,N)
t	Time, s
t_b	Breakthrough time, s
V_f	Superficial velocity of bulk fluid in single column (N=1), m/s
$V_{f,i}$	Superficial velocity of bulk fluid in section S_i (i=1,2..,N) of stratified column, m/s
$V_{p,i}$	Volume of adsorbent particle of radius $R_{p,i}$ (i=1,2,..,N), m^3
x	Axial coordinate along the column, m

Greek Letters

δ	Proportionality constant
α_i	L_i/L_{i+1} for i=1,2,..,N-1
β_i	$R_{p,i}/R_{p,i+1}$ for i=1,2,..,N-1

ε	Packed bed porosity in column
ε_i	Packed bed porosity in section S_i (i=1,2,..,N) of stratified column
$\varepsilon_{p,i}$	Porosity of particles of radius $R_{p,i}$ where i =1,2,3,..,N
$\varepsilon_{p,i,j+1}$	Porosity of particles of radius $R_{m,i,j+1}$ where i=1,2,..,N and j=0,1,2,..,N′-1
$\varepsilon_{p,i,N'+1}$	Porosity of the smallest porous microspheres where i=1,2,…,N
τ_i	Ratio of the radii between smaller and larger microspheres that make up the partially fractal particle of radius $R_{p,i}$ where i=1,2,3,..,N (see Eq. (1))
$1/\tau_i$	Ratio of the radii between larger and smaller microspheres that make up the partially fractal particle of radius $R_{p,i}$ where i=1,2,3,..,N

Subscripts

i	denotes the section number in a stratified column, i = 1,2,..,N
j	denotes the division (recursion) number of the fractal, j =0,1,2,..,N′

6. References

[1] Li, M., Liapis, A. I., *J. Sep. Sci.* 2012, *35*, 947-956.

[2] Li, M., Liapis, A. I., *J. Sep. Sci.* 2012, *35*, 3439-3446.

[3] Do, D. D., *Adsorption Analysis: Equilibria and Kinetics*, Imperial College Press, London, United Kingdom 1998.

[4] Harrison, R. G., Todd, P., Rudge, S. R., Petrides, D. R., *Bioseparation Science and Engineering*, Oxford University Press, New York 2003.

[5] Mathews, A. P., in: Myers, A. L., Belfort, G.(Eds.), *Fundamentals of Adsorption*, Engineering Foundation, New York 1984, pp. 345-354.

[6] Liapis, A. I., *Math. Model. Sci. Comput.* 1993, *1*, 397-414.

[7] Riccardi, E., Wang, J.-C., Liapis, A. I., *J. Chem. Phys.* 2010, *133*, 084904-1-084904-12.

[8] Wang, J.-C., Liapis, A. I., *Chemie Ingenieur Technik*, 2011, *83*, 152-165.

[9] Unger, K. K., Liapis, A. I., *J. Sep. Sci.* 2012, *35*, 1201-1212.

[10] Liapis, A. I., Xu, Y., Crosser, O. K., Tongta, A., *J. Chromatogr. A.* 1995, *702*, 45-57.

[11] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A.* 1995, *711*, 3-21.

[12] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A.* 1996, *734*, 105-123.

[13] Heeter, G. A., Liapis, A. I., *J. Chromatogr. A.* 1996, *743*, 3-14.

[14] Meyers, J. J., Liapis, A. I., *J. Chromatogr. A.* 1998, *827*, 197-213.

[15] Liapis, A. I., Riccardi, E., Wang, J.-C., *J. Sep. Sci.* 2010, *33*, 2749-2756.

[16] M. Li., Report No. 51, Department of Chemical and Biochemical Engineering, Missouri University of Science and Technology, Rolla, Missouri, USA 2012.

[17] Arnold, F. H., Blanch, H. W., Wilke, C. R., *Chem. Eng. J.* 1985, *30*, B9-B23.

[18] Arnold, F. H., Blanch, H. W., Wilke, C. R., *Chem. Eng. J.* 1985, *30*, B25-B36.

[19] Arve, B. H., Liapis, A. I., *AIChE J*. 1987, *33*, 179-193.

[20] Riccardi, E., Liapis, A. I., *J*. *Sep*. *Sci*. 2009, *32*, 4059-4068.

[21] Afeyan, N. B., Fulton, S. P., Gordon, N. F., Mazaroff, I., Varady, L., Regnier, F. E., *Biotechnol*. 1990, *8*, 203-206.

[22] Grimes, B. A., Liapis, A. I., *J*. *Coll*. *Interfac*e. *Sci*. 2002, *248*, 504-520.

[23] Liapis, A. I., Grimes, B. A., *J*. *Sep*. *Sci*. 2005, *28*, 1909-1926.

[24] Villadsen, J., Michelsen, M. L., *Solution of Differential Equation Models by Polynomial Approximation*, Prentice Hall, Englewood Cliffs, New Jersey 1978.

[25] Holland, C. D., Liapis, A. I., *Computer Methods for Solving Dynamic Separation Problems*, McGraw-Hill Book Company, New York 1983.

[26] Liapis, A. I., Anspach, B., Findley, M. E., Davies, J., Hearn, M. T. W., Unger, K. K., *Biotechnol*. *Bioeng*. 1989, *34*, 467-477.

[27] Wilson, E. J., Geankoplis, C. J., *Ind*. *Eng*. *Chem*. *Fundam*. 1966, *5*, 9-14.

[28] Liapis, A. I., Bruttini, R., *Int*. *J*. *of Heat Mass Transfer*. 2009, *52*, 100-111.

[29] Poole, C. F., *The Essence of Chromatography*, Elsevier, Amsterdam, The Netherlands 2003.

[30] Sober H. A.(Ed.), *Handbook of Biochemistry: Selected Data for Molecular Biology*, second ed., The Chemical Rubber Company, Cleveland, OH 1970, page C-10.

Table 1. Common values of the parameters used in the adsorption systems of this study. The adsorbate considered in this work is lysozyme [26, 30].

$C_{d,in} = 25.10\times10^{-3}\ \mathrm{kg/m^3}$

$D_{fm} = 11.2\times10^{-11}\ \mathrm{m^2/s}$

$D_{L_i} \cong 0\ \mathrm{m^2/s}$ for i = 1,2,3,…,N

$D_{p,i,j+1} = 4.04\times10^{-11}\ \mathrm{m^2/s}$ for i = 1,2,3,…,N and j = 0,1,2,…,N′

$k_{1,i,j+1} = 3.088\ \mathrm{m^3/(kg\ s)}$ for i = 1,2,3,…,N and j = 0,1,2,…,N′

$k_{2,i,j+1} = 0.5483\ \mathrm{s^{-1}}$ for i = 1,2,3,…,N and j = 0,1,2,…,N′

$L = 0.20$ m

N = 1 and N = 2 in this study

N′ = 1 and N′ = 2 in this study

$R_{p,1} = 50\times10^{-6}$ m

$T = 293.15$ K

$\alpha_i = 1.5$ for i = 1,2,3,…,N

$\beta_i = 1.5$ for i = 1,2,3,…,N

$\varepsilon_i = 0.35$ for i = 1,2,3,…,N

$\varepsilon_{p,i} = 0.60$ for i =1,2,3,…,N

$\varepsilon_{p,i,j+1} = 0.60$ for i = 1,2,3,…,N and j = 0,1,2,…,N′

$\mu = 1.0019\times10^{-3}\ \mathrm{kg/(m\ s)}$

$\rho = 997\ \mathrm{kg/m^3}$

Table 2. Values of the parameter $C_{T,i,j+1}$ where i = 1,2 and j = 0,1,2 employed in the adsorption systems of this study. The indicated values of $1/\tau_i$ are the same for both sections (i=1,2) of the stratified column. The units of $C_{T,1,1}$, $C_{T,1,2}$ and $C_{T,1,3}$ are given in the Nomenclature section.

Single column (N=1) of total length L = 0.2 m

N'	$1/\tau_1$	$C_{T,1,1}$	$C_{T,1,2}$	$C_{T,1,3}$
1	5	0.89	1.34	
1	10	1.79	2.68	
1	20	3.57	5.36	
1	30	5.36	8.04	
2	5	0.89	1.34	2.01
2	10	1.79	2.68	4.02
2	20	3.57	5.36	8.04
2	30	5.36	8.04	12.06

Stratified column with two sections (N=2) and total length $L=\sum_{i=1}^{2} L_i = 0.2$ m

N'	L_1 (m)	L_2 (m)	$R_{p,1}$ (m)	$R_{p,2}$ (m)	$1/\tau_i$	Section of length L_1			Section of length L_2		
						$C_{T,1,1}$	$C_{T,1,2}$	$C_{T,1,3}$	$C_{T,2,1}$	$C_{T,2,2}$	$C_{T,2,3}$
1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5	0.89	1.34		1.34	2.01	
1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	10	1.79	2.68		2.68	4.02	
1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	20	3.57	5.36		5.36	8.04	
1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	30	5.36	8.04		8.04	12.06	
2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5	0.89	1.34	2.01	1.34	2.01	3.01
2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	10	1.79	2.68	4.02	2.68	4.02	6.03
2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	20	3.57	5.36	8.04	5.36	8.04	12.06
2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	30	5.36	8.04	12.06	8.04	12.06	18.08

Table 3. Number of minutes needed for the outlet concentration, $C_{d,out}$, of the adsorbate from a column bed comprised of one section (N=1) to be equal to 1% (breakthrough time, t_b), 5%, and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column for various values of N′, $1/\tau_1$, and $V_{f,1}$. In all cases, $C_{d,in} = 25.10\times10^{-3}$ kg/m^3 and L=0.2 m.

N	N'	L (m)	$R_{p,1}$ (m)	$V_{f,1}$ (m/s)	$1/\tau_1$	$\varepsilon_{p,1}$	Time, t (min)		
							1%	5%	10%
1	1	0.20	5.00×10^{-5}	2.778×10^{-3}	5	0.60	3.48	4.88	5.81
1	1	0.20	5.00×10^{-5}	2.778×10^{-3}	10	0.60	6.41	9.02	10.76
1	1	0.20	5.00×10^{-5}	2.778×10^{-3}	20	0.60	12.25	17.27	20.65
1	1	0.20	5.00×10^{-5}	2.778×10^{-3}	30	0.60	18.07	25.53	30.53
1	2	0.20	5.00×10^{-5}	2.778×10^{-3}	5	0.60	4.11	5.81	6.95
1	2	0.20	5.00×10^{-5}	2.778×10^{-3}	10	0.60	7.73	10.90	13.03
1	2	0.20	5.00×10^{-5}	2.778×10^{-3}	20	0.60	14.89	21.03	25.15
1	2	0.20	5.00×10^{-5}	2.778×10^{-3}	30	0.60	22.03	31.14	37.26
1	1	0.20	5.00×10^{-5}	5.556×10^{-3}	5	0.60	1.04	1.62	20.73
1	1	0.20	5.00×10^{-5}	5.556×10^{-3}	10	0.60	1.90	2.99	3.82
1	1	0.20	5.00×10^{-5}	5.556×10^{-3}	20	0.60	3.61	5.69	7.29
1	1	0.20	5.00×10^{-5}	5.556×10^{-3}	30	0.60	5.31	8.39	10.77
1	2	0.20	5.00×10^{-5}	5.556×10^{-3}	5	0.60	1.19	1.91	2.46
1	2	0.20	5.00×10^{-5}	5.556×10^{-3}	10	0.60	2.27	3.59	4.61
1	2	0.20	5.00×10^{-5}	5.556×10^{-3}	20	0.60	4.37	6.92	8.87
1	2	0.20	5.00×10^{-5}	5.556×10^{-3}	30	0.60	6.47	10.23	13.13
1	1	0.20	5.00×10^{-5}	8.334×10^{-3}	5	0.60	0.47	0.80	1.06
1	1	0.20	5.00×10^{-5}	8.334×10^{-3}	10	0.60	0.87	1.47	1.95
1	1	0.20	5.00×10^{-5}	8.334×10^{-3}	20	0.60	1.66	2.79	3.72
1	1	0.20	5.00×10^{-5}	8.334×10^{-3}	30	0.60	2.44	4.11	5.48
1	2	0.20	5.00×10^{-5}	8.334×10^{-3}	5	0.60	0.54	0.93	1.25
1	2	0.20	5.00×10^{-5}	8.334×10^{-3}	10	0.60	1.03	1.76	2.35
1	2	0.20	5.00×10^{-5}	8.334×10^{-3}	20	0.60	2.00	3.38	4.52
1	2	0.20	5.00×10^{-5}	8.334×10^{-3}	30	0.60	2.96	5.00	6.68

Table 4. Number of minutes needed for the outlet concentration, $C_{d,out}$, of the adsorbate from a stratified column bed comprised of two sections (N=2) to be equal to 1% (breakthrough time, t_b), 5% and 10% of the inlet concentration, $C_{d,in}$, of the adsorbate in the column for various values of N′, $1/\tau_i$ (i=1,2), and $V_{f,i}$ (i=1,2). In all cases, $C_{d,in} = 25.10\times10^{-3}$ kg/m^3 and $L=\sum_{i=1}^{2} L_i = 0.2$ m. The values of $V_{f,i}$, $1/\tau_i$, and $\varepsilon_{p,i}$ are the same in both sections of the stratified column bed.

N	N'	L_1 (m)	L_2 (m)	$R_{p,1}$ (m)	$R_{p,2}$ (m)	$V_{f,i}$ (m/s)	$1/\tau_i$	$\varepsilon_{p,i}$	Time, t (min)		
									1%	5%	10%
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	5	0.60	5.07	6.72	7.75
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	10	0.60	9.55	12.65	14.59
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	20	0.60	18.48	24.49	28.25
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	30	0.60	27.39	36.32	41.90
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	5	0.60	6.06	8.07	9.32
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	10	0.60	11.57	15.35	17.71
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	20	0.60	22.52	29.86	34.45
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	30	0.60	33.47	44.39	51.22
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	5	0.60	1.61	2.40	2.96
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	10	0.60	3.05	4.52	5.56
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	20	0.60	5.89	8.73	10.75
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	30	0.60	8.73	12.93	15.93
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	5	0.60	1.91	2.87	3.54
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	10	0.60	3.68	5.47	6.74
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	20	0.60	7.17	10.63	13.10
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	30	0.60	10.65	15.79	19.46
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	5	0.60	0.77	1.23	1.58
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	10	0.60	1.46	2.32	2.97
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	20	0.60	2.82	4.47	5.74
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	30	0.60	4.19	6.62	8.50
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	5	0.60	0.89	1.46	1.89
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	10	0.60	1.75	2.80	3.60
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	20	0.60	3.43	5.44	6.99
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	30	0.60	5.11	8.09	10.38

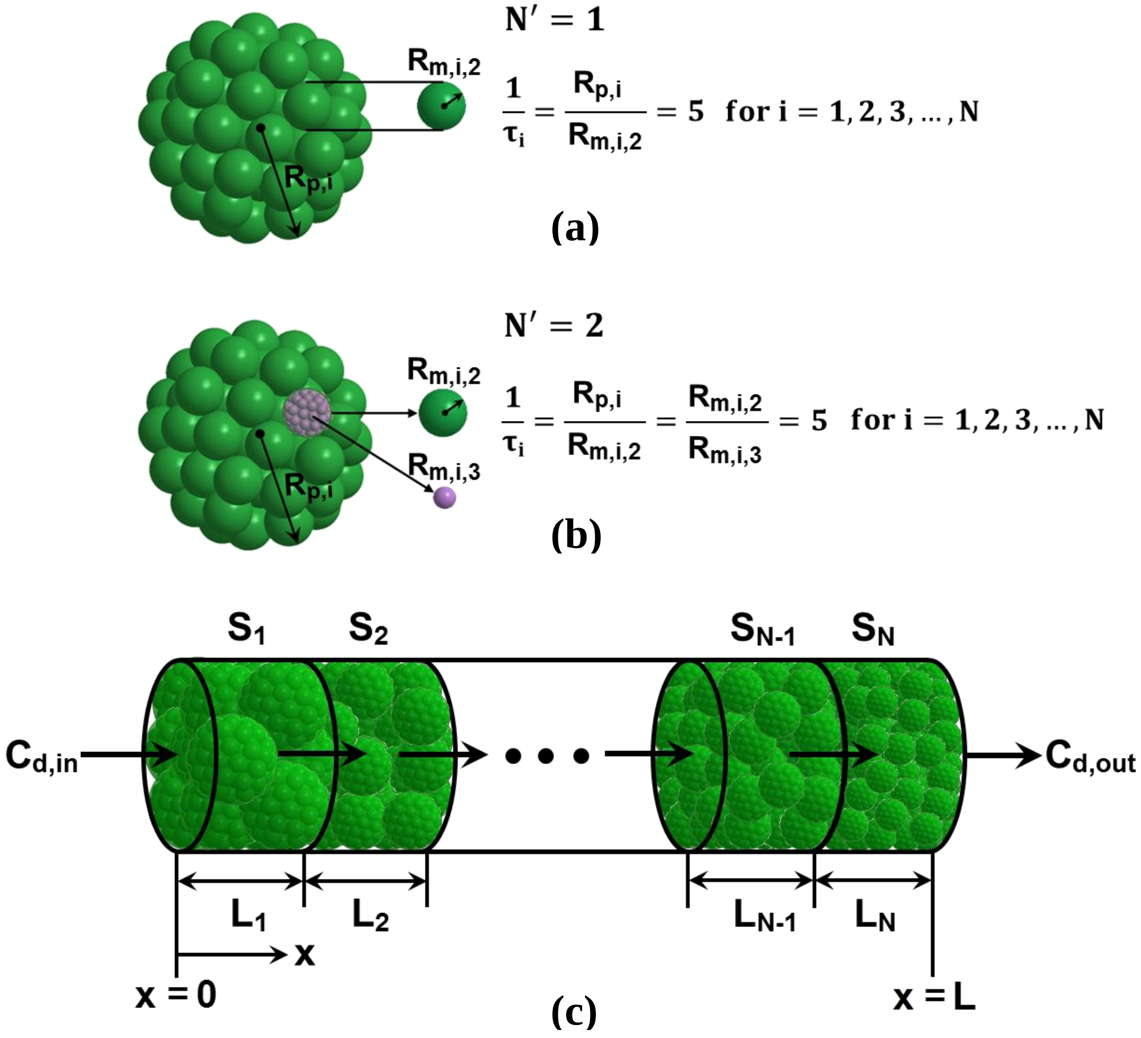


Figure 1. Schematic representation of partially fractal porous adsorbent particles with the total number N′ of recursions of the fractal being (a) N′=1, and (b) N′=2, and (c) schematic representation of a stratified column bed of N sections.

