Research note

Determination of Adsorption Isotherm for L-Lysine Imprinted Polymer

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Abstract
The optimization of adsorption-based operations requires an accurate model to represent the separation process. In the present study, single-component adsorption data of L-lysine on its imprinted polymer were fitted to Freundlich, Langmuir-type and Jovanovic-type models. L-Lysine imprinted polymer (LLIP) was prepared by free radical solution polymerization. The best estimate of the parameters of these models by regression analysis was obtained. The statistical analysis of results showed that the experimental data fit the Jovanovic-Freundlich mode, better than other models in terms of f value. The best prediction of retention capacity equal to 0.186 mmol lysine per g of LLIP, which is the nearest value to the experimental data, was obtained by applying the Jovanovic model.

Keywords: *Molecular imprinting, Isotherm model, Jovanovic-Freundlich, Lysine adsorption*

Introduction

Adsorption-based operations are important for large-scale industrial separations and are becoming more and more sophisticated. One example is the development of preparative chromatography in the pharmaceutical industry. The optimization of these operations requires an accurate model for representation of the separation [1]. For obvious economic reasons, preparative chromatography should be carried out at a high concentration, in which case a non-linear equilibrium takes place and the thermodynamic factors play an important role in the course of the separations [1].

Molecular imprinting of cross-linked polymers is now widely used for the design of recognition materials for various chiral, analytical and preparative separations [2, 3]. The most widely applied method of preparation of molecularly imprinted polymers (MIPs) is based on the formation of noncovalent interaction between a template molecule and functional monomers. These prepolymer complexes are then immobilized into a polymer matrix by copolymerization with a high concentration of cross-linking monomers in the presence of an initiator. After polymerization, the template is extracted from the polymer matrix, leaving behind cavities that have complementary size, shape and functionalities toward the template and can readily adsorb it [3].

The major problem encountered in the

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synthesis of MIPs by this method, is the heterogeneous character of their binding sites, the presence of several different types of binding sites with various association constants, and densities on the MIP surface [3].

The purpose of the present study was to fit the experimental results of L-lysine adsorption onto imprinted polymer to several adsorption models and determine the most suitable to properly describe the separation process.

Theory
Adsorption isotherm models
The adsorption isotherm models relate the equilibrium concentrations of the studied component in the bulk liquid phase, F (mM), and in the adsorbent, B (mmol/g of adsorbent) [4]. Different models have been used to correlate experimental adsorption data. Some of them consider an ideal behavior of the system, without taking into account the possible source of nonideal behavior, like the adsorbate-adsorbate interactions in the adsorbed phase, the heterogeneity of the adsorbent surface, the loss of symmetry, clustering or dissociation of the adsorbates, the interactions among the components of the bulk liquid phase leading, in some cases, to the formation of associates, the limited solubility of the components in the bulk liquid phase, the irreversibility of the adsorption, or even the existence of synergistic effects [1].

Langmuir-type and empirical isotherm models
One of the simple models is Langmuir adsorption isotherm (Table 1) where the adsorbent is assumed to contain only one type of site, adsorbate–adsorbate interactions are assumed not to occur and the system is assumed ideal. This isotherm depends on two parameters: the theoretical saturation capacity, q (mmol of adsorbate/g of adsorbent), and the equilibrium constant, k

[5-7]. The nature of MIPs indicates the importance of accounting for the heterogeneity of the adsorption sites. Another model of this type includes a number of classical models for the heterogeneous surface with continuous energy distribution such as Langmuir-Freundlich [8] (Table 1).

The Langmuir-Freundlich model was analyzed by Sipe, who found that its energy distribution function corresponds to a symmetrical quasi-Gaussian function. The model reduces to the monolayer but does not obey the Henry's law. At low concentrations, the model reduces to the Freundlich model. The Langmuir–Freundlich model reduces to the Langmuir model for the case of a homogeneous surface [9]. In this equation, q and k have the same meaning as in the Langmuir isotherm model and n is the heterogeneity parameter ($0<n<1$). This parameter increases with the decreasing degree of surface heterogeneity [9, 10].

