



생물흡착의 평형모델에 대한 고찰

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Review for Equilibrium Model of Biosorption

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ABSTRACT

Recent research on heavy metal biosorption has been focused on its mechanisms and principles. For effective metal removal/recovery the process design has to be optimized for every type of application. That is most efficiently carried out based on computer simulations by means of mathematical models of the process. Therefore, the study on sorption equilibrium isotherm is important and the methodology was summarized here involving both one metal and multi-metal systems.

Keywords : Biosorption, Mathematical modeling, Sorption performance, Ion exchange model

초록

중금속 생물흡착에 대한 최근의 연구는 흡착 기작과 원리에 중점을 두고 있다. 효과적인 금속 제거/회수 공정설계를 위하여 모든 형태의 적용에 최적화가 되어지고 있다. 그 최적화는 공정의 수학적 모델에 의한 컴퓨터 모사에 바탕을 두고 효과적으로 수행되어지고 있다. 그래서 등온흡착평형에 대한 연구가 중요하며 단일성분과 다성분계를 포함하는 방법이 소개하였다.

핵심용어 : 생물흡착, 수학적 모델링, 흡착 성능, 이온 교환 모델

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1. Introduction

Mathematical modeling and computer simulation of biosorption offers an extremely powerful tool for a number of tasks on different levels. It is essential for process design and optimization where the equilibrium and dynamic test information comes together representing a multivariable system which cannot be effectively handled without appropriate modeling and computer-based techniques. The dynamic nature of sorption process applications such as columns, flow-through contactors makes this approach mandatory. When reaction kinetics is combined with mass transfer which is in turn dependent on the particle and fluid flow properties only a reasonably sophisticated apparatus can make sense out of the web of variables. Biosorption process modeling is particularly useful for predicting the process performance according to different conditions. Computer simulations can then replace numerous tedious and expensive experiments to the extent that only the key experiments can be selected and need to be carried out to verify the predictions. Needless to say, the simulations are only as good as the model behind them is. However, advanced sophistication in this area and availability of very powerful computer hardware and software makes contribution of the process modeling/simulation activity very realistic and indispensable indeed. Biosorption process modeling then can perform as follows:

- guide experimental research
- optimize a given process
- provide basis for process control strategies
- provide a process diagnostic tool

In general, metal ion binding mechanism in biosorption may involve different processes such as complexation, coordination, electrostatic attraction,

microprecipitation, and ion exchange. Until now, many biosorption models based on these mechanisms have been reported. So we are going to try to review for Equilibrium Model of Biosorption.

2. Equilibrium modeling

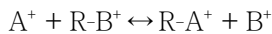
2.1 Multicomponent equilibrium model

Most of the biosorption models have been described using Langmuir or Freundlich sorption isotherms, where binding of metal ions is determined as a function of the equilibrium metal ion concentration in the metal solution. The major advantage of these models is their simplicity however, both models fail to predict the effect of important factors, such as pH and ionic strength. Some models have been reported recently to overcome these problems. Crist et al.¹⁾ utilized a multicomponent Langmuir model that considers the effect of competing ions. The deficiency of this model is that it assumes a constant number of free sites, which is true at constant pH system, but does not hold for a system with changing pH. Extended Langmuir model was applied to the three-metal system by Chong and Volesky²⁾. However, when there were three metals in a solution, the model was no longer effective for describing the system.

2.2 Ion exchange model

Schiewer and Volesky³⁾ observed that ion exchange plays an important role in metal sorption by algal biomass and modeled the binding of heavy metal ions and protons as a function of metal concentration and equilibrium pH. Therefore, many researchers introduced ion exchange model with equilibrium constants that took into account the reversibility of the ion exchange reactions to

describe biosorption mechanisms. Ion exchange is a stoichiometric process, which means that in a binary ion exchange system if one ion enters the solid phase, another ion must leave the solid based on the charge of these ions. Also, ion exchange mechanism assumes that all sites to which metal ions are sorbed are initially occupied, i.e., the number of free sites stays constant. For monovalent ion exchange:



where R is biosorbent and A^+ and B^+ are metal ions, respectively.

If the activity coefficient is all 1.0, the law of mass action gives an equilibrium expression as follows:

$$C_{RA} = \frac{C_{Rtotal} K_{AB} C_A}{C + (K_{AB} - 1) C_A}$$

where C_{Rtotal} is the total resin capacity in equivalents per bulk volume and c is the total concentration of ions in the liquid in equivalents per liter. It is convenient to work in terms of fractions:

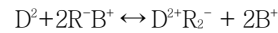
$$y_i = \frac{C_{Ri}}{C_{Rtotal}} \quad X_i = \frac{C_i}{C}$$

Thus, for monovalent ions can be expressed as followed.

$$y_A = \frac{K_{AB} X_A}{1 + (K_{AB} - 1) X_A}$$

For monovalent ions above equation does not depend on either the total ionic strength of the solution or the resin capacity (except for secondary effects due to the activity coefficients). Note that above equation is a Langmuir-type form which will be favorable for A if $K_{AB} > 1$.

For removal of a divalent ion the situation is different. Now the reaction is as follows:



And the equilibrium expression is as following:

$$\frac{y_B^2}{1 - y_B} = \left[\frac{1}{K_{DB} \frac{C_{Rtotal}}{C}} \right] \frac{X_B^2}{1 - X_B}$$

The general Langmuir form has been lost but the isotherm will be favorable for D if $(K_{DB} C_{Rtotal} / C) > 1$. Note that the isotherm now depends on both the total resin capacity and the liquid concentration. This is important in the chemical regeneration of these systems. In real systems, K_{DB} may not be constant.