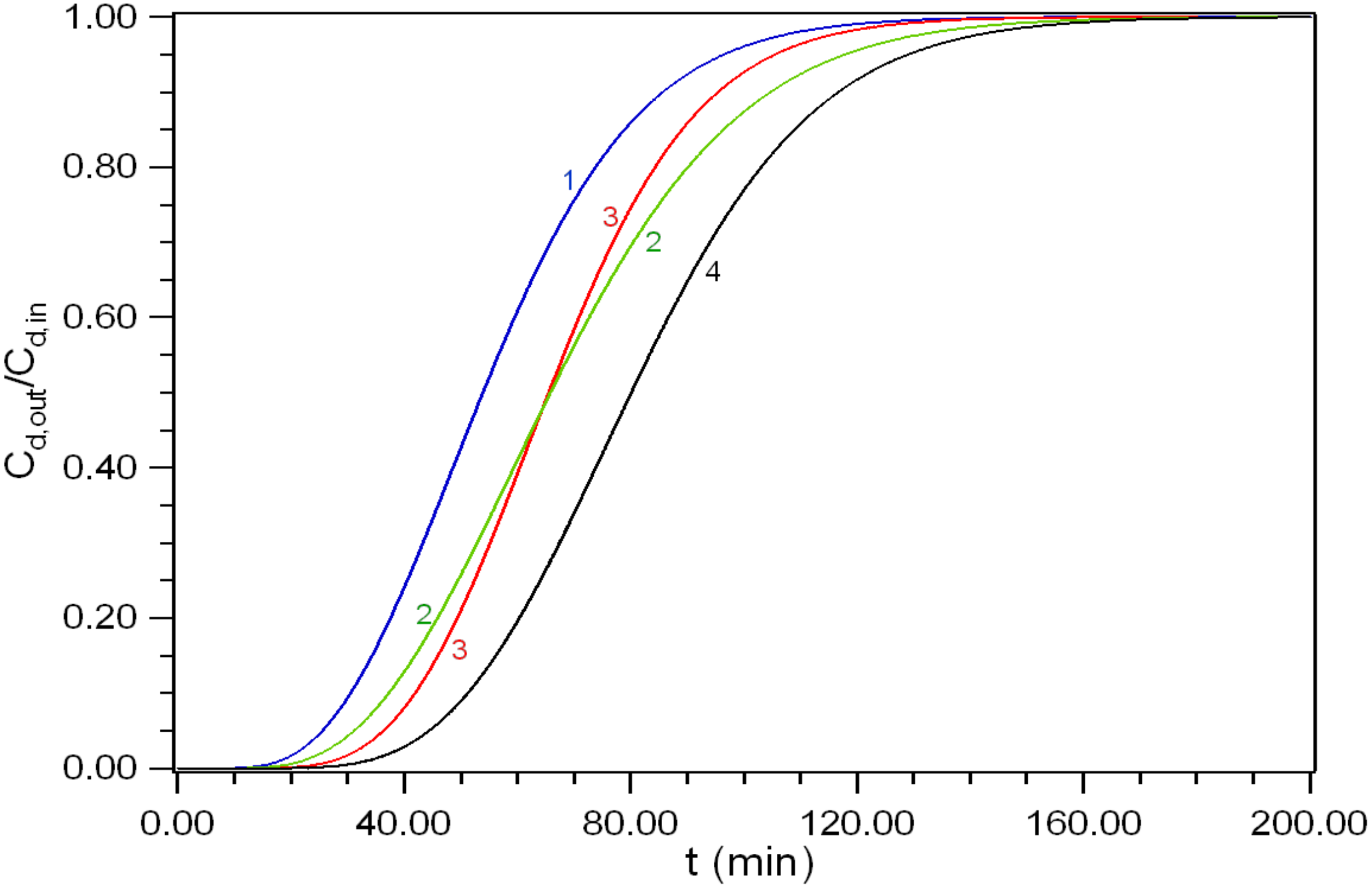


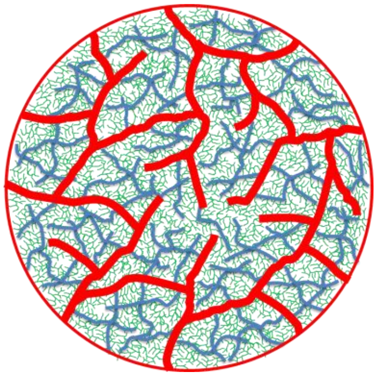
Figure 2. Breakthrough curves from a single column (N=1) and a stratified column of two sections (N=2) packed with partially fractal porous adsorbent particles. Both the single and the stratified columns have the same total length L=0.2 m.

Curve 1: N = 1, N′ = 1, $1/\tau_1 = 30$; Curve 2: N = 1, N′ =2, $1/\tau_1 = 30$
Curve 3: N = 2, N′ = 1, $1/\tau_i = 30$ for i = 1, 2; Curve 4: N = 2, N′ = 2, $1/\tau_i = 30$ for i = 1, 2

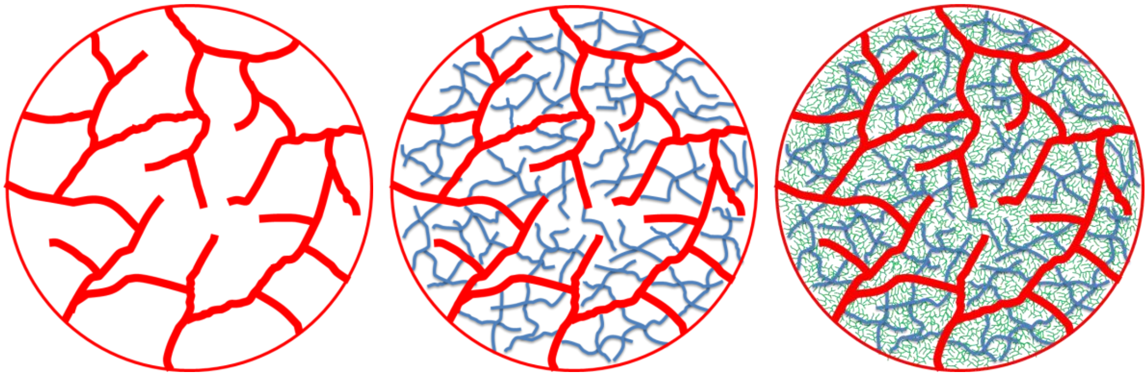
APPENDIX

Quasi-Partially Fractal Porous Particle

Depiction of quasi-partially fractal porous particle constructed through a sequence of cross-linking operations.



The above quasi-partially fractal porous particle was constructed by combining the cross-linking operations shown below, which represent a three-stage process.



2. CONCLUSIONS

Mathematical models are constructed and solved in order to study the dynamic behavior of adsorption in column bed systems packed with partially fractal porous adsorbent particles. The models account for the mechanisms of external film mass and intraparticle diffusional of adsorbate in partially fractal particles as well as for the mechanism of the adsorption of the adsorbate onto the immobilized adsorption sites (ligands) on the pore surfaces of the particles.

The results obtained in this dissertation clearly show that:

(1) Conventional columns packed with partially fractal porous adsorbent particles provide larger breakthrough times and dynamic utilization of the adsorptive capacity of the column than conventional columns packed with conventional porous adsorbent particles.

(2) Stratified column beds provide larger breakthrough times and significantly sharper in shape breakthrough curves than those obtained from conventional columns because the stratified column provides larger average external and intraparticle mass transfer rates per unit length of packed column, and this effect increases as the number, N, of the sections of the stratified column increases, the value of β_i ($\beta_i = R_{p,i}/R_{p,i+1}$) increases, and the value of α_i ($\alpha_i = L_i/L_{i+1}$) decreases.

(3) When the spatial distribution of immobilized ligand in the partially fractal particles is nonuniform and satisfies a certain functional form, then the breakthrough times and dynamic utilization of the adsorptive capacity of the particles obtained from a stratified column, especially when the throughput is increased, are significantly larger

than those obtained from a stratified column packed with partially fractal particles having a uniform spatial distribution of immobilized ligand. The proper form of the nonuniform spatial distribution of immobilized ligand increases the intraparticle mass transfer and adsorption rates.

(4) The breakthrough times and the dynamic utilization of the adsorptive capacity of the partially fractal particles obtained from a stratified column increases as the total number, N', of the recursion of the fractal and the value of the ratio $1/\tau_i$ between the radii of the larger and smaller microspheres from which the particle is made from, increase.

(5) The effect that increasing values of throughput have on the breakthrough time and dynamic utilization of the adsorptive capacity of the column, becomes smaller as the values of N' and $1/\tau_i$ increase, because the intraparticle mass transfer and adsorption rates increase as the values of N' and $1/\tau_i$ increase.

(6) Partially fractal porous adsorbent particles and stratified column beds provide to the designer and user of adsorbent media and column systems more degrees of freedom with respect to the number of parameters and variables that could be controlled in the design, construction, and operation of adsorption systems.

The physical and modeling concepts which are relevant to stratified column beds and porous media having a partially fractal structure could also prove useful in the design, construction, and operation of packed bed reactors involving chemical catalysis and biocatalysis, as well as in fluidized and expanded beds.

APPENDIX A.

ESTIMATION OF SURFACE AREAS IN PARTIALLY FRACTAL PARTICLES

APPENDIX A represents

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for the

Department of Chemical and Biochemical Engineering

In the following section, the estimation of the surface area of the pores in the partially fractal particles packed in a stratified column bed is presented. The adsorption columns considered in this work are packed with spherical porous adsorbent particles which have a partially fractal structure. The radius of the particles packed in section S_i (i=1,2,..,N) of the column is $R_{p,i}$ (i=1,2,..,N), the microspheres that make up the particle of radius $R_{p,i}$ have radius $R_{m,i,j+1}$ and it is related to $R_{p,i}$ through the expression shown in Eq. (1):

$$R_{m,i,j+1} = \tau_i^j R_{p,i}\text{, for } i = 1,2,3,..,N \text{ and } j = 0,1,2,3,..,N' \qquad (1)$$

In Eq. (1) i denotes the adsorbent particles packed in section S_i of a stratified column bed [1, 2] and $R_{m,i,j+1}$ represents the radius of the microspheres that make up the adsorbent particle of radius $R_{p,i}$ after j divisions, N′ denotes the total number of divisions (the total number of recursions of the fractal), and τ_i represents the ratio of the radii between the smaller and larger microspheres that make up the adsorbent particles of radius $R_{p,i}$. The value of τ_i is less than unity ($\tau_i < 1$) because the partially fractal particles of radii $R_{p,i}$ are comprised of the microparticles of radius $R_{m,i,j+1}$ (i = 1,2,..,N and j = 0,1,2,..,N′), and the value of the total number of recursions of the fractal, N′, has to be finite [3] and have a magnitude such that all pores in the partially fractal adsorbent particles have linear dimensions (sizes) that could allow the effective transport of solvent and adsorbate solute. It is noted that the porosity $\varepsilon_{p,i,j+1}$ of each microsphere of radius $R_{m,i,j+1}$ has the same value of the porosity $\varepsilon_{p,i}$ of the adsorbent particle of radius $R_{p,i.}$

In the following paragraphs, we present the approach for estimating the surface area, $A_{pores,i,j+1}$, of the pores in the microspheres of radius $R_{m,i,j+1}$ in one single partially fractal particle of radius $R_{p,i}$ where i = 1,2,..,N and j = 0,1,2,..,N′. It is worth mentioning here that $A_{pores,i,1}$ represents the surface area of the pores (macropores) of the partially fractal particle $R_{p,i}$ as it is indicated in Eq. (1) where $R_{m,i,1} = R_{p,i}$ when $j = 0$.

As an approximation, the geometry of each recursion of the pores in the partially fractal particles is considered to be cylindrical, and, furthermore, it is taken that the pores in the microspheres of radius $R_{m,i,j+1}$ have a quasi-uniform pore size distribution. The radius (effective linear dimension) of the pores in the microspheres of radius $R_{m,i,j+1}$ is taken to be $\lambda_{pore,i,j+1}$ and the length of the cylindrical pores in the microspheres of radius $R_{m,i,j+1}$ is taken to be $L_{pore,i,j+1}$ which is related to $\lambda_{pore,i,j+1}$ (i=1,2,..,N and j = 0,1,2,..,N′) by the following expression:

$$L_{pore,i,j+1} = \gamma\, \lambda_{pore,i,j+1} \qquad \text{for } i = 1,2,..,N \text{ and } j = 0,1,2,..,N' \tag{2}$$

In Eq. (2), γ is a proportionality constant which characterizes the relationship of length $L_{pore,i,j+1}$ and radius $\lambda_{pore,i,j+1}$ of the cylindrical pores in the microspheres of radius $R_{m,i,j+1}$.