The empirical Freundlich expression (Table 1) is an exponential equation and therefore assumes that as the adsorbate concentration increases, so too does the concentration of adsorbate on the adsorbent surface. This isotherm may be used to describe heterogeneous systems with continuous energy distribution [11-13]. Theoretically, using this expression, an infinite amount of adsorption can occur [14]. The Freundlich equation agrees well with the Langmuir equation over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants [13].

Jovanovic-type models
The Jovanovic model keeps the same assumptions contained in the Langmuir model, only considering, in addition the possibility of some mechanical contacts

between the adsorbing and desorbing molecules [15]. Moreover, a different extension of Jovanovic model for heterogeneous surface, the Jovanovic-Freundlich model, has been applied as a semiempirical model to the adsorption data of imprinted polymers (Table 2).

The Jovanovic-Freundlich model for single component adsorption was derived from a differential relationship relating the surface coverage and the bulk concentration of the adsorbate [16]. The model reduces to the Jovanovic model when the surface is homogeneous. It reduces to the monolayer isotherm at high concentrations but does not obey the Henry's law at low concentrations. The energy distribution corresponding to this model for Jovanovic local behavior is a quasi-Gaussian function skewed in the direction of high adsorption energies [1].

Materials and Methods
Preparation of L-Lysine Imprinted Polymer (LLIP)
LLIP was prepared by the non-covalent method, and the batch rebinding study was carried out at equilibrium and optimum conditions with a temperature of 25 °C, as described in our previous work [17].

Nonlinear least squares analysis
Calculation of adsorption isotherm was performed by the CurveExpert (Version 1.34) program. The program uses non-linear least square fitting of the averaged experimental data by using the Marquardt-Levemberg algorithm. This algorithm seeks the values of the parameters that minimize the sum of the squared differences (SSD) between the values of the observed (β_{ex}) and predicted values of the dependent variable (β_t):

Table 1. Langmuir-type and empirical models

Model	Equation	Eq.no .
Langmuir	$B = \dfrac{qkF}{1+kF}$	(1)
Langmuir-Freundlich	$B = \dfrac{qkF^n}{1+kF^n}$	(2)
Freundlich	$B = aF^n$	(3)

F, B: equilibrium concentrations of the studied component in the bulk liquid phase and in the adsorbed phase, respectively; *q*: the theoretical maximum adsorption capacity for corresponding models; *k*: equilibrium constant; *n*: heterogeneity parameter; *a*: constant parameter.

Table 2. Jovanovic-type models

Model	Equation	Eq. no.
Jovanovic	$B = q(1-\exp(-kF))$	(4)
Jovanovic-Freundlich	$B = q(1-\exp(-kF^n))$	(5)

$$SSD = \sum_{i=1}^{m}(B_{ex,i} - B_{t,i})^2 \qquad (6)$$

where m is the number of the experimental data points.

For fitting the single component data (especially to four parameter models), the response surface of the optimization problem often exhibits several minima such as real (global) and/or unreal (local). To avoid being trapped in unreal (local) minima, the identification process was carried out several times, using a different initial guess vector at each time. This is a convenient empirical way to determine if the solution converges toward the global minima [1].

The selection of the most adequate adsorption isotherm model was performed using the Fisher test [18]. According to this test, the model with better data correlation is the one that exhibits the highest value of the Fisher parameter, f, defined as:

$$f = \frac{(m-p)}{(m-1)} \frac{\sum_{i=1}^{m}(B_{ex,i} - \overline{B_{ex}})^2}{\sum_{i=1}^{m}(B_{ex,i} - B_{t,i})^2} \qquad (7)$$

where p is the number of adjusted parameters of the model, and $\overline{B_{ex}}$ is the average of the experimental data points.