Crist et al.⁴⁾ compared the fit of the Langmuir sorption isotherm model and the one using ion exchange constants. The differences between the two models were especially pronounced at low metal ion concentrations because of the effect of the reverse reaction involving the displaced ion. Correspondingly, it has been postulated that the Langmuir model applies only at higher metal ion concentrations where binding of the displaced ion is low. Therefore, the ion exchange approach is perhaps somewhat closer to the reality than the simple Langmuir model.

Many isotherm equations have been developed for adsorption. Crittenden et al.⁵⁾, Yu and Wang⁶⁾, Gu et al.⁷⁾, Poltzer and Fuentes⁸⁾, Poltzer et al.⁹⁾, and Zheng et al.¹⁰⁾ used adsorption isotherms to represent ion exchange, although ion exchange is quite different from adsorption. An ion exchange isotherm was derived by Holland and Anthony¹¹⁾. Using adsorption isotherms in ion exchange is empirical, and the functional form of an adsorption isotherm is used to summarize the ion exchange equilibrium data. Therefore, the ability to predict the parameters of the isotherm in different situations is poor. Poltzer et al.⁹⁾ used a modified Langmuir for ion

exchange on volcanic tuff media and then later applied the Gaines–Tomas theory on the modified Langmuir isotherm to make the parameters predictable. Bellot and Condoret¹²⁾ have defined in the Langmuir model an interaction i , which is a characteristic of each species and depends on the other components. Zheng et al.¹⁰⁾ successfully modified Langmuir isotherm method for distribution coefficients for the ion exchange of cesium by using basic solutions where the competitive effect of other cations is negligible. Zheng et al.¹³⁾ reported that the existence of two types of ion exchange sites has been demonstrated; one exhibits exothermic ion exchange, and the other exhibits endothermic ion exchange by using TAM-5. A macroporous resin containing iminodiacetic groups (Lewatit) was investigated for its sorption properties towards proton and nickel(II) by Raffaella Biesuz et al.¹⁴⁾ The stoichiometry, the exchange coefficients and the intrinsic constants of the sorption equilibria were obtained from the experimental data by using the Gibbs–Donnan model for the ion exchange resin. Arevalo et al.¹⁵⁾ carried out experiments of binary and ternary ion exchange equilibrium of heavy metals and sodium using iminodiacetic resin Lewatit TP 207. First binary equilibrium data were obtained at different temperatures and ionic strength and fixed to models considering two different ion exchange–stoichiometries by using Gibbs–Donnan model. For ternary equilibrium data, distinct simple models were applied. A systematic study with the charged cation–exchange resin Amberlite 200 was performed to investigate the influence of anion type on cation exchange by David A et al.¹⁶⁾ The Gaines–Thoma provided the best predictions of binary and ternary cation exchange on the sulfonate resin for

the different anionic media and ionic strength. A thermodynamic model was developed to describe phase equilibria for aqueous amino acid/polyelectrolyte gel systems. In gel phase, activities of all exchangeable species (charged and neutral) are calculated with the generalized Flory–Huggins model by Bellot and Condoret et al.¹⁷⁾

However, these synthetic resins are chemically rather simple compounds that mostly employ only one active group, making mathematical models describing their performance not applicable in the case of more complex materials used as biosorbents. Therefore, most of these ion exchange models were limited to the consideration for mono functional group only while most of the biosorbents have various functional groups in them. Jeon et al.¹⁸⁾ described and applied a new biosorption model for binary adsorption sites using alginic acid [Table 1] shows various ion–exchange model equation using alginic acid^{19,20,21)}.

3. Conclusions

Equilibrium sorption data provide a crucial input in predicting the performance of an actual sorption process.

A new generation of equilibrium isotherm models for ion exchange based biosorption is being developed including also the effect of the process pH.

Most of ion exchange models were limited to the consideration for mono functional group only while most of the biosorbents have various functional groups in them.

Sophisticated multispecies and structured mathematical models for computer simulation of biosorption processes are still lacking.

[Table 1] Various ion-exchange model using alginic acid

	Model equation	Advantage	Dis- advantage
Jeon et al. ¹⁸	$qT = \frac{(4Q_{COOH}K_{e,COOH}C_M + C_H^2) - C_H\sqrt{C_H^2 + 8Q_{COOH}K_{e,COOH}C_M}}{8K_{e,COOH}C_M} + \frac{(4Q_{OH}K_{e,OH}C_M + C_H^2) - C_H\sqrt{C_H^2 + 8Q_{OH}K_{e,OH}C_M}}{8K_{e,OH}C_M}$	Considering two functional groups of alginic acid	Eq' n is Somewhat complex
Seki and Suzuki et al. ²²	$q = \frac{N_{MA}(P_A - \sqrt{P_A^2 - 4})}{4}$ $(P_A = 2 + [K_{MA}[M^{2+}][\frac{K_A}{K_A + [H^+]}]^2]^{-1})$	Explain the adsorption mechanism of lead on the adsorbent.	Consedering carboxyl groups only
Kornsh et al. ²³	$q = -(\frac{1}{n})(\frac{1}{K_M})^{1/n}D_M^{1/n}[H^+] + (\frac{1}{n})Q$	Prediction of maximum adsorption capacity From the eq' n	Considering carboxyl groups only
Jang et al. ²⁴	$Q_{Cu} = (\frac{K_{Cu}[Cu^{2+}]}{K_H^2[H^+]^2})Q_H^2$	Considering multi metal ion and hydrogen ion	Considering carboxyl groups only

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