By employing the concept of the construction of partially fractal particles [1, 2, 3] where the microspheres of radius $R_{m,i,j+1}$ are formed through the gluing of the microspheres whose radius is $R_{m,i,j+2}$ and satisfies the relationship

$$R_{m,i,j+2} = \frac{R_{m,i,j+1}}{\left(\frac{1}{\tau_i}\right)} \qquad \text{for } i = 1,2,..,N \text{ and } j=0,1,2,..,N' \tag{3}$$

it becomes apparent that the surface of the pores in the microspheres of radius $R_{m,i,j+1}$ are made from the microspheres of radius $R_{m,i,j+2}$. An important aspect in the fractal structure is the concept of self-similarity [4] and it could be appropriately related to the concept of geometrical (physical) similarity of the radius of pores $\lambda_{pore,i,j+1}$ in the microspheres of radius $R_{m,i,j+1}$ (i=1,2,..,N and j=0,1,2,..,N′) through Eq. (4)

$$\lambda_{pore,i,j+1} = \delta\left(\frac{\varepsilon_{m,i,j+1}}{1-\varepsilon_{m,i,j+1}}\right)R_{m,i,j+2} \qquad \text{for i =1,2,..,N and j=0,1,2,..,N'} \qquad (4)$$

In Eq. (4), the parameter δ is a proportionality constant that characterizes the packing structure of microspheres of recursion j into a sphere of recursion j-1. One can then consider that the volume of a single cylindrical pore of radius $\lambda_{pore,i,j+1}$ is $\pi\lambda_{pore,i,j+1}^{2}L_{pore,i,j+1}$, the surface area of a single cylindrical pore of radius $\lambda_{pore,i,j+1}$ is $2\pi\lambda_{pore,i,j+1}L_{pore,i,j+1}$, and the total volume $V_{pores,i,j+1}$ of the pores of size $\lambda_{pore,i,j+1}$ in a partially fractal particle of radius $R_{p,i}$ is determined from the expression

$$V_{pores,i,j+1} = V_{p,i}(1-\varepsilon_{p,i})^{j}\varepsilon_{p,i} \qquad \text{for i =1,2,..,N and j=0,1,2,..,N'} \qquad (5)$$

where $V_{p,i}$ is the volume of a single partially fractal particle of radius $R_{p,i}$ and $\varepsilon_{p,i}$ is the porosity of the particle which is taken to satisfy the condition $\varepsilon_{p,i} = \varepsilon_{p,i,j+1}$ (i=1,2,..,N and j = 0,1,2,..,N′), as indicated above. By combining Eqs (3)-(5) and considering that in a single partially fractal particle of radius $R_{p,i}$ the total surface area, $A_{pores,i,j+1,}$ of the pores of size $\lambda_{pore,i,j+1}$ formed by gluing microspheres of radius $R_{m,i,j+2}$, is the product of the total number of pores of radius $\lambda_{pore,i,j+1}$ in the particle times the surface area of a single pore of radius $\lambda_{pore,i,j+1}$, one obtains

$$A_{pores,i,j+1} = \frac{2V_{p,i}(1-\varepsilon_{p,i})^{j+1}}{\delta R_{m,i,j+1}\tau_{i}} \qquad \text{for i=1,2,..,N and j=0,1,2,..,N'} \qquad (6)$$

When partially fractal particles of radius $R_{p,i}$ with N′ = 2 are considered, then from Eq. (6) the surface areas of the pores in (a) the microspheres of radius $R_{m,i,3}$, (b) the microspheres of radius $R_{m,i,2}$ formed by gluing the microspheres of radius $R_{m,i,3}$, and (c) the pores of the particle of radius $R_{p,i}$ formed by gluing the microspheres of radius $R_{m,i,2}$, could be determined from Eqs. (7)-(9), respectively:

$$A_{pores,i,3} = \frac{2V_{p,i}(1-\varepsilon_{p,i})^3}{\delta R_{m,i,3}\tau_i} \qquad \text{for i=1,2,..,N} \qquad (7)$$

$$A_{pores,i,2} = \frac{2V_{p,i}(1-\varepsilon_{p,i})^2}{\delta R_{m,i,2}\tau_i} \qquad \text{for i=1,2,..,N} \qquad (8)$$

$$A_{pores,i,1} = \frac{2V_{p,i}(1-\varepsilon_{p,i})}{\delta R_{p,i}\tau_i} \qquad \text{for i=1,2,..,N} \qquad (9)$$

It is observed from Eqs (6) – (9) that the surface area, $A_{pores,i,N'+1}$, of the pores in the smallest microspheres of a partially fractal porous adsorbent particle with the total number of the recursion of the fractal being equal to N′, could be determined from the expression

$$A_{pores,i,N'+1} = (1-\varepsilon_{p,i})^{N'}(\frac{1}{\tau_i})^{N'}A_{pores,i,1}, \quad \text{for i = 1,2,..,N and j=0,1,2,..,N'} \qquad (10)$$

The relationship of the surface area, $A_{pores,i,j+1}$, of the pores in a given recursion j of a partially fractal porous particle of radius $R_{p,i}$ is related to the surface area, $A_{pores,i,1}$, of the macropores of the partially fractal particles of radius $R_{p,i}$ through the following equation:

$$A_{pores,i,j+1} = (1-\varepsilon_{p,i})^{j}(\frac{1}{\tau_i})^{j}A_{pores,i,1}, \quad \text{for i = 1,2,..,N and j=0,1,2,..,N'} \qquad (11)$$

Thus, for given values of i (i = 1,2,..,N) and $R_{p,i}$ of a partially fractal porous adsorbent particle, the surface area $A_{pores,i,j+1}$ increases as (i) the value of $1/\tau_i$ increases (which means the value of τ_i is decreasing), and this means that the ratio of the radii between the larger microspheres and the smaller microspheres from which the larger microspheres are made from, increases and (ii) the number of the recursion of the fractal, j, increases.

It is important to note here that the total internal pore surface area, $A_{ws,i}$, of the partially fractal particle of radius $R_{p,i}$ is the summation of the surface areas, $A_{pores,i,j+1}$ (j=0,1,2,..,N′), of the pores in the particle, that is

$$A_{ws,i} = \sum_{j=0}^{N'} A_{pores,i,j+1,} \quad \text{for } i = 1,2,..,N \tag{12}$$

Eq. (12) indicates that the value of $A_{ws,i}$ increases as the total number, N′, of the recursion of the fractal increases.

In Table 1, estimates of the values of $A_{pores,i,j+1}$ when i = 1,2 and j = 0,1,2 are presented.

In the partially fractal porous adsorbent particle whose radius is $R_{p,i}$, $A_{pores,i,j+1}$ is the surface area of the pores in the microspheres of radius $R_{m,i,j+1}$. The volume, $V_{m,i,j+1}$, of the microspheres of radius $R_{m,i,j+1}$, in the particle of radius $R_{p,i}$ is determined from the expression

$$V_{m,i,j+1} = V_{p,i}(1-\varepsilon_{p,i})^{j} \qquad \text{for } i = 1,2,..,N \text{ and } j = 0,1,2,...,N' \tag{13}$$

Considering that the surface area $A_{pores,i,j+1}$, is covered by a monolayer coverage of adsorption sites (ligands), then the total molar amount of adsorption sites (ligands), $n_{i,j+1}$, on the pore surface area, $A_{pores,i,j+1}$, is given by the expression

$$n_{i,j+1} = \frac{A_{pores,i,j+1}}{\pi R_{ads}^{2}} \frac{1}{N_A} \qquad \text{for } i=1,2,..,N \text{ and } j = 0,1,2,..,N' \tag{14}$$

where R_{ads} is the radius of the adsorbed adsorbate (ligands), πR_{ads}^{2} is the projected surface area of an adsorbed adsorbate onto the surface of the pores, N_A is the Avogadro number and its value is 6.022×10^{23} mol $^{-1}$.

Thus, the maximum equilibrium concentration, $C_{T,i,j+1}$, of adsorbate in the adsorbed phase of particles of radius $R_{m,i,j+1}$ could be estimated by Eq. (15):

$$C_{T,i,j+1} = \frac{n_{i,j+1}}{V_{m,i,j+1}} = \frac{A_{pores,i,j+1}}{\pi R_{ads}^{2} N_A} \frac{1}{V_{p,i}(1-\varepsilon_{p,i})^{j}} \quad \text{for } i=1,2,..,N \text{ and } j = 0,1,2,..,N' \tag{15}$$

References

[1] Li, M., Liapis, A. I., *J. Sep. Sci*. 2012, *35*, 947-956.

[2] Li, M., Liapis, A. I., *J. Sep. Sci.* 2012, *35*, 3439-3446.

[3] Liapis, A. I., *Math*. *Model*. *Sci*. *Comput*. 1993, *1*, 397-414.

[4] Avnir, D. (ed), *The Fractal Approach to Heterogeneous Chemistry: Surfaces, Colloids*, *Polymers*, John Wiley and Sons, New York, 1989

Table 1. Examples of the values of $A_{pores,i,j+1}$ (i = 1,2 and j = 0,1,2)

N	N'	L_1 (m)	L_2 (m)	$R_{p,1}$ (m)	$R_{p,2}$ (m)	$\varepsilon_{p,i}$	$1/\tau_i$	Section 1			Section 2		
								$A_{pores,i,1}(m^2)$	$A_{pores,i,2}(m^2)$	$A_{pore,i,3}(m^3)$	$A_{pores,i,1}(m^2)$	$A_{pores,i,2}(m^2)$	$A_{pore,i,3}(m^3)$
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	5	1.884×10^{-7}	5.652×10^{-7}		8.373×10^{-8}	2.512×10^{-7}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	10	3.768×10^{-7}	2.261×10^{-6}		1.675×10^{-7}	1.005×10^{-6}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	20	7.536×10^{-7}	9.043×10^{-6}		3.349×10^{-7}	4.019×10^{-6}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	30	1.130×10^{-6}	2.035×10^{-5}		5.024×10^{-7}	9.043×10^{-6}	
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	5	1.884×10^{-7}	5.652×10^{-7}	1.696×10^{-6}	8.373×10^{-8}	2.512×10^{-7}	7.536×10^{-7}
2	2	0.12.	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	10	3.768×10^{-7}	2.261×10^{-6}	1.357×10^{-5}	1.675×10^{-7}	1.005×10^{-6}	6.029×10^{-6}
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	20	7.536×10^{-7}	9.043×10^{-6}	1.085×10^{-4}	3.349×10^{-7}	4.019×10^{-6}	4.823×10^{-5}
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.40	30	1.130×10^{-6}	2.035×10^{-5}	3.663×10^{-4}	5.024×10^{-7}	9.043×10^{-6}	1.628×10^{-4}
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	5	1.570×10^{-7}	3.925×10^{-7}		6.978×10^{-8}	1.744×10^{-7}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	10	3.140×10^{-7}	1.570×10^{-6}		1.397×10^{-7}	6.978×10^{-7}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	20	6.280×10^{-7}	6.280×10^{-6}		2.791×10^{-7}	2.791×10^{-6}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	30	9.420×10^{-7}	1.413×10^{-5}		4.187×10^{-7}	6.280×10^{-6}	
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	5	1.570×10^{-7}	3.925×10^{-7}	9.813×10^{-7}	6.978×10^{-8}	1.744×10^{-7}	4.361×10^{-7}
2	2	0.12.	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	10	3.140×10^{-7}	1.570×10^{-6}	7.850×10^{-6}	1.396×10^{-7}	6.978×10^{-7}	3.489×10^{-6}
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	20	6.280×10^{-7}	6.280×10^{-6}	6.280×10^{-5}	2.791×10^{-7}	2.791×10^{-6}	2.791×10^{-5}
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.50	30	9.420×10^{-7}	1.413×10^{-5}	2.120×10^{-4}	4.187×10^{-7}	6.280×10^{-6}	9.420×10^{-5}
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	5	1.256×10^{-7}	2.512×10^{-7}		5.582×10^{-8}	1.116×10^{-7}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	10	2.512×10^{-7}	1.005×10^{-6}		1.116×10^{-7}	4.466×10^{-7}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	20	5.024×10^{-7}	4.019×10^{-6}		2.233×10^{-7}	1.786×10^{-6}	
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	30	7.536×10^{-7}	9.043×10^{-6}		3.349×10^{-7}	4.019×10^{-6}	
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	5	1.256×10^{-7}	2.512×10^{-7}	5.024×10^{-7}	5.582×10^{-8}	1.116×10^{-7}	2.233×10^{-7}
2	2	0.12.	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	10	2.512×10^{-7}	1.005×10^{-6}	4.019×10^{-6}	1.116×10^{-7}	4.466×10^{-7}	1.786×10^{-6}
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	20	5.024×10^{-7}	4.019×10^{-6}	3.215×10^{-5}	2.233×10^{-7}	1.786×10^{-6}	1.429×10^{-5}
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	0.60	30	7.536×10^{-7}	9.043×10^{-6}	1.085×10^{-4}	3.349×10^{-7}	4.019×10^{-6}	4.823×10^{-5}

APPENDIX B.

ESTIMATION OF THE EFFECTIVE DIFFUSION COEFFICIENT OF ADSORBATES IN THE PORES OF THE PARTICLES

In this work, partially fractal porous adsorbent particles are packed in stratified column beds. There are pores in each recursion, j, of the partially fractal porous adsorbent particles which are formed by the surrounding of the microspheres of recursion j+1 in the particle. Diffusion of the adsorbate is taken place in the pores of each recursion of the microspheres, and, thus, the adsorbate can be transported onto the surfaces of the pores and then adsorption of the adsorbate occurs and adsorbate-ligand complexes are formed.

In this work, the pores in the partially fractal porous adsorbent particles are considered to be of cylindrical geometry so that they can be characterized by a single parameter, namely the pore radius. They are a series of tortuous, interconnecting paths of pore bodies and pore throats with varying cross-sectional areas. Diffusive transport typically is described using Fick's law to relate the diffusive solute flux to the difference in adsorbate concentration between adjacent regions by means of a diffusion coefficient [1]. To consider the diffusion process within each and every of the tortuous pathways in the particles individually is tedious and not fruitful [2], and, thus, an effective pore diffusion coefficient is used to describe the diffusion process taking place at any position in the particle. Because of the constriction of transport of a solute in a pore and the tortuous flow paths in the pores, the effective pore diffusion coefficient, $D_{p,i,j+1}$, is much lower than the free molecular diffusion coefficient, D_{fm}. An expression that relates $D_{p,i,j+1}$ to D_{fm} is given by the following equation:

$$D_{p,i,j+1} = \frac{D_{fm}\varepsilon_{p,i,j+1}\sigma_c}{\tau} \tag{1}$$

In Eq. (1) $D_{p,i,j+1}$ is the effective pore diffusion coefficient of the adsorbate in the pores of the microspheres whose radius is $R_{m,i,j+1}$, $\varepsilon_{p,i,j+1}$ is the porosity of the microspheres whose radius is $R_{m,i,j+1}$, σ_c is a constriction factor to account for the constricted transport of a solute in the pores of small radii, and τ is a tortuosity factor that accounts for the reduction in diffusive flux caused by the tortuous path lengths. The tortuosity factor is the ratio of the actual distance the adsorbate travels between two points to the straight line distance between those two points, and, thus, the tortuosity factor is always greater than one ($\tau > 1$).

For the BSA adsorption system studied in this work, the free molecular diffusion coefficient of BSA has the value $D_{fm} = 6.70\times10^{-12}$ m^2/s, the porosity of the microspheres in each recursion of the particle has the value $\varepsilon_{p,i,j+1} = 0.60$, the value of the constriction factor σ_c was chosen to be equal to 0.88 and the tortuosity factor τ was taken to be equal to 1.414. Combining these parameters in Eq. (1), the effective pore diffusion coefficient of BSA in this study is determined and $D_{p,i,j+1} = 2.50\times10^{-12}$ m^2/s.

For the lysozyme adsorption system studied in this work, the free molecular diffusion coefficient of lysozyme has the value $D_{fm} = 11.2\times10^{-11}$ m^2/s, the porosity of the microspheres in each recursion of the particle has the value $\varepsilon_{p,i,j+1} = 0.60$, the value of the constriction factor for the lysozyme is taken to be equal to 0.85, and the tortuosity factor τ is taken to be equal to 1.414. By combining these parameters in Eq. (1), the effective pore diffusion coefficient of lysozyme in this study is obtained and $D_{p,i,j+1} = 4.04\times10^{-11}$ m^2/s.

When the value of the free molecular diffusion coefficient of the adsorbate is not known from experimental measurements, its value could be estimated by the following Stokes-Einstein relation which assumes that the adsorbate is a spherical molecule:

$$D_{fm} = \frac{kT}{6\pi r\eta} \tag{2}$$

In Eq. (2), k represents the Boltzman constant whose value is 1.38×10^{-23} J/K, r is the radius of the molecule, η is the viscosity of the solvent, and T is the temperature of the system.

Young and others [3] have also suggested a correction to calculate the diffusion coefficient D_{fm} of a protein, and this correction is given by the expression

$$D_{fm} = 8.34\times10^{-8}\frac{T}{\eta M^{1/3}} \tag{3}$$

where T is the absolute temperature of the system (K), M is the molecular weight (g/mol) of the protein and η represents the viscosity of the solvent (cP).

References

[1] Saripalli, K., Serne, R., Meyer, P., McGrail, B., *Ground Water*. 2002, *40*, 346 – 352.

[2] Fogler, H. S., *Elements of Chemical Reaction Engineering, fourth ed.*, Prentice Hall, Upper Saddle River, NJ, 2006, pp 813-816.

[3] Young, M. E., Carroad, P. A., Bell, R. L., *Biotechno and Bioeng* . 1980, *22*, 947-955.

APPENDIX C.

RELATIONSHIP BETWEEN LIGAND DENSITY CONCENTRATIONS $C_{T,i,j+1,U}$ AND $C_{T,max,i,j+1}$ IN THE PARTIALLY FRACTAL POROUS ADSORBENT PARTICLES PACKED IN STRATIFIED COLUMN BED SYSTEMS

Porous adsorbent particles with partially fractal structure [1, 2] are packed in the stratified column bed systems and the size of the particles, $R_{p,i}$, in each section S_i is decreasing along the flow direction. Adsorption sites (ligands) exist on the intraparticle pores of the partially fractal porous adsorbent particles and, thus, adsorption of the adsorbate onto the adsorbed phase of the particles occurs.