Results and discussion
Retention capacity studies
The experimental results indicated that the retention capacity increased with increasing the initial concentration of L-lysine in the feed solution and reached constant values of 27.26 mg lysine per g of LLIP at an initial feed concentration greater than 180 mg lysine per 100 mL of aqueous solution [17].

The fitting of the experimental data to isotherm models
Fitting of the experimental data to different isotherm models are shown in Figs. 1 and 2. The isotherm models can be applied in two different ways, as fitting equations for the experimental data or as actual physical models of the equilibrium observed. However, it should be noted that an excellent fit of experimental data to a model is never a demonstration of the physical validity of this model [2]. The results of the regression analysis of the evaluated models are reported in Tables 3 and 4. The corresponding values of the parameters, Fisher parameter (*f*) and *SSD* are listed in these Tables.
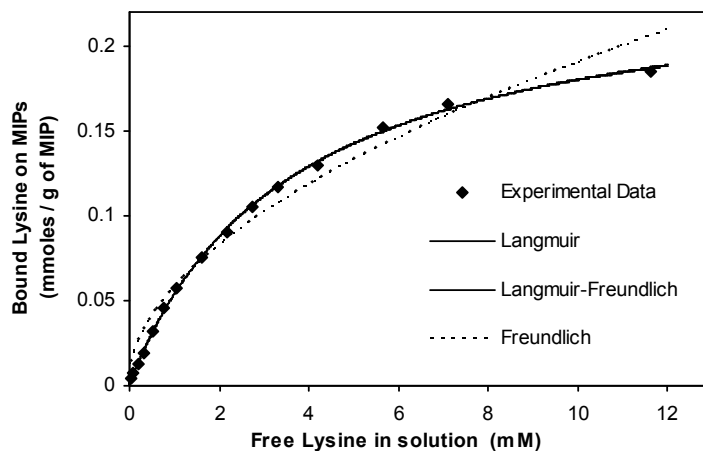

Figure 1. Comparison of experimental data with calculated values of Langmuir-type and empirical models
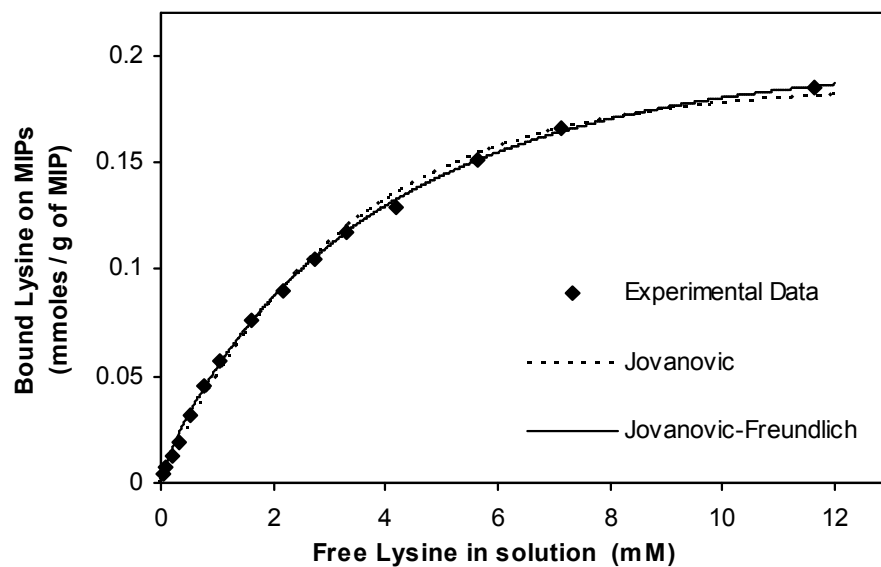
Figure 2. Comparison of experimental data with calculated values of Jovanovic-type models.