There are at least two different approaches which could be employed for the immobilization of adsorption sites (ligands) on the intraparticle pore surfaces of the partially fractal porous adsorbent particles. Both approaches depend on the construction procedures of the partially fractal particles. In approach (A), partially fractal porous particles with recursion N' of the fractal is constructed from base matrices and then ligands are introduced to the pores of the partially fractal particle, and, thus, adsorption sites could be attached on the pore surfaces of the spherical particles of recursion number j = 0,1,2,…,N'. In Approach (B) the adsorption sites (ligands) are only introduced to the pores of the microspheres of recursion number N' (smallest microspheres), then these smallest microspheres are glued together to form spheres of recursion numbers N'-1, N'-2,…,1, and 0. Thus, in Approach (B), there are no adsorption sites (ligands) on the surface of the pores in the microspheres of recursion numbers N'-1, N'-2, N'-3,…,1 and 0, and adsorption sites (ligands) are only immobilized on the pore surfaces of the microspheres of recursion number N'.

In many studies as well as in the work of Li and Liapis [2], the distribution of the adsorption sites (ligands) on the pores of particles is considered to be uniform and has the same value in every spatial position. However, recently obtained results [3-5] determined from molecular dynamic modeling and simulation studies of the polymeric particles of which the charged ligands are immobilized onto the pore surfaces, indicate that the spatial density distribution of the immobilized ligands is likely to be non-uniform. Furthermore, Liapis et al. [6] showed that the dynamic adsorption performance of the conventional columns packed with porous adsorbent particles having conventional pore structures depends largely on the spatial density distribution of the immobilized ligands, and better adsorption performance can be achieved when the packed porous adsorbent particles in the adsorption column systems employ non-uniform ligand density distribution and the concentration of the immobilized ligands increases monotonically from the center of the particle to the outer particle surface when compared with the adsorption performance of the column in which the packed adsorbent particles have uniform ligand density distribution.

Therefore, it is interesting to analyze the dynamic performance of the stratified column bed systems whose sections are packed with partially fractal porous adsorbent particles employing non-uniform ligand density distribution on the pore surfaces of the particles and compare it with the dynamic adsorption performance of the stratified column beds whose packed partially fractal porous adsorbent particles have uniform ligand density distribution. In order to make a fair comparison of the performance between the uniform ligand density distribution system and the non-uniform ligand density distribution system, it is necessary to require that the total number of adsorption sites (ligands) in both systems be the same.

The expression of the adsorption of the adsorbate onto the immobilized ligand on the pore surfaces of the particles of radius $R_{p,i}$ and $R_{m,i,j+1}$ is considered to follow a second-order adsorption mechanism given by the form

$$\frac{\partial C_{s,i,j+1}}{\partial t}=k_{1,i,j+1}C_{p,i,j+1}(C_{T,i,j+1}-C_{s,i,j+1})-k_{2,i,j+1}C_{s,i,j+1} \quad \text{for i=1,2,..,N and j=0,1,2,..,N'-1} \qquad (1)$$

It is important to mention here that, $R_{p,i} = R_{m,i,1}$ (i=1,2,..,N). The adsorption of the adsorbate onto the immobilized ligand on the pore surfaces of the smallest microspheres of radius $R_{m,i,N'+1}$ takes the form

$$\frac{\partial C_{s,i,N'+1}}{\partial t}=k_{1,i,N'+1}C_{p,i,N'+1}(C_{T,i,N'+1}-C_{s,i,N'+1})-k_{2,i,N'+1}C_{s,i,N'+1} \quad \text{for i=1,2,..,N} \qquad (2)$$

The terms $C_{T,i,j+1}$ and $C_{T,i,N'+1}$ in Eq. (1) and Eq. (2), respectively, denote the local maximum equilibrium concentration of adsorbate in the adsorbed phase of the pores in the spherical particles of radii $R_{m,i,j+1}$ (i=1,2,..,N and j = 0,1,2,..,N′-1) and $R_{m,i,N'+1}$ (i=1,2,..,N). When monovalent adsorbate-ligand adsorption is considered, $C_{T,i,j+1}$ and $C_{T,i,N'+1}$ also represent the local maximum concentration of the immobilized ligands in the microspheres $R_{m,i,j+1}$ (i=1,2,..,N and j = 0,1,2,..,N′-1) and $R_{m,i,N'+1}$ (i=1,2,..,N).

For the adsorption system whose packed adsorbent particles have uniform ligand density distribution, the term $C_{T,i,j+1}$ has the same value along every radial position, r, of the microspheres $R_{m,i,j+1}$ (i=1,2,..,N and j = 0,1,2,..,N′) and, thus,

$$C_{T,i,j+1} = C_{T,i,j+1,U} \quad \text{for i = 1,2,...,N and j = 0,1,2,..,N'-1} \qquad (3)$$

$$C_{T,i,N'+1} = C_{T,i,N'+1,U} \quad \text{for i = 1,2,...,N} \qquad (4)$$

But for the adsorption systems whose spatial ligand density distribution on the surface of the pores in each recursion j of the microspheres is not uniform, the value of $C_{T,i,j+1}$ in Eq. (1) and the value of $C_{T,i,N'+1}$ in Eq. (2) need to vary along the radial position r of the microspheres $R_{m,i,j+1}$ and $R_{m,i,N'+1}$, respectively.

For the non-uniform ligand density distribution on the pores of the partially fractal porous adsorbent particles, different ligand density distribution functional forms could be employed for each recursion, j, corresponding to the microspheres packed in each section, S_i, of the stratified column bed system, and, thus, the $C_{T,i,j+1}$ and $C_{T,i,N'+1}$ could be represented in the following forms

$$C_{T,i,j+1}=C_{T,\max,i,j+1}\, f_{i,j}\left(\frac{r}{R_{m,i,j+1}}\right) \qquad \text{for } 0 \le r \le R_{m,i,j+1},\ i=1,2,..,N \text{ and } j=0,1,2,..,N'-1 \tag{5}$$

$$C_{T,i,N'+1}=C_{T,\max,i,N'+1}\, f_{i,N'}\left(\frac{r}{R_{m,i,N'+1}}\right) \qquad \text{for } 0 \le r \le R_{m,i,N'+1},\ i=1,2,..,N \tag{6}$$

where $C_{T,\max,i,j+1}$ and $C_{T,\max,i,N'+1}$ denote the maximum adsorption sites (ligands) concentration on the pores of the microspheres of radius $R_{m,i,j+1}$ and $R_{m,i,N'+1}$, respectively, and $f_{i,j}\left(\frac{r}{R_{m,i,j+1}}\right)$ and $f_{i,N'}\left(\frac{r}{R_{m,i,N'+1}}\right)$ are dimensionless functional forms.

The amount of adsorption sites (ligands) on the pore surfaces of the microspheres of radii $R_{m,i,j+1}$ ($i=1,2,..,N$ and $j=0,1,2,..,N'-1$) and $R_{m,i,N'+1}$ in a partially fractal porous adsorbent particle, is given by expressions (7) and (8), respectively,

$$m_{s,i,j+1} = \int_0^{R_{m,i,j+1}} 4\pi\, C_{T,i,j+1}\, r^2 dr \qquad \text{for } i = 1,2,..,N \text{ and } j = 0,1,2,..,N'-1 \tag{7}$$

$$m_{s,i,N'+1} = \int_0^{R_{m,i,N'+1}} 4\pi\, C_{T,i,N'+1}\, r^2 dr \qquad \text{for } i = 1,2,..,N \tag{8}$$

The total amount of adsorption sites (ligands) in a partially fractal porous adsorbent particle of radius $R_{p,i}$ is determined from the summation of the amount of adsorption sites (ligands) in every recursion, j, of the particle, and is given by expression (9)

$$m_{s,i} = m_{s,i,1}+m_{s,i,2}+...+m_{s,i,N'}+m_{s,i,N'+1} \qquad \text{for } i = 1,2,..,N \tag{9}$$

By combining Eqs. (3), (4), (7)-(9) together, the total amount of adsorption sites (ligands), $m_{s,i,U}$, in the partially fractal porous adsorbent particle of radius $R_{p,i}$ whose microspheres employ uniform ligand density distribution, could be obtained. Furthermore, by combining Eqs. (5), (6), (7)-(9) together, the total amount of adsorption sites (ligands), $m_{s,i,D}$, in the partially fractal porous adsorbent particle of radius $R_{p,i}$ whose microspheres employ non-uniform ligand density distribution could be obtained. By equating the values of $m_{s,i,U}$ and $m_{s,i,D,}$ which means that the total amount of adsorption sites (ligands) in the particle whose microspheres have uniform ligand density distribution is equal to the total amount of adsorption sites (ligands) in the particle whose microspheres have non-uniform ligand density distributions, the relationship between $C_{T,i,j+1,U}$ and $C_{T,max,i,j+1}$ could be obtained.

Eqs. (1)-(9) represent a quantitative approach for the determination of the total amount of adsorption sites (ligands) in a partially fractal porous adsorbent particle of radius $R_{p,i}$ which has ligand molecules immobilized on the surface of the pores in the microspheres of each division (recursion) number j = 0,1,2,..,N′, and it consideres that the immobilization of the ligands in the adsorbent particles took place by approach (A). If the immobilization of the ligands in the adsorbent particles took place by approach (B) so that there are only ligands immobilized on the surface of the pores in the smallest microspheres of radius $R_{m,i,N'+1}$, then the values of $m_{s,i,j+1}$ for i=1,2,..,N and j = 0,1,2,..,N′-1 are all equal to zero and Eq. (9) takes the form

$$m_{s,i} = m_{s,i,N'+1} \qquad \text{for } i = 1,2,..,N \tag{9-a}$$

Then by combining Eqs. (4), (6), (8) and (9-a), the relationship between $C_{T,i,N'+1,U}$ and $C_{T,max,i,N'+1}$ in the partially fractal porous adsorbent particles whose construction process employed approach (B), is obtained.

For example, if a partially fractal porous adsorbent is constructed by approach (B) and the spatial distribution of the immobilized ligand in the smallest microspheres of radius $R_{m,i,N'+1}$ has the form

$$C_{T,i,N'+1} = C_{T,max,i,N'+1}\left(\frac{r}{R_{m,i,N'+1}}\right)^4 \qquad \text{for } 0 \leq r \leq R_{m,i,N'+1} \text{ and } i=1,2,3,..,N \tag{10}$$

then by combining Eqs. (4), (8) and (10) the following expressions are obtained for $m_{s,i,U}$ and $m_{s,i,D}$:

$$m_{s,i,U} = \frac{4}{3}\pi C_{T,i,N'+1,U} R^3_{m,i,N'+1} \qquad \text{for } i = 1,2,3,..,N \tag{11}$$

$$m_{s,i,D} = \frac{4}{7}\pi C_{T,max,i,N'+1} R^3_{m,i,N'+1} \qquad \text{for } i = 1,2,3,..,N \tag{12}$$

Therefore, one can now easily show that the relationship between the ligand density concentrations of $C_{T,i,N'+1,U}$ and $C_{T,max,i,N'+1}$ is given by expression (13)

$$C_{T,max,i,N'+1} = \left(\frac{7}{3}\right)C_{T,i,N'+1,U} \qquad \text{for } i = 1,2,3,..,N \tag{13}$$

References

[1] Liapis, A. I., Math. Model. Sci. Comput 1993, *1*, 397-414.

[2] Li, M., Liapis, A. I., J. Sep. Sci. 2012, *35*, 947-956.

[3] Riccardi, E., Wang, J.-C., Liapis, A. I., J. Sep. Sci. 2009, *32*, 3084-3098.

[4] Riccardi, E., Wang, J.-C., Liapis, A. I., J. Phys. Chem. B 2008, *112*, 7478-7488.

[5] Riccardi, E., Wang, J.-C., Liapis, A. I., J. Chromatogr. Sci. 2009, *47*, 459-466.

[6] Liapis, A. I., Riccardi, E., Wang, J.-C., J. Sep. Sci. 2010, *33*, 2749-2756.

APPENDIX D.

EQUILIBRIUM LANGMUIR ISOTHERM CURVES FOR THE BOVINE SERUM ALBUMIN (BSA) AND LYSOZYME ADSORPTION SYSTEMS

It is assumed that in the stratified column bed packed with porous adsorbent particles of fractal structures, only one-site adsorbate-ligand complexes are considered to be formed from the interaction between the adsorbate molecules and the immobilized ligands, and, thus, the interaction between unbound adsorbate, $A_{ads,i,j+1,}$ and vacant immobilized ligand, $L_{lig,i,j+1,}$ is considered to be of the form

$$A_{ads,i,j+1} + L_{lig,i,j+1} \underset{k_{2,i,j+1}}{\overset{k_{1,i,j+1}}{\rightleftarrows}} A_{ads,i,j+1}L_{lig,i,j+1} \qquad (1)$$

where $A_{ads,i,j+1}L_{lig,i,j+1}$ represents the one-site adsorbate-ligand complex. The dynamic adsorption mechanism which can quantitatively describe expression (1), is given by

$$\frac{\partial C_{s,i,j+1}}{\partial t} = k_{1,i,j+1}C_{p,i,j+1}(C_{T,i,j+1} - C_{s,i,j+1}) - k_{2,i,j+1}C_{s,i,j+1} \quad \text{for } i=1,2,..,N \text{ and } j=0,1,2,..,N' \qquad (2)$$

which is, of course, a second-order adsorption mechanism. In Eq. (2), $C_{p,i,j+1}$ represents the concentration of the adsorbate in the microspheres $R_{m,i,j+1}$, $C_{s,i,j+1}$ represents the concentration of the adsorbate in the adsorbed phase in the microspheres $R_{m,i,j+1}$ and $C_{T,i,j+1}$ represents the concentration of the adsorption sites (ligands) in the microspheres $R_{m,i,j+1}$ ($i = 1,2..,N$ and $j = 0,1,2,..,N'$).

If the left hand side of Eq. (2) is set equal to zero, this could imply that the adsorption step occurs in effect infinitely fast and adsorption equilibrium takes place and follows the Langmuir equilibrium adsorption isotherm, and, therefore, the relationship of $C_{p,i,j+1}$, $C_{s,i,j+1}$ and $C_{T,i,j+1}$ is shown as follows

$$C_{s,i,j+1} = \frac{k_{1,i,j+1}C_{p,i,j+1}C_{T,i,j+1}}{k_{1,i,j+1}C_{p,i,j+1} + k_{2,i,j+1}} \qquad (3)$$

For BSA adsorption systems studied in this work, $k_{1,i}$ = 1.05 m^3/(kg s) and $k_{2,i}$ = 0.131 s^{-1}; for the Lysozyme adsorption systems studied in this work, $k_{1,i,j+1}$ = 3.088 m^3 /(kg s) and $k_{2,i,j+1}$ = 0.5483 s^{-1} (i = 1,2,..,N and j = 0,1,2,..,N').

When one uses k_1 and k_2 to represent the terms $k_{1,i,j+1}$ and $k_{2,i,j+1,}$ respectively, in Eq. (3) and replaces $C_{s,i,j+1}$, $C_{T,i,j+1,}$ $C_{p,i,j+1}$ with the more general terms C_s, C_T, and C_p, respectively in Eq. (3), then Eq. (3) acquires the form

$$C_s = \frac{k_1 C_p C_T}{k_1 C_p + k_2} \tag{3-a}$$

where k_1 and k_2 denote the forward and backward adsorption rate constants of the adsorption mechanism, C_p is the concentration of the adsorbate in the pores of the particle, C_T denotes the maximum equilibrium concentration of adsorbate in the adsorbed phase of the particle, and C_s represents the concentration of the adsorbate in the adsorbed phase of the particle.

In Figs. 1-4, for given values of C_T, the equilibrium values (Eq. (3-a)) of C_s as a function of the value of C_p for the BSA and lysozyme adsorption systems, are plotted.

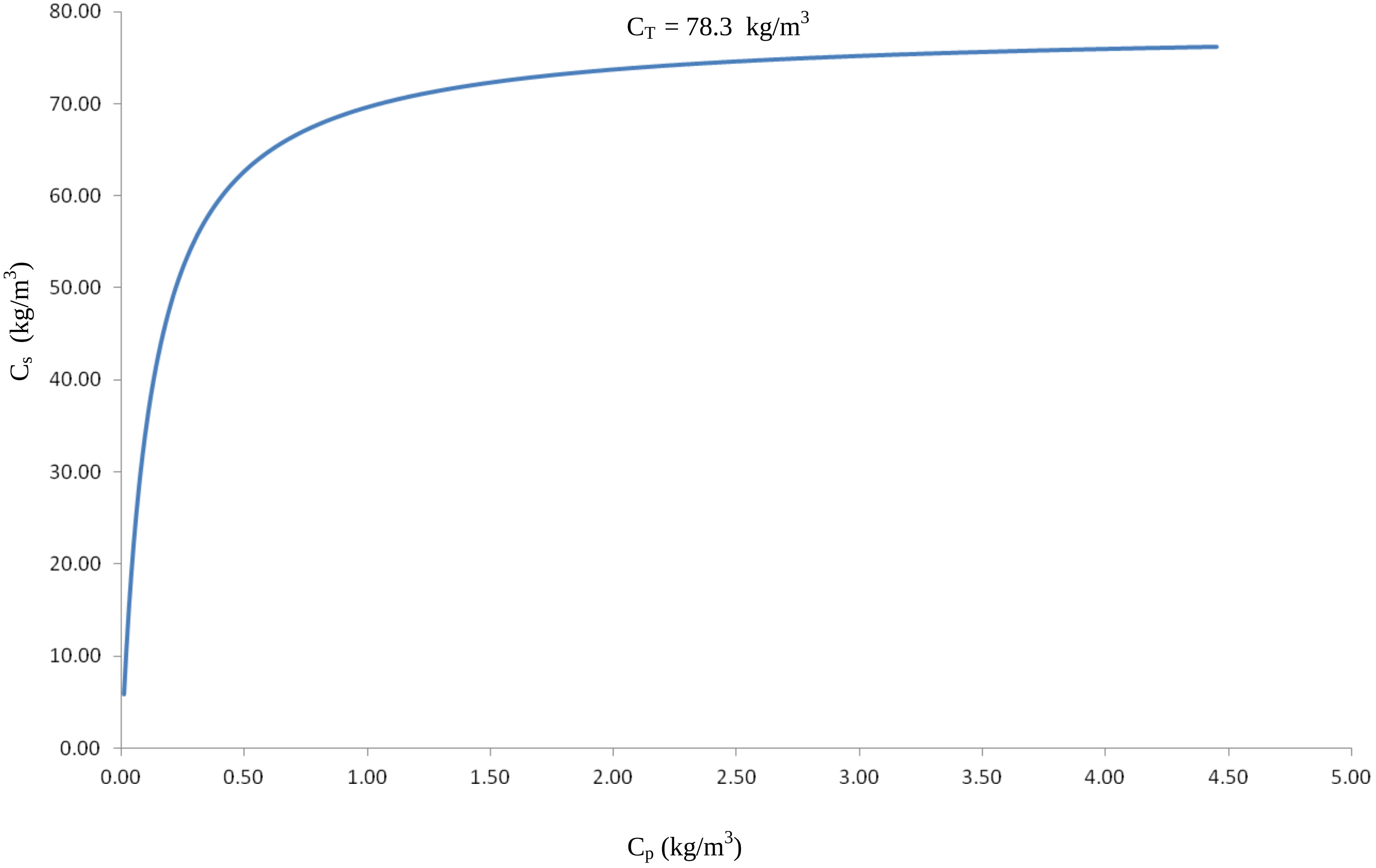

Figure. 1 Equilibrium Langmuir adsorption isotherm curve for BSA system

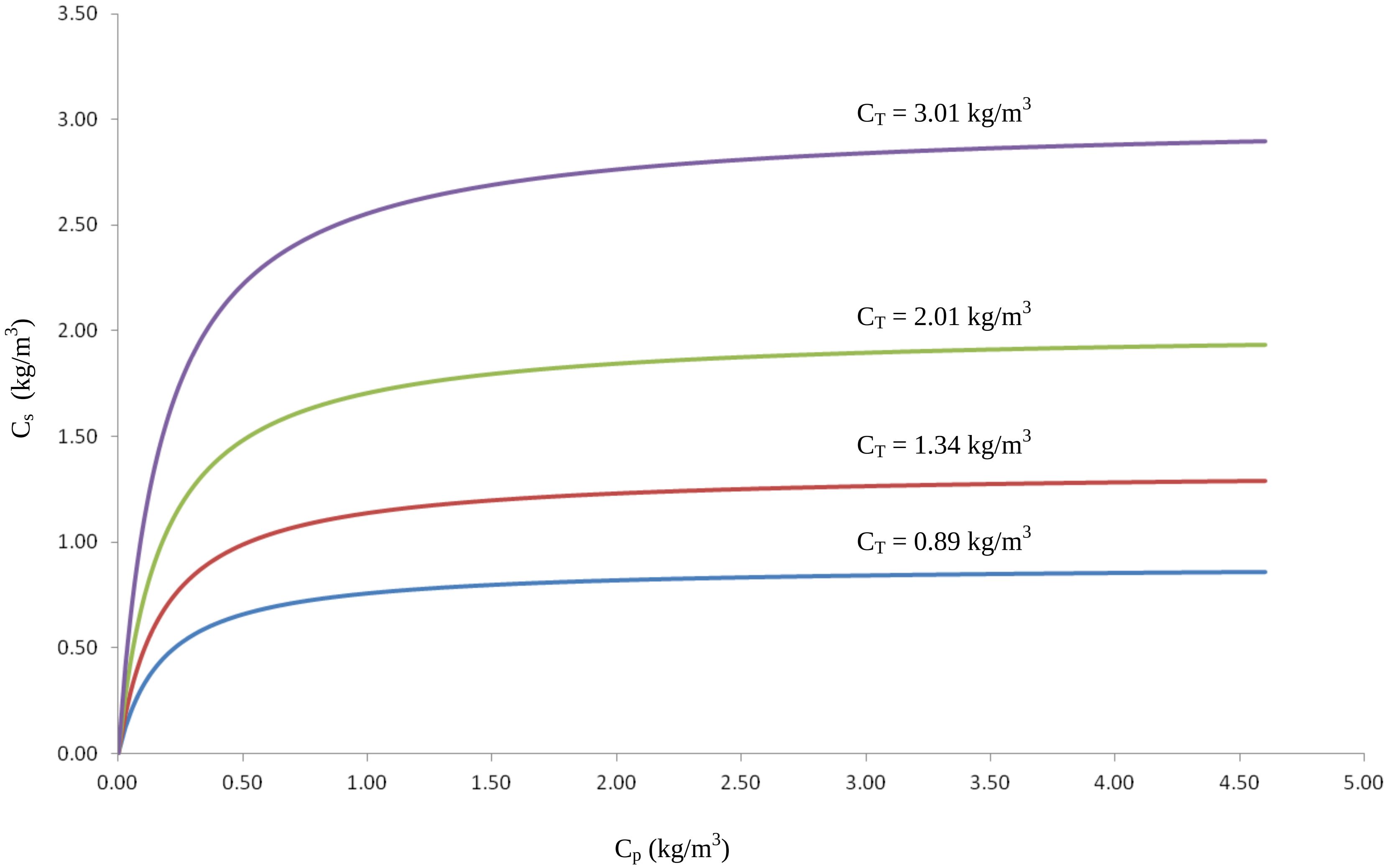

Figure. 2 Equilibrium Langmuir adsorption isotherm curve for lysozyme system

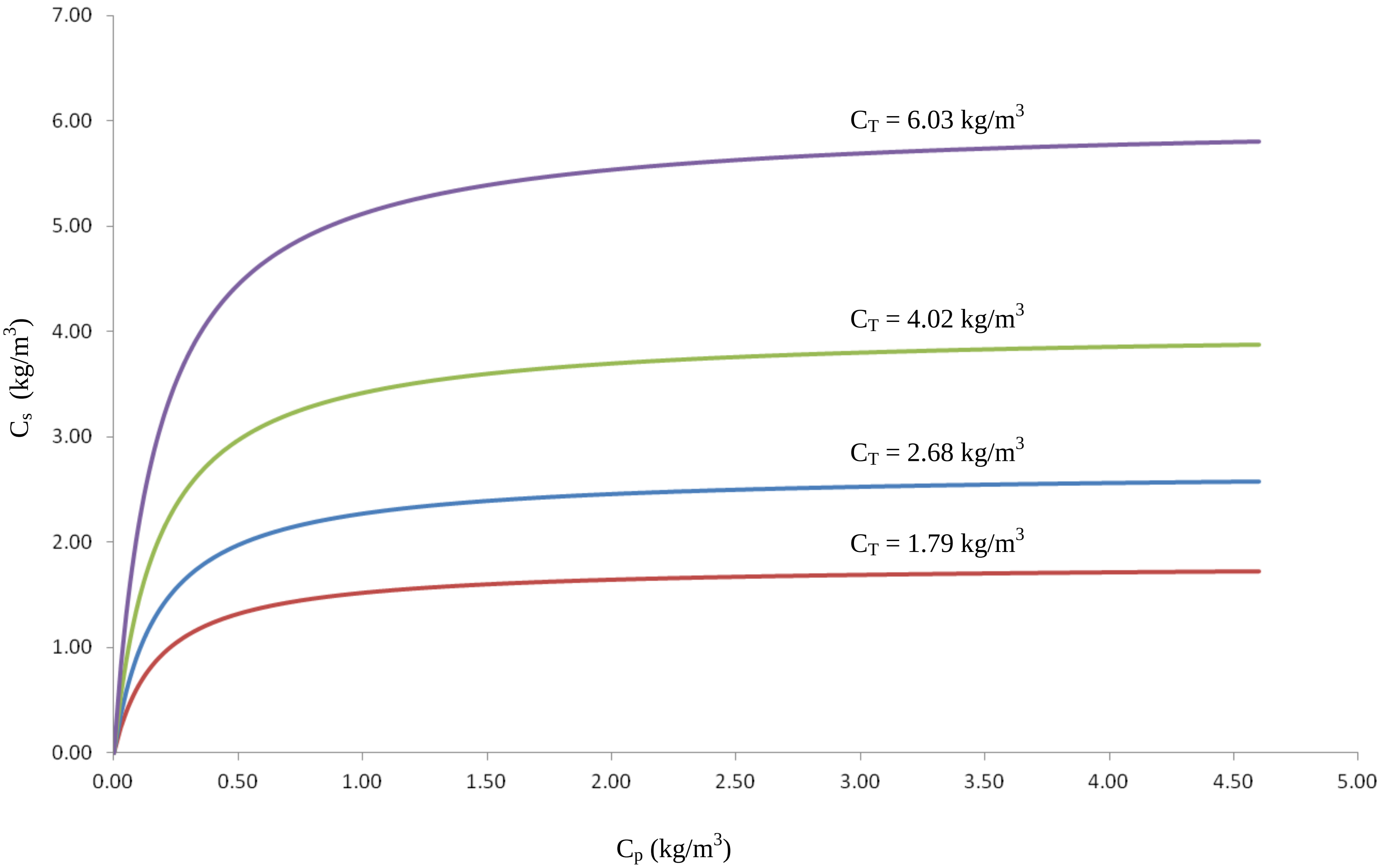

Figure. 3 Equilibrium Langmuir adsorption isotherm curve for lysozyme system

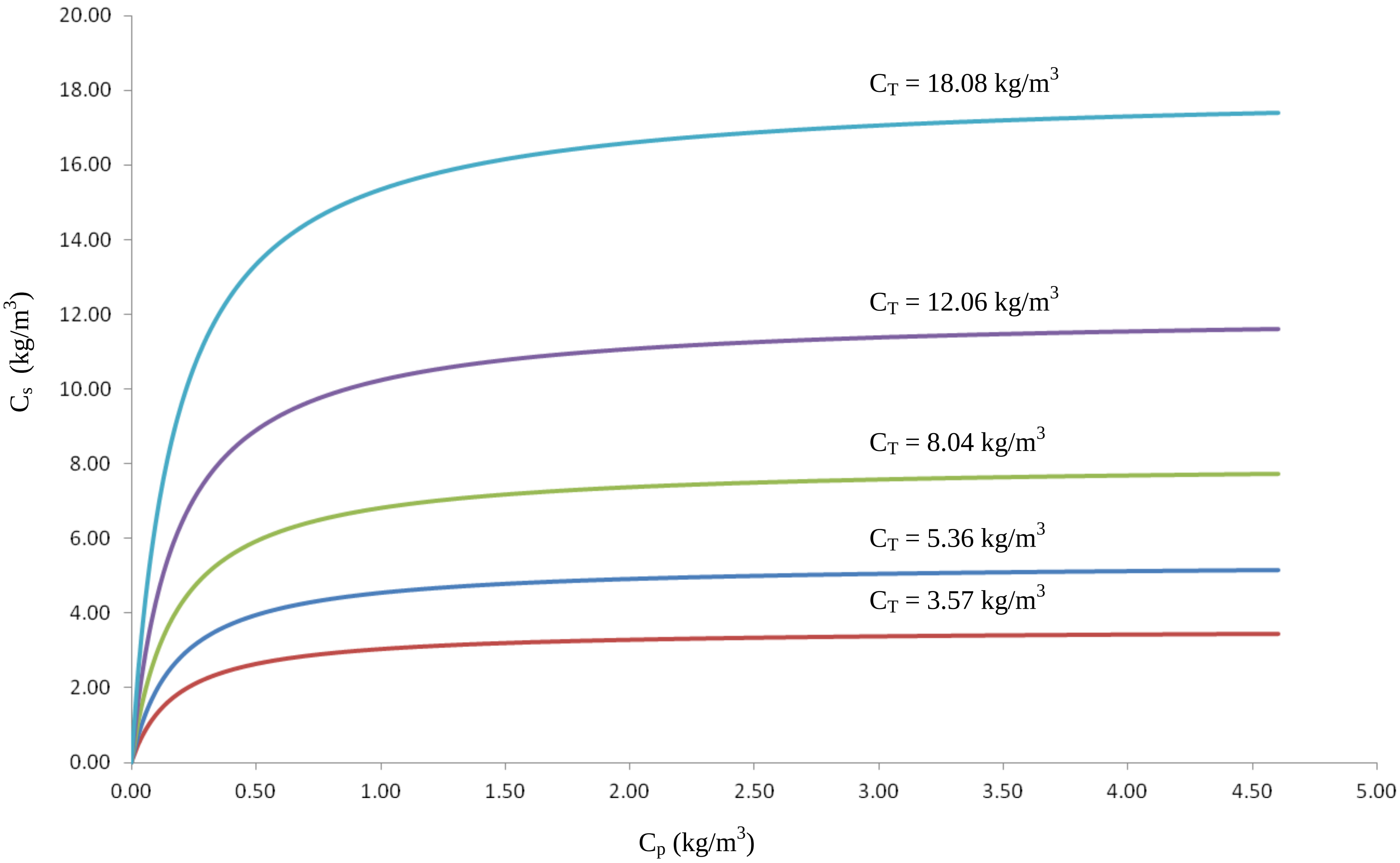

Figure. 4 Equilibrium Langmuir adsorption isotherm curve for lysozyme system

APPENDIX E.

ADDITIONAL RESULTS

APPENDIX E present additional results for the Bovine Serum Albumin (BSA) and lysozyme adsorption systems of this work. Tables 1-6 show additional results for the BSA adsorption system (Paper 1) whose packed porous adsorbent particles employ uniform ligand density distribution; Tables 7 and 8 show additional results for the BSA adsorption system in which the packed porous adsorbent particles employ non-uniform ligand density distribution (see Paper 2); Tables 9 and 10 show additional results of the lysozyme adsorption system (Paper 3) when $N' = 1$ and $N' = 2$.