Table 3. The calculation of the Langmuir-type and empirical models

Model	Parameters	*SSD* $\times 10^7$	*f*
Langmuir	$q = 0.24365$ $k = 0.28288$	351.9	794.4
Langmuir-Freundlich	$q = 0.24844$ $k = 0.27794$ $n = 0.97906$	333.0	789.8
Freundlich	$a = 0.05764$ $n = 0.51876$	14000	34.82

Table 4. The calculation of the Jovanovic-type models

Model	Parameters	*SSD* $\times 10^7$	*f*
Jovanovic	$q = 0.18588$ $k = 0.31237$	1675	255
Jovanovic-Freundlich	$q = 0.19973$ $k = 0.31108$ $n = 0.87428$	271.0	879.8

Overall results show that the experimental data have not been fitted well to the Freundlich model. Comparison of the Fisher and *SSD* values indicates that it is the least suitable model, as this expression cannot consider the occurrence of a limited adsorption and some mechanical contacts between adsorbate and desorbate molecules. In addition, it has 2 parameters. But it can, specifically, predict the moderate equilibrium concentration range [11-13].

Also, the Langmuir-Freundlich model shows less SSD value than the Langmuir model does for fitting of adsorption data. However the former model has 3 parameters, while the Langmuir model is 2-parametric. The number of parameters has affected the Fisher values and the Langmuir model is, consequently, more suitable than the Freundlich-Langmuir model.

In addition, the Jovanovic-Freundlich model is clearly the best model in terms of *SSD* and *f* values. It can be ascribed to the heterogeneity of polymer particles and the possibility of some mechanical contacts between the adsorbate and desorbate molecules due to the existence of carboxyl and amine groups in the lysine molecule, although this model is 3-parameteric.

The consideration of the heterogeneity parameters shows that LLIP have a limited binding site type, although it is heterogeneous. This confirms a strong need for optimization of the synthesis method to improve the binding performance of the MIPs and their surface homogeneity, and to shift toward higher values of energy of the different sites. Some of these attempts include the optimization of the experimental condition used in chromatography [3], such as mobile phase pH [2] or adsorption pH of batch rebinding as reported in our previous work [17].

Theoretical results show that the Jovanovic model gives the best prediction of retention capacity (q) equal to 27.26 mg (0.186 mmol) lysine per g of LLIP, as the nearest value to the experimental data, in comparison with other models. However, this is very close to that obtained by the Jovanovic-Freundlich model.

Conclusion

Since the optimization of adsorption-based operations requires an accurate model for the representation of the separation, in the present study different models were applied to fit the equilibrium adsorption isotherm of L-lysine separation by its imprinted polymers.

SSD values of the regression analysis indicated that the Jovanovic-Freundlich model, which takes into account the heterogeneity of the LLIP, is superior to the other models. The goodness of data fit to this model can be related to considering the possibility of some mechanical contacts between the adsorbing and desorbing molecules [15] because of the existence of carboxyl and amine groups in adsorbate molecules (lysine).

The consideration of heterogeneity parameters shows that LLIPs have a limited binding site, although they are hetero-geneous. This confirms a strong need for optimization of the synthesis method to improve the binding performance of the MIPs and their surface homogeneity and to shift toward higher values of energy of different sites.

The best prediction of retention capacity, obtained by applying the Jovanovic model, was approved with the experimental data. Also, this model behaved quite similar to the Jovanovic-Freundlich model for fitting experimental data of L-lysine separation by its imprinted polymers.

Nomenclature

a   Constant parameter
B   Equilibrium concentration of lysine in the adsobed phase
B_{ex} Experimental adsorption value
$\overline{B_{ex}}$ Average of experimental adsorption value

B_t Theoretical adsorption value

f Fisher parameter

F Equilibrium concentrations of lysine in the bulk liquid phase

k Equilibrium constant

m Number of the experimental data points

p Number of adjusted parameters of model

q Theoretical saturation capacity

SSD Sum of the squared differences between the experimental and theoretical values of adsorption

Superscript

n Heterogeneity parameter

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