Table 1. BSA adsorption systems with uniform ligand density distribution

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	V_f (m/s)	$C_{d,in}$ = 0.1kg/m^3			$C_{d,in}$ = 1.5kg/m^3		
							Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%
2	0.3	75×10^{-6}	1.5	1.5	3	2.778×10^{-3}	3.28	11.96	27.28	2.40	5.81	10.99
2	0.3	50×10^{-6}	1.5	1.5	3	2.778×10^{-3}	26.62	87.45	163.10	14.76	35.78	55.32
2	0.3	25×10^{-6}	1.5	1.5	3	2.778×10^{-3}	343.85	546.11	669.61	120.60	135.61	141.90
2	0.25	75×10^{-6}	1	1.5	3	2.778×10^{-3}	3.96	14.84	33.52	2.80	7.20	13.22
2	0.25	50×10^{-6}	1	1.5	3	2.778×10^{-3}	32.68	103.53	187.61	18.00	41.70	62.22
2	0.25	25×10^{-6}	1	1.5	3	2.778×10^{-3}	375.50	577.76	697.99	123.90	136.80	142.46
2	0.3	75×10^{-6}	1.5	1.5	10	2.778×10^{-3}	20.20	68.05	121.11	11.67	27.30	39.00
2	0.3	50×10^{-6}	1.5	1.5	10	2.778×10^{-3}	111.90	220.52	305.62	49.59	70.49	82.38
2	0.3	25×10^{-6}	1.5	1.5	10	2.778×10^{-3}	473.45	643.03	744.41	136.20	143.20	146.48
2	0.25	75×10^{-6}	1	1.5	10	2.778×10^{-3}	25.04	79.63	136.58	14.10	31.20	42.64
2	0.25	50×10^{-6}	1	1.5	10	2.778×10^{-3}	126.59	240.46	328.37	54.60	75.60	87.17
2	0.25	25×10^{-6}	1	1.5	10	2.778×10^{-3}	501.91	670.88	769.52	137.40	143.70	146.71
2	0.3	75×10^{-6}	1.5	1.5	20	2.778×10^{-3}	42.08	98.44	147.32	21.00	34.50	42.85
2	0.3	50×10^{-6}	1.5	1.5	20	2.778×10^{-3}	139.20	239.09	318.07	56.97	73.48	83.45
2	0.3	25×10^{-6}	1.5	1.5	20	2.778×10^{-3}	486.09	650.81	749.99	138.10	143.60	146.69
2	0.25	75×10^{-6}	1	1.5	20	2.778×10^{-3}	49.09	109.38	160.91	23.70	37.50	46.16
2	0.25	50×10^{-6}	1	1.5	20	2.778×10^{-3}	152.99	257.85	339.98	61.50	78.30	88.17
2	0.25	25×10^{-6}	1	1.5	20	2.778×10^{-3}	513.94	678.36	774.91	139.20	144.30	146.91
2	0.3	75×10^{-6}	1.5	3	3	2.778×10^{-3}	33.44	98.60	169.27	18.60	39.60	56.10
2	0.3	50×10^{-6}	1.5	3	3	2.778×10^{-3}	160.21	300.59	401.13	75.60	99.41	110.09
2	0.3	25×10^{-6}	1.5	3	3	2.778×10^{-3}	580.15	736.22	818.15	150.90	154.10	155.57
2	0.25	75×10^{-6}	1	3	3	2.778×10^{-3}	52.97	142.03	228.29	28.20	53.70	70.09
2	0.25	50×10^{-6}	1	3	3	2.778×10^{-3}	216.11	372.50	476.95	91.22	110.75	119.46
2	0.25	25×10^{-6}	1	3	3	2.778×10^{-3}	663.25	806.74	877.40	151.50	154.10	155.83
2	0.3	75×10^{-6}	1.5	3	10	2.778×10^{-3}	111.73	208.95	285.50	52.18	69.27	78.68
2	0.3	50×10^{-6}	1.5	3	10	2.778×10^{-3}	278.10	415.84	506.36	105.05	116.06	121.32
2	0.3	25×10^{-6}	1.5	3	10	2.778×10^{-3}	685.93	816.36	881.60	154.50	156.00	156.81
2	0.25	75×10^{-6}	1	3	10	2.778×10^{-3}	146.69	259.67	343.19	63.90	80.99	90.12
2	0.25	50×10^{-6}	1	3	10	2.778×10^{-3}	337.57	482.54	573.74	115.06	124.20	128.64
2	0.25	25×10^{-6}	1	3	10	2.778×10^{-3}	760.22	877.31	932.39	154.80	156.10	156.91
2	0.3	75×10^{-6}	1.5	3	20	2.778×10^{-3}	136.00	229.29	301.12	57.90	71.70	79.84
2	0.3	50×10^{-6}	1.5	3	20	2.778×10^{-3}	297.26	428.62	515.86	107.74	117.07	121.83
2	0.3	25×10^{-6}	1.5	3	20	2.778×10^{-3}	696.18	822.94	886.42	155.10	156.30	156.88
2	0.25	75×10^{-6}	1	3	20	2.778×10^{-3}	172.00	277.38	356.38	69.30	83.10	91.05
2	0.25	50×10^{-6}	1	3	20	2.778×10^{-3}	354.47	493.74	582.13	117.44	125.09	129.06
2	0.25	25×10^{-6}	1	3	20	2.778×10^{-3}	769.13	882.98	936.55	155.12	156.30	156.97

Table 2. BSA adsorption systems with uniform ligand density distribution

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	V_f (m/s)	$C_{d,in}$ = 0.1kg/m^3			$C_{d,in}$ = 1.5kg/m^3		
							Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%
2	0.3	75×10^{-6}	1.5	1.5	3	5.556×10^{-3}	0.60	1.16	2.31	0.56	0.85	1.27
2	0.3	50×10^{-6}	1.5	1.5	3	5.556×10^{-3}	2.21	8.39	18.74	1.48	3.97	7.30
2	0.3	25×10^{-6}	1.5	1.5	3	5.556×10^{-3}	63.51	142.30	205.96	30.60	47.70	56.27
2	0.25	75×10^{-6}	1	1.5	3	5.556×10^{-3}	0.61	1.36	2.83	0.58	0.95	1.48
2	0.25	50×10^{-6}	1	1.5	3	5.556×10^{-3}	2.72	10.37	22.84	1.80	4.80	8.74
2	0.25	25×10^{-6}	1	1.5	3	5.556×10^{-3}	73.66	157.41	222.07	34.50	51.00	58.57
2	0.3	75×10^{-6}	1.5	1.5	10	5.556×10^{-3}	1.52	6.50	15.25	1.20	3.30	6.06
2	0.3	50×10^{-6}	1.5	1.5	10	5.556×10^{-3}	14.35	43.49	72.84	7.82	16.61	22.48
2	0.3	25×10^{-6}	1.5	1.5	10	5.556×10^{-3}	132.81	207.51	259.73	49.18	57.60	62.03
2	0.25	75×10^{-6}	1	1.5	10	5.556×10^{-3}	1.89	8.14	18.65	1.40	3.90	7.22
2	0.25	50×10^{-6}	1	1.5	10	5.556×10^{-3}	17.52	50.03	81.10	9.60	18.60	24.37
2	0.25	25×10^{-6}	1	1.5	10	5.556×10^{-3}	143.98	220.61	273.35	51.59	59.89	63.94
2	0.3	75×10^{-6}	1.5	1.5	20	5.556×10^{-3}	4.00	15.74	30.01	2.70	6.90	10.24
2	0.3	50×10^{-6}	1.5	1.5	20	5.556×10^{-3}	27.13	58.31	84.68	12.75	19.72	24.08
2	0.3	25×10^{-6}	1.5	1.5	20	5.556×10^{-3}	142.40	213.23	263.61	50.30	58.49	62.24
2	0.25	75×10^{-6}	1	1.5	20	5.556×10^{-3}	5.07	18.75	34.28	3.30	7.80	11.30
2	0.25	50×10^{-6}	1	1.5	20	5.556×10^{-3}	31.12	64.28	92.03	14.38	21.50	25.84
2	0.25	25×10^{-6}	1	1.5	20	5.556×10^{-3}	153.05	226.02	277.06	53.98	60.59	64.15
2	0.3	75×10^{-6}	1.5	3	3	5.556×10^{-3}	2.93	10.84	23.09	2.10	5.10	8.79
2	0.3	50×10^{-6}	1.5	3	3	5.556×10^{-3}	22.34	61.38	100.45	12.03	24.01	32.12
2	0.3	25×10^{-6}	1.5	3	3	5.556×10^{-3}	177.26	259.04	308.30	64.79	69.00	71.50
2	0.25	75×10^{-6}	1	3	3	5.556×10^{-3}	4.89	17.61	35.91	3.00	7.80	13.06
2	0.25	50×10^{-6}	1	3	3	5.556×10^{-3}	34.58	86.00	132.04	17.76	31.27	39.24
2	0.25	25×10^{-6}	1	3	3	5.556×10^{-3}	215.75	297.94	344.53	67.80	71.70	73.33
2	0.3	75×10^{-6}	1.5	3	10	5.556×10^{-3}	17.25	44.67	70.03	9.60	17.36	22.06
2	0.3	50×10^{-6}	1.5	3	10	5.556×10^{-3}	66.41	118.70	158.64	29.85	38.21	42.73
2	0.3	25×10^{-6}	1.5	3	10	5.556×10^{-3}	237.31	309.86	351.17	70.67	72.80	73.89
2	0.25	75×10^{-6}	1	3	10	5.556×10^{-3}	26.31	60.72	90.53	13.50	21.90	26.92
2	0.25	50×10^{-6}	1	3	10	5.556×10^{-3}	86.70	145.53	188.60	35.96	44.11	48.38
2	0.25	25×10^{-6}	1	3	10	5.556×10^{-3}	273.27	344.24	382.69	72.58	74.38	75.27
2	0.3	75×10^{-6}	1.5	3	20	5.556×10^{-3}	27.85	56.84	81.66	13.80	19.80	23.51
2	0.3	50×10^{-6}	1.5	3	20	5.556×10^{-3}	78.62	128.31	165.84	32.47	39.26	43.24
2	0.3	25×10^{-6}	1.5	3	20	5.556×10^{-3}	244.31	314.47	354.61	71.40	72.90	74.00
2	0.25	75×10^{-6}	1	3	20	5.556×10^{-3}	38.16	72.50	100.90	17.40	24.00	28.04
2	0.25	50×10^{-6}	1	3	20	5.556×10^{-3}	98.15	153.83	194.71	38.32	45.02	48.79
2	0.25	25×10^{-6}	1	3	20	5.556×10^{-3}	279.40	348.26	385.69	73.10	74.50	75.36

Table 3. BSA adsorption systems with uniform ligand density distribution

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	V_f (m/s)	$C_{d,in} = 0.1 kg/m^3$			$C_{d,in} = 1.5 kg/m^3$		
							Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%
2	0.3	75×10^{-6}	1.5	1.5	3	8.334×10^{-3}	0.35	0.38	0.67	0.35	0.38	0.50
2	0.3	50×10^{-6}	1.5	1.5	3	8.334×10^{-3}	0.58	1.95	4.47	0.49	1.08	1.96
2	0.3	25×10^{-6}	1.5	1.5	3	8.334×10^{-3}	18.36	51.76	86.38	9.88	19.80	27.01
2	0.25	75×10^{-6}	1	1.5	3	8.334×10^{-3}	0.36	0.41	0.78	0.36	0.40	0.54
2	0.25	50×10^{-6}	1	1.5	3	8.334×10^{-3}	0.68	2.41	5.53	0.60	1.21	2.35
2	0.25	25×10^{-6}	1	1.5	3	8.334×10^{-3}	22.06	59.52	96.39	11.39	22.20	29.21
2	0.3	75×10^{-6}	1.5	1.5	10	8.334×10^{-3}	0.41	1.42	3.50	0.39	0.86	1.61
2	0.3	50×10^{-6}	1.5	1.5	10	8.334×10^{-3}	4.12	15.38	29.66	2.68	6.60	10.09
2	0.3	25×10^{-6}	1.5	1.5	10	8.334×10^{-3}	56.85	99.07	130.53	23.40	29.89	33.48
2	0.25	75×10^{-6}	1	1.5	10	8.334×10^{-3}	0.47	1.78	4.39	0.40	0.90	1.95
2	0.25	50×10^{-6}	1	1.5	10	8.334×10^{-3}	17.52	50.03	81.10	3.27	12.75	25.49
2	0.25	25×10^{-6}	1	1.5	10	8.334×10^{-3}	62.84	106.65	138.91	24.90	31.50	35.08
2	0.3	75×10^{-6}	1.5	1.5	20	8.334×10^{-3}	0.83	3.89	9.03	0.60	2.00	3.59
2	0.3	50×10^{-6}	1.5	1.5	20	8.334×10^{-3}	8.18	22.70	36.14	4.37	8.38	10.95
2	0.3	25×10^{-6}	1.5	1.5	20	8.334×10^{-3}	64.96	104.10	133.87	25.20	30.60	33.72
2	0.25	75×10^{-6}	1	1.5	20	8.334×10^{-3}	1.06	4.86	10.89	0.78	2.40	4.19
2	0.25	50×10^{-6}	1	1.5	20	8.334×10^{-3}	9.86	25.67	39.88	5.40	9.30	11.86
2	0.25	25×10^{-6}	1	1.5	20	8.334×10^{-3}	70.56	111.37	142.05	27.00	32.10	35.30
2	0.3	75×10^{-6}	1.5	3	3	8.334×10^{-3}	0.73	2.58	5.84	0.60	1.43	2.45
2	0.3	50×10^{-6}	1.5	3	3	8.334×10^{-3}	5.65	18.83	35.64	3.24	7.97	12.50
2	0.3	25×10^{-6}	1.5	3	3	8.334×10^{-3}	78.53	130.04	164.03	33.90	39.60	41.96
2	0.25	75×10^{-6}	1	3	3	8.334×10^{-3}	1.15	4.30	9.56	0.90	2.10	3.80
2	0.25	50×10^{-6}	1	3	3	8.334×10^{-3}	9.28	28.67	51.05	5.10	11.55	16.89
2	0.25	25×10^{-6}	1	3	3	8.334×10^{-3}	100.70	155.47	189.35	37.80	42.30	44.24
2	0.3	75×10^{-6}	1.5	3	10	8.334×10^{-3}	4.36	14.87	26.86	2.70	6.30	9.15
2	0.3	50×10^{-6}	1.5	3	10	8.334×10^{-3}	24.95	51.46	73.63	12.29	18.02	21.28
2	0.3	25×10^{-6}	1.5	3	10	8.334×10^{-3}	119.27	167.24	196.83	41.00	43.48	44.66
2	0.25	75×10^{-6}	1	3	10	8.334×10^{-3}	7.29	22.07	37.00	4.20	8.70	11.85
2	0.25	50×10^{-6}	1	3	10	8.334×10^{-3}	34.64	65.88	90.75	15.77	21.65	24.94
2	0.25	25×10^{-6}	1	3	10	8.334×10^{-3}	141.18	190.19	219.03	43.20	45.30	46.46
2	0.3	75×10^{-6}	1.5	3	20	8.334×10^{-3}	9.32	22.65	34.99	5.10	8.70	10.83
2	0.3	50×10^{-6}	1.5	3	20	8.334×10^{-3}	33.08	59.21	80.07	14.70	19.12	21.81
2	0.3	25×10^{-6}	1.5	3	20	8.334×10^{-3}	124.92	170.97	199.61	41.65	43.70	44.79
2	0.25	75×10^{-6}	1	3	20	8.334×10^{-3}	13.79	30.28	44.84	6.90	10.80	13.22
2	0.25	50×10^{-6}	1	3	20	8.334×10^{-3}	42.87	72.83	96.19	17.94	22.59	25.38
2	0.25	25×10^{-6}	1	3	20	8.334×10^{-3}	146.12	193.45	221.47	43.79	45.60	46.56

Table 4. BSA adsorption systems with uniform ligand density distribution

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	V_f	$C_{d,in}$ = 0.1kg/m^3			$C_{d,in}$ = 1.5kg/m^3		
							Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%
3	0.237	75×10^{-6}	1.5	1.5	3	2.778×10^{-3}	8.35	30.99	65.45	5.16	13.95	24.58
3	0.237	50×10^{-6}	1.5	1.5	3	2.778×10^{-3}	63.18	168.67	271.03	33.64	66.95	87.12
3	0.237	25×10^{-6}	1.5	1.5	3	2.778×10^{-3}	461.52	654.63	763.15	143.51	149.78	152.46
3	0.1667	75×10^{-6}	1.0	1.5	3	2.778×10^{-3}	14.66	51.87	101.29	8.56	22.36	37.13
3	0.1667	50×10^{-6}	1.0	1.5	3	2.778×10^{-3}	99.01	234.14	349.52	50.61	85.47	103.72
3	0.1667	25×10^{-6}	1.0	1.5	3	2.778×10^{-3}	546.88	731.20	828.39	144.66	149.87	152.37
3	0.237	75×10^{-6}	1.5	1.5	10	2.778×10^{-3}	48.18	121.55	187.31	25.69	45.12	56.25
3	0.237	50×10^{-6}	1.5	1.5	10	2.778×10^{-3}	176.58	303.67	397.33	74.88	93.68	103.75
3	0.237	25×10^{-6}	1.5	1.5	10	2.778×10^{-3}	579.31	741.09	829.88	149.95	152.94	154.36
3	0.1667	75×10^{-6}	1.0	1.5	10	2.778×10^{-3}	73.78	162.86	236.79	36.58	56.20	67.51
3	0.1667	50×10^{-6}	1.0	1.5	10	2.778×10^{-3}	226.31	365.47	464.45	89.72	107.32	116.45
3	0.1667	25×10^{-6}	1.0	1.5	10	2.778×10^{-3}	655.90	808.89	887.46	150.08	152.91	154.28
3	0.237	75×10^{-6}	1.5	1.5	20	2.778×10^{-3}	75.06	147.32	206.98	34.94	49.25	58.01
3	0.237	50×10^{-6}	1.5	1.5	20	2.778×10^{-3}	199.86	318.47	407.43	79.66	95.26	104.36
3	0.237	25×10^{-6}	1.5	1.5	20	2.778×10^{-3}	590.40	748.20	835.20	150.73	153.22	154.45
3	0.1667	75×10^{-6}	1.0	1.5	20	2.778×10^{-3}	101.53	85.26	252.87	44.50	59.57	68.84
3	0.1667	50×10^{-6}	1.0	1.5	20	2.778×10^{-3}	246.83	378.12	473.15	93.90	108.69	116.94
3	0.1667	25×10^{-6}	1.0	1.5	20	2.778×10^{-3}	665.62	815.10	891.98	150.85	153.18	154.38
3	0.237	75×10^{-6}	1.5	3.0	3	2.778×10^{-3}	280.03	400.85	475.58	100.35	107.31	110.36
3	0.237	50×10^{-6}	1.5	3.0	3	2.778×10^{-3}	421.49	542.00	610.92	136.71	138.73	139.66
3	0.237	25×10^{-6}	1.5	3.0	3	2.778×10^{-3}	794.38	903.98	950.37	159.49	159.79	159.96
3	0.1667	75×10^{-6}	1.0	3.0	3	2.778×10^{-3}	421.91	551.96	624.18	122.89	127.19	129.22
3	0.1667	50×10^{-6}	1.0	3.0	3	2.778×10^{-3}	603.65	716.59	772.23	145.33	146.90	147.70
3	0.237	75×10^{-6}	1.5	3.0	10	2.778×10^{-3}	331.64	442.80	509.08	116.58	119.81	121.37
3	0.237	50×10^{-6}	1.5	3.0	10	2.778×10^{-3}	523.01	635.66	696.27	142.95	143.92	144.43
3	0.237	25×10^{-6}	1.5	3.0	10	2.778×10^{-3}	883.20	971.40	1003.20	157.44	158.67	160.08
3	0.1667	75×10^{-6}	1.0	3.0	10	2.778×10^{-3}	487.51	601.94	663.25	132.81	134.91	135.95
3	0.1667	50×10^{-6}	1.0	3.0	10	2.778×10^{-3}	696.86	795.17	840.51	149.32	150.15	150.59
3	0.237	75×10^{-6}	1.5	3.0	20	2.778×10^{-3}	350.31	457.72	521.37	117.80	120.57	121.99
3	0.237	50×10^{-6}	1.5	3.0	20	2.778×10^{-3}	537.95	646.29	704.53	143.37	144.22	144.68
3	0.237	25×10^{-6}	1.5	3.0	20	2.778×10^{-3}	926.67	982.23	1008.76	157.49	158.72	160.08
3	0.1667	75×10^{-6}	1.0	3.0	20	2.778×10^{-3}	502.42	613.18	672.37	133.44	135.35	136.29
3	0.1667	50×10^{-6}	1.0	3.0	20	2.778×10^{-3}	708.23	803.02	846.62	149.64	150.36	150.76

Table 5. BSA adsorption systems with uniform ligand density distribution

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	V_f	$C_{d,in}$ = 0.1kg/m^3			$C_{d,in}$ = 1.5kg/m^3		
							Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%
3	0.237	75×10^{-6}	1.5	1.5	3	5.556×10^{-3}	0.83	2.67	5.99	0.74	1.49	2.71
3	0.237	50×10^{-6}	1.5	1.5	3	5.556×10^{-3}	5.83	21.05	42.83	3.47	9.23	15.69
3	0.237	25×10^{-6}	1.5	1.5	3	5.556×10^{-3}	110.21	200.41	262.73	49.94	62.90	68.00
3	0.1667	75×10^{-6}	1.0	1.5	3	5.556×10^{-3}	1.30	4.59	10.48	0.98	2.38	4.33
3	0.1667	50×10^{-6}	1.0	1.5	3	5.556×10^{-3}	10.21	34.35	65.51	5.79	14.45	22.97
3	0.1667	25×10^{-6}	1.0	1.5	3	5.556×10^{-3}	146.04	241.57	302.55	59.01	67.71	71.10
3	0.237	75×10^{-6}	1.5	1.5	10	5.556×10^{-3}	4.31	16.86	33.91	2.68	7.54	12.41
3	0.237	50×10^{-6}	1.5	1.5	10	5.556×10^{-3}	31.47	72.68	107.85	16.12	25.89	31.39
3	0.237	25×10^{-6}	1.5	1.5	10	5.556×10^{-3}	178.42	257.95	309.44	62.95	68.59	71.15
3	0.1667	75×10^{-6}	1.0	1.5	10	5.556×10^{-3}	7.84	27.25	49.84	4.58	11.46	16.93
3	0.1667	50×10^{-6}	1.0	1.5	10	5.556×10^{-3}	46.23	94.90	133.96	21.92	31.69	37.25
3	0.1667	25×10^{-6}	1.0	1.5	10	5.556×10^{-3}	212.27	294.06	344.37	68.08	71.83	73.50
3	0.237	75×10^{-6}	1.5	1.5	20	5.556×10^{-3}	10.67	30.26	49.09	6.03	11.85	15.42
3	0.237	50×10^{-6}	1.5	1.5	20	5.556×10^{-3}	45.53	84.81	116.71	20.42	27.66	32.12
3	0.237	25×10^{-6}	1.5	1.5	20	5.556×10^{-3}	186.36	262.82	312.92	64.11	68.94	71.28
3	0.1667	75×10^{-6}	1.0	1.5	20	5.556×10^{-3}	17.15	41.83	63.79	9.00	15.18	18.94
3	0.1667	50×10^{-6}	1.0	1.5	20	5.556×10^{-3}	60.14	105.29	141.22	25.55	33.16	37.85
3	0.1667	25×10^{-6}	1.0	1.5	20	5.556×10^{-3}	219.20	298.37	347.50	69.02	72.13	73.61
3	0.237	75×10^{-6}	1.5	3.0	3	5.556×10^{-3}	55.79	101.60	134.46	27.72	35.79	39.27
3	0.237	50×10^{-6}	1.5	3.0	3	5.556×10^{-3}	131.34	187.87	222.92	53.56	56.45	57.73
3	0.237	25×10^{-6}	1.5	3.0	3	5.556×10^{-3}	301.27	361.79	392.60	77.45	77.84	78.02
3	0.1667	75×10^{-6}	1.0	3.0	3	5.556×10^{-3}	110.60	171.71	210.25	44.48	49.96	52.41
3	0.1667	50×10^{-6}	1.0	3.0	3	5.556×10^{-3}	210.49	272.21	306.16	63.51	65.35	66.21
3	0.237	75×10^{-6}	1.5	3.0	10	5.556×10^{-3}	96.76	146.25	179.34	40.88	44.87	46.75
3	0.237	50×10^{-6}	1.5	3.0	10	5.556×10^{-3}	179.94	235.87	268.69	60.75	62.10	62.75
3	0.237	25×10^{-6}	1.5	3.0	10	5.556×10^{-3}	351.00	403.73	428.36	78.50	78.72	78.85
3	0.1667	75×10^{-6}	1.0	3.0	10	5.556×10^{-3}	159.17	217.97	253.34	53.85	56.54	57.85
3	0.1667	50×10^{-6}	1.0	3.0	10	5.556×10^{-3}	259.68	315.91	345.47	67.85	68.75	69.21
3	0.237	75×10^{-6}	1.5	3.0	20	5.556×10^{-3}	106.84	155.43	187.53	42.24	45.67	47.37
3	0.237	50×10^{-6}	1.5	3.0	20	5.556×10^{-3}	189.14	243.05	274.53	61.25	62.42	63.02
3	0.237	25×10^{-6}	1.5	3.0	20	5.556×10^{-3}	356.78	407.60	431.28	78.57	78.77	78.89
3	0.1667	75×10^{-6}	1.0	3.0	20	5.556×10^{-3}	168.02	225.21	259.49	54.72	57.00	58.18
3	0.1667	50×10^{-6}	1.0	3.0	20	5.556×10^{-3}	266.93	321.28	349.80	68.20	68.96	69.38

Table 6. BSA adsorption system with uniform ligand density distribution

N	L_1 (m)	$R_{p,1}$ (m)	α_i	β_i	$1/\tau_i$	V_f (m/s)	$C_{d,in}$ = 0.1kg/m^3			$C_{d,in}$ = 1.5kg/m^3		
							Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%
3	0.237	75×10^{-6}	1.5	1.5	3	8.334×10^{-3}	0.36	0.71	1.47	0.36	0.55	0.80
3	0.237	50×10^{-6}	1.5	1.5	3	8.334×10^{-3}	1.34	5.13	11.43	0.91	2.45	4.51
3	0.237	25×10^{-6}	1.5	1.5	3	8.334×10^{-3}	38.45	86.19	125.38	19.46	31.17	36.92
3	0.1667	75×10^{-6}	1.0	1.5	3	8.334×10^{-3}	0.38	1.14	2.46	0.38	0.71	1.19
3	0.1667	50×10^{-6}	1.0	1.5	3	8.334×10^{-3}	2.35	8.88	18.98	1.47	4.02	7.15
3	0.1667	25×10^{-6}	1.0	1.5	3	8.334×10^{-3}	55.95	111.19	152.67	26.63	36.80	41.25
3	0.237	75×10^{-6}	1.5	1.5	10	8.334×10^{-3}	0.94	4.02	9.35	0.70	2.00	3.78
3	0.237	50×10^{-6}	1.5	1.5	10	8.334×10^{-3}	8.78	26.39	44.33	4.91	10.60	14.29
3	0.237	25×10^{-6}	1.5	1.5	10	8.334×10^{-3}	82.30	129.80	163.06	32.27	37.79	40.61
3	0.1667	75×10^{-6}	1.0	1.5	10	8.334×10^{-3}	1.71	7.15	15.52	1.12	3.32	5.89
3	0.1667	50×10^{-6}	1.0	1.5	10	8.334×10^{-3}	14.50	37.59	58.56	7.70	13.92	17.61
3	0.1667	25×10^{-6}	1.0	1.5	10	8.334×10^{-3}	101.53	152.28	186.42	37.19	41.93	44.21
3	0.237	75×10^{-6}	1.5	1.5	20	8.334×10^{-3}	2.49	9.65	18.28	1.60	4.29	6.49
3	0.237	50×10^{-6}	1.5	1.5	20	8.334×10^{-3}	16.58	36.09	52.71	8.22	12.57	15.22
3	0.237	25×10^{-6}	1.5	1.5	20	8.334×10^{-3}	89.02	133.90	165.89	33.47	38.17	40.76
3	0.1667	75×10^{-6}	1.0	1.5	20	8.334×10^{-3}	4.55	14.89	25.64	2.68	6.10	8.40
3	0.1667	50×10^{-6}	1.0	1.5	20	8.334×10^{-3}	23.54	46.52	65.52	10.84	15.48	18.36
3	0.1667	25×10^{-6}	1.0	1.5	20	8.334×10^{-3}	107.38	155.85	188.93	38.24	42.26	44.33
3	0.237	75×10^{-6}	1.5	3.0	3	8.334×10^{-3}	19.57	43.55	63.18	10.35	16.49	19.70
3	0.237	50×10^{-6}	1.5	3.0	3	8.334×10^{-3}	60.45	95.42	118.44	27.56	31.06	32.54
3	0.237	25×10^{-6}	1.5	3.0	3	8.334×10^{-3}	165.08	205.76	228.05	48.46	48.97	49.20
3	0.1667	75×10^{-6}	1.0	3.0	3	8.334×10^{-3}	45.74	82.64	108.33	20.88	26.57	29.11
3	0.1667	50×10^{-6}	1.0	3.0	3	8.334×10^{-3}	106.00	147.88	172.36	36.95	39.13	40.12
3	0.237	75×10^{-6}	1.5	3.0	10	8.334×10^{-3}	42.97	71.24	91.81	19.72	23.45	25.32
3	0.237	50×10^{-6}	1.5	3.0	10	8.334×10^{-3}	90.88	126.82	149.12	34.43	36.06	36.85
3	0.237	25×10^{-6}	1.5	3.0	10	8.334×10^{-3}	199.19	236.12	254.99	49.92	50.18	50.32
3	0.1667	75×10^{-6}	1.0	3.0	10	8.334×10^{-3}	76.73	113.62	137.81	29.31	32.11	33.46
3	0.1667	50×10^{-6}	1.0	3.0	10	8.334×10^{-3}	139.07	178.17	200.05	41.37	42.47	43.00
3	0.237	75×10^{-6}	1.5	3.0	20	8.334×10^{-3}	49.55	77.66	97.86	21.07	24.18	25.86
3	0.237	50×10^{-6}	1.5	3.0	20	8.334×10^{-3}	97.50	132.37	153.81	34.97	36.40	37.13
3	0.237	25×10^{-6}	1.5	3.0	20	8.334×10^{-3}	202.20	238.24	256.00	50.00	50.25	50.39
3	0.1667	75×10^{-6}	1.0	3.0	20	8.334×10^{-3}	82.99	118.99	142.53	30.22	32.61	33.83
3	0.1667	50×10^{-6}	1.0	3.0	20	8.334×10^{-3}	144.50	182.39	203.53	41.77	42.70	43.18

Table 7. BSA adsorption system with non-uniform ligand density distribution

$C_{d,in}$ = 0.1 kg/m^3					$R_P = 7.5\times10^{-5}$ m			$R_P = 5.0\times10^{-5}$ m			$R_P = 2.5\times10^{-5}$ m		
					Non-Uniform ligand density distribution			Non-Uniform ligand density distribution			Non-Uniform ligand density distribution		
N	α_i	β_i	$1/\tau_i$	$V_{f,i}$ (m/s)	Time, t (min)			Time, t (min)			Time, t (min)		
					1%	5%	10%	1%	5%	10%	1%	5%	10%
1	1.5	1.5	3	2.778×10^{-3}	2.37	8.60	20.54	19.93	71.76	139.97	297.39	479.68	598.06
1	1.5	1.5	3	5.556×10^{-3}	0.53	0.87	1.71	1.58	6.17	14.54	53.69	123.51	179.25
1	1.5	1.5	3	8.334×10^{-3}	0.35	0.36	0.48	0.44	1.47	3.32	14.68	44.47	75.55
1	1.5	1.5	10	2.778×10^{-3}	12.95	48.48	88.01	79.94	161.39	228.27	369.41	528.00	632.87
1	1.5	1.5	10	5.556×10^{-3}	0.95	4.16	10.42	9.66	31.51	53.23	98.44	159.80	206.15
1	1.5	1.5	10	8.334×10^{-3}	0.36	0.90	2.26	2.06	8.91	18.65	41.41	74.12	100.01
1	1.5	1.5	20	2.778×10^{-3}	26.95	66.55	102.15	95.35	171.24	234.55	375.77	531.70	635.39
1	1.5	1.5	20	5.556×10^{-3}	2.22	10.20	20.29	17.86	40.04	59.51	103.54	162.68	207.99
1	1.5	1.5	20	8.334×10^{-3}	0.41	2.33	5.89	5.17	15.35	24.93	45.88	76.73	101.66
2	1.5	1.5	3	2.778×10^{-3}	6.11	24.61	55.05	53.01	151.85	247.98	423.48	609.65	719.81
2	1.5	1.5	3	5.556×10^{-3}	0.66	1.97	4.56	4.40	17.24	36.99	99.84	183.32	242.01
2	1.5	1.5	3	8.334×10^{-3}	0.36	0.54	1.10	0.98	3.95	9.25	33.99	78.74	114.96
2	1.5	1.5	10	2.778×10^{-3}	35.02	92.08	142.80	133.60	235.75	315.92	483.77	649.39	748.97
2	1.5	1.5	10	5.556×10^{-3}	2.79	12.17	25.78	23.45	55.37	82.67	140.59	212.19	262.91
2	1.5	1.5	10	8.334×10^{-3}	0.61	2.71	6.72	6.21	20.13	34.10	63.38	103.19	133.28
2	1.5	1.5	20	2.778×10^{-3}	52.03	105.88	152.24	145.86	242.86	320.45	488.73	652.40	751.12
2	1.5	1.5	20	5.556×10^{-3}	6.94	21.32	35.12	32.07	61.70	86.87	144.46	214.38	264.37
2	1.5	1.5	20	8.334×10^{-3}	1.46	6.61	13.06	11.51	25.85	38.38	66.80	105.11	134.52
3	1.5	1.5	3	2.778×10^{-3}	16.93	60.89	118.63	111.75	244.94	350.91	535.33	711.55	807.92
3	1.5	1.5	3	5.556×10^{-3}	1.39	5.27	12.37	11.97	40.17	73.96	149.10	237.22	293.94
3	1.5	1.5	3	8.334×10^{-3}	0.37	1.25	2.82	2.71	10.53	22.48	60.44	112.70	150.11
3	1.5	1.5	10	2.778×10^{-3}	68.30	142.40	203.66	195.35	315.84	405.68	588.30	746.81	834.06
3	1.5	1.5	10	5.556×10^{-3}	8.09	26.59	45.84	42.20	82.55	115.21	184.88	261.91	312.26
3	1.5	1.5	10	8.334×10^{-3}	1.74	7.49	15.66	14.25	34.03	51.23	87.74	133.15	165.37
3	1.5	1.5	20	2.778×10^{-3}	83.83	152.97	210.64	205.19	321.49	409.43	592.56	749.49	836.01
3	1.5	1.5	20	5.556×10^{-3}	15.11	35.08	52.80	49.73	87.38	118.35	188.03	263.78	313.58
3	1.5	1.5	20	8.334×10^{-3}	4.28	13.11	21.75	19.86	38.52	54.32	90.48	134.72	166.44

Table 8. BSA adsorption system with non-uniform ligand density distribution

$C_{d,in}$ = 1.5 kg/m^3					$R_P = 7.5\times10^{-5}$ m			$R_P = 5.0\times10^{-5}$ m			$R_P = 2.5\times10^{-5}$ m		
					Non-Uniform ligand density distribution			Non-Uniform ligand density distribution			Non-Uniform ligand density distribution		
N	α_i	β_i	$1/\tau_i$	$V_{f,i}$ (m/s)	Time, t (min)			Time, t (min)			Time, t (min)		
					1%	5%	10%	1%	5%	10%	1%	5%	10%
1	1.5	1.5	3	2.778×10^{-3}	1.83	4.46	8.53	11.18	29.06	45.62	98.15	117.38	126.67
1	1.5	1.5	3	5.556×10^{-3}	0.53	0.71	1.02	1.14	3.03	5.78	23.93	38.24	46.51
1	1.5	1.5	3	8.334×10^{-3}	0.35	0.36	0.43	0.39	0.85	1.51	7.61	15.98	21.92
1	1.5	1.5	10	2.778×10^{-3}	7.52	18.69	27.50	33.80	51.35	62.09	113.18	124.46	130.22
1	1.5	1.5	10	5.556×10^{-3}	0.79	2.19	4.30	5.23	11.50	16.05	36.44	45.35	50.36
1	1.5	1.5	10	8.334×10^{-3}	0.35	0.62	1.13	1.31	3.86	6.33	16.40	22.44	26.01
1	1.5	1.5	20	2.778×10^{-3}	12.90	23.29	30.20	39.00	53.51	62.74	114.95	124.93	130.33
1	1.5	1.5	20	5.556×10^{-3}	1.52	4.38	6.89	8.14	13.61	17.18	38.12	45.83	50.47
1	1.5	1.5	20	8.334×10^{-3}	0.40	1.28	2.41	2.72	5.59	7.61	17.89	22.95	26.13
2	1.5	1.5	3	2.778×10^{-3}	3.93	11.30	20.90	28.02	56.81	74.81	130.02	140.48	145.09
2	1.5	1.5	3	5.556×10^{-3}	0.62	1.20	2.15	2.68	7.65	13.63	41.73	54.36	60.43
2	1.5	1.5	3	8.334×10^{-3}	0.36	0.46	0.66	0.74	1.94	3.73	16.47	26.45	31.74
2	1.5	1.5	10	2.778×10^{-3}	18.21	33.11	42.30	55.47	72.99	83.31	130.70	143.73	146.65
2	1.5	1.5	10	5.556×10^{-3}	1.83	5.56	9.38	11.55	19.18	23.86	50.80	58.25	62.21
2	1.5	1.5	10	8.334×10^{-3}	0.51	1.44	2.82	3.51	7.82	10.67	24.73	30.42	33.68
2	1.5	1.5	20	2.778×10^{-3}	23.95	35.67	43.34	58.76	73.98	83.59	138.52	143.95	146.70
2	1.5	1.5	20	5.556×10^{-3}	3.96	8.26	11.07	14.23	20.32	24.27	51.70	58.47	62.27
2	1.5	1.5	20	8.334×10^{-3}	1.03	2.99	4.59	5.58	9.01	11.21	25.59	30.66	33.75
3	1.5	1.5	3	2.778×10^{-3}	9.86	26.21	42.48	56.27	85.54	99.78	147.39	151.76	153.73
3	1.5	1.5	3	5.556×10^{-3}	1.04	2.69	5.05	6.77	16.87	25.73	58.49	66.83	70.31
3	1.5	1.5	3	8.334×10^{-3}	0.37	0.77	1.32	1.65	4.73	8.43	27.52	35.84	39.67
3	1.5	1.5	10	2.778×10^{-3}	33.11	48.55	57.76	78.76	95.00	104.26	150.56	153.15	154.42
3	1.5	1.5	10	5.556×10^{-3}	4.76	11.02	15.02	19.58	27.37	32.02	63.89	68.87	71.25
3	1.5	1.5	10	8.334×10^{-3}	1.16	3.50	5.93	7.45	12.26	15.09	33.25	38.10	40.73
3	1.5	1.5	20	2.778×10^{-3}	37.12	49.91	58.26	80.69	95.54	104.46	150.90	153.25	154.44
3	1.5	1.5	20	5.556×10^{-3}	7.86	12.65	15.66	21.39	27.96	32.23	64.35	69.00	71.29
3	1.5	1.5	20	8.334×10^{-3}	2.56	5.28	7.06	9.14	12.91	15.34	33.73	38.23	40.78

Table 9. Lysozyme adsorption system, N' = 1 and N' = 2

							$C_{d,in}$=25.1×10^{-3} kg/m^3			$C_{d,in}$= 25.1×10^{-2} kg/m^3			$C_{d,in}$ = 0.5 kg/m^3			$C_{d,in}$ = 1.0 kg/m^3		
N	N'	L (m)	$R_{p,1}$ (m)	$V_{f,1}$ (m/s)	1/τ_1	$\varepsilon_{p,1}$	Time, t (min)			Time, t (min)			Time, t (min)			Time, t (min)		
							1%	5%	10%	1%	5%	10%	1%	5%	10%	1%	5%	10%
1	1	0.2	5.00×10^{-5}	2.778×10^{-3}	5	0.6	3.48	4.88	5.81	2.96	3.77	4.22	2.54	3.05	3.31	2.06	2.35	2.49
1	1	0.2	5.00×10^{-5}	2.778×10^{-3}	10	0.6	6.41	9.02	10.76	5.30	6.71	7.47	4.38	5.18	5.57	3.30	3.69	3.88
1	1	0.2	5.00×10^{-5}	2.778×10^{-3}	20	0.6	12.25	17.27	20.65	9.95	12.56	13.96	8.02	9.39	10.07	5.71	6.31	6.61
1	1	0.2	5.00×10^{-5}	2.778×10^{-3}	30	0.6	18.07	25.53	30.53	14.60	18.41	20.44	11.65	13.60	14.55	8.10	8.92	9.32
1	2	0.2	5.00×10^{-5}	2.778×10^{-3}	5	0.6	4.11	5.81	6.95	3.47	4.46	5.00	2.97	3.58	3.88	2.37	2.71	2.88
1	2	0.2	5.00×10^{-5}	2.778×10^{-3}	10	0.6	7.73	10.90	13.03	6.36	8.07	8.99	5.23	6.19	6.66	3.89	4.35	4.58
1	2	0.2	5.00×10^{-5}	2.778×10^{-3}	20	0.6	14.89	21.03	25.15	12.07	15.24	16.94	9.70	11.35	12.16	6.84	7.56	7.91
1	2	0.2	5.00×10^{-5}	2.778×10^{-3}	30	0.6	22.03	31.14	37.26	17.77	22.41	24.88	14.14	16.50	17.66	9.77	10.75	11.23
1	1	0.2	5.00×10^{-5}	5.556×10^{-3}	5	0.6	1.04	1.62	20.73	0.91	1.31	1.58	0.82	1.11	1.29	0.70	0.89	1.00
1	1	0.2	5.00×10^{-5}	5.556×10^{-3}	10	0.6	1.90	2.99	3.82	1.62	2.33	2.79	1.41	1.89	2.18	1.13	1.42	1.58
1	1	0.2	5.00×10^{-5}	5.556×10^{-3}	20	0.6	3.61	5.69	7.29	3.03	4.35	5.21	2.57	3.44	3.96	1.99	2.46	2.73
1	1	0.2	5.00×10^{-5}	5.556×10^{-3}	30	0.6	5.31	8.39	10.77	4.44	6.36	7.63	3.74	4.99	5.74	2.84	3.50	3.86
1	2	0.2	5.00×10^{-5}	5.556×10^{-3}	5	0.6	1.19	1.91	2.46	1.05	1.54	1.86	0.93	1.29	1.51	0.79	1.02	1.15
1	2	0.2	5.00×10^{-5}	5.556×10^{-3}	10	0.6	2.27	3.59	4.61	1.93	2.79	3.35	1.67	2.25	2.60	1.33	1.67	1.87
1	2	0.2	5.00×10^{-5}	5.556×10^{-3}	20	0.6	4.37	6.92	8.87	3.67	5.27	6.32	3.10	4.16	4.78	2.38	2.95	3.27
1	2	0.2	5.00×10^{-5}	5.556×10^{-3}	30	0.6	6.47	10.23	13.13	5.39	7.73	9.28	4.53	6.05	6.96	3.43	4.22	4.66
1	1	0.2	5.00×10^{-5}	8.334×10^{-3}	5	0.6	0.47	0.80	1.06	0.43	0.66	0.83	0.39	0.57	0.69	0.35	0.47	0.55
1	1	0.2	5.00×10^{-5}	8.334×10^{-3}	10	0.6	0.87	1.47	1.95	0.76	1.17	1.46	0.67	0.97	0.17	0.56	0.75	0.87
1	1	0.2	5.00×10^{-5}	8.334×10^{-3}	20	0.6	1.66	2.79	3.72	1.41	2.17	2.71	1.22	1.76	2.02	0.97	1.29	1.49
1	1	0.2	5.00×10^{-5}	8.334×10^{-3}	30	0.6	2.44	4.11	5.48	2.06	3.17	3.96	1.77	2.54	3.05	1.38	1.84	2.11
1	2	0.2	5.00×10^{-5}	8.334×10^{-3}	5	0.6	0.54	0.93	1.25	0.48	0.77	0.97	0.44	0.66	0.80	0.39	0.54	0.63
1	2	0.2	5.00×10^{-5}	8.334×10^{-3}	10	0.6	1.03	1.76	2.35	0.89	1.39	1.75	0.79	1.15	1.39	0.65	0.88	1.02
1	2	0.2	5.00×10^{-5}	8.334×10^{-3}	20	0.6	2.00	3.38	4.52	1.70	2.62	3.28	1.46	2.11	2.54	1.16	1.55	1.78
1	2	0.2	5.00×10^{-5}	8.334×10^{-3}	30	0.6	2.96	5.00	6.68	2.50	3.85	4.82	2.14	3.07	3.69	1.66	2.21	2.54

Table 10. Lysozyme adsorption system, N' = 1 and N' = 2

									$C_{d,in} = 25.1\times10^{-3}$ kg/m^3			$C_{d,in} = 25.1\times10^{-2}$ kg/m^3			$C_{d,in} = 0.5$ kg/m^3			$C_{d,in} = 1.0$ kg/m^3		
N	N'	L_1 (m)	L_2 (m)	$R_{p,1}$ (m)	$R_{p,2}$ (m)	$V_{f,i}$ (m/s)	$1/\tau_i$	$\varepsilon_{p,i}$	Time, t (min)			Time, t (min)			Time, t (min)			Time, t (min)		
									1%	5%	10%	1%	5%	10%	1%	5%	10%	1%	5%	10%
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	5	0.6	5.07	6.72	7.75	4.25	5.09	5.50	3.56	4.00	4.20	2.75	2.96	3.06
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	10	0.6	9.55	12.65	14.59	7.79	9.23	9.91	6.23	6.89	7.18	4.44	4.71	4.83
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	20	0.6	18.48	24.49	28.25	14.82	17.47	18.71	11.50	12.60	13.09	7.72	8.13	8.33
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	30	0.6	27.39	36.32	41.90	21.85	25.70	27.50	16.75	18.30	18.99	10.99	11.54	11.81
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	5	0.6	6.06	8.07	9.32	5.06	6.08	6.56	4.20	4.73	4.96	3.20	3.44	3.56
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	10	0.6	11.57	15.35	17.71	9.41	11.16	11.98	7.47	8.27	8.61	5.27	5.58	5.73
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	20	0.6	22.52	29.86	34.45	18.03	21.25	22.75	13.93	15.26	15.85	9.29	9.77	10.01
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	2.778×10^{-3}	30	0.6	33.47	44.39	51.22	26.66	31.35	33.53	20.38	22.26	23.09	13.29	13.96	14.67
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	5	0.6	1.61	2.40	2.96	1.40	1.91	2.21	1.23	1.57	1.76	1.01	1.22	1.32
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	10	0.6	3.05	4.52	5.56	2.57	3.47	4.00	2.19	2.75	3.05	1.70	2.00	2.14
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	20	0.6	5.89	8.73	10.75	4.91	6.58	7.56	4.10	5.10	5.62	3.05	3.52	3.74
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	30	0.6	8.73	12.93	15.93	7.23	9.69	11.13	6.00	7.44	8.18	4.39	5.03	5.33
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	5	0.6	1.91	2.87	3.54	1.65	2.62	2.63	1.44	1.85	2.07	1.18	1.42	1.54
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	10	0.6	3.68	5.47	6.74	3.10	4.19	4.83	2.63	3.31	3.66	2.02	2.37	2.54
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	20	0.6	7.17	10.63	13.10	5.96	8.00	9.20	4.97	6.18	6.81	3.68	4.23	4.50
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	5.556×10^{-3}	30	0.6	10.65	15.79	19.46	8.82	11.82	15.76	7.30	9.05	9.96	5.32	6.09	6.89
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	5	0.6	0.77	1.23	1.58	0.68	1.00	1.21	0.61	0.84	0.98	0.52	0.67	0.75
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	10	0.6	1.46	2.32	2.97	1.25	1.81	2.18	1.08	1.47	1.71	0.87	1.10	1.23
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	20	0.6	2.82	4.47	5.74	2.38	3.44	4.13	2.21	2.73	3.15	1.57	1.95	2.16
2	1	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	30	0.6	4.19	6.62	8.50	3.51	5.06	6.07	2.97	3.98	4.59	2.26	2.80	3.10
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	5	0.6	0.89	1.46	1.89	0.79	1.18	1.41	0.70	0.98	1.16	0.59	0.77	0.87
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	10	0.6	1.75	2.80	3.60	1.49	2.18	2.63	1.29	1.77	2.05	1.03	1.31	1.46
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	20	0.6	3.43	5.44	6.99	2.89	4.17	5.02	2.45	3.31	3.81	1.89	2.35	2.60
2	2	0.12	0.08	5.00×10^{-5}	3.33×10^{-5}	8.334×10^{-3}	30	0.6	5.11	8.09	10.38	4.28	6.16	7.40	3.61	4.85	5.58	2.74	3.39	3.75

APPENDIX F.

FORTRAN CODES ON CD-ROM

Included with this dissertation is a CD-ROM which contains Fortran 77 codes employed in obtaining the numerical results in the three papers published (papers 1-3). The codes are included in the following folders:

1. Uniform Ligand density distribution

   Fortran 77 code used for the computations for the paper titled “Adsorption in a stratified column bed packed with porous particles having partially fractal structures and a distribution of particle diameters”.

2. Non-uniform Ligand density distribution

   Fortran 77 code used for the computations for the paper titled “The dynamic behavior of a stratified column bed packed with porous adsorbent particles having partially fractal structures and a non-uniform ligand density distribution”.

3. Stratified column beds packed with partially fractal particles (recursion greater than one)

   Fortran 77 code used for the computations for the paper titled “Adsorption in columns packed with porous adsorbent particles having partially fractal structures”.

VITA

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