**THE ROLE OF MODELING IN SCALING UP**

**THE FIXED-BED ADSORPTION COLUMN SYSTEMS**

 **Introduction**

Adsorption is a widely used method to treat industrial waste gas and effluent due to its low cost, high efficiency and easy operation. Particularly, the adsorption process is suitable for decontaminating those compounds of low concentration or high toxicity, which are not readily treated by biological processes. Based on the operation mode, adsorption can be generally classified into static adsorption and dynamic adsorption.

Static adsorption, also called batch adsorption, occurs in a closed system containing a desired amount of adsorbent contacting with a certain volume of adsorbate solution, while dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent. For column adsorption, how to determine the breakthrough curve is a very important issue because it provides the basic but predominant information for the design of a column adsorption system.

Without the information of the breakthrough curve one cannot determine a rational scale of a column adsorption for practical application. There are two widely used approaches to obtain the breakthrough curve of a given adsorption system: direct experimentation or mathematical modeling.

The experimental method could provide a direct and concise breakthrough curve of a given system. However, it is usually a time-consuming and economical undesirable process, particularly for the trace contaminants and long residence time. Also, it greatly depends upon the experimental conditions, such as ambient temperature and residence time.

Comparatively, mathematical modeling is simple and readily realized with no experimental apparatus required, and thus, it has attracted increasing interest in the past decades. Currently, a variety of mathematical models have been used to describe and predict the breakthrough curves of a column adsorption system in liquid or gaseous phase but there is still lack of a comprehensive review of these models[ 28,29,30].

The main objective of the present review is to introduce the modeling of dynamic adsorption in liquid phase. Different from the gas-solid adsorption, liquid-solid adsorption is more theoretically difficult to give an unambiguous description because the solvent accompanies more intricate interaction between the species involved. Moreover, the salvation effect results in a more complicated behavior of the process. To model a liquid-solid column adsorption, it is necessary to divide it into four basic steps (Fig.1):

(1) liquid phase mass transfer including convective mass transfer and molecular diffusion

 (2) interface diffusion between liquid phase and the exterior surface of the adsorbent (i.e., film diffusion)

(3) intrapellet mass transfer involving pore diffusion and surface diffusion; and, (4) the adsorption- desorption reactio[31,32].

(1) Liquid phase mass transfer. Molecules or ions in the column can move in both axial and radial directions. For simplification, it is common to postulate that all cross-sections are homogeneous and the radial movement could be neglected. Thus, a macroscopic mass conservation equation is acquired to represent the relationship between the corresponding variations (i.e., concentration of the adsorbed adsorbate

q; concentration of the bulk solution C; distance to the inlet z; superficial velocity u; and axial dispersion coefficient Dz (if the axial dispersion is not ignored).

Regarding a control volume as shown in Fig.3. 2, one has to use the equation[33] :

 (eq.1)

where initial and boundary conditions are :



 When the axial dispersion is ignored,[33]

  (eq.2)

The initial and boundary conditions turn to:



where:

ε = the bed porosity

t = the time,

ρa = the adsorbent density

CF = the initial concentration of the influent and

 H = the bed height. [33].



Figure 1: Macroscopic adsorption process of an adsorbent pellet [33]



Figure 2: Schematic diagram of the mass conservation of a control volume [33]

Eqs. (1) and (2) are based on the following assumptions:

(1) the process is isothermal

(2) no chemical reaction occurs in the column

 (3) the packing material is made of porous particles that are spherical and uniform in size

(4) the bed is homogenous and the concentration gradient in the radial direction of the bed is negligible

(5) the flow rate is constant and invariant with the column position and,

 (6) the activity coefficient of each species is unity [34].

(2) Film diffusion. The driving force of film diffusion is the concentration gradient located at the interface region between the exterior surface of adsorbent pellets and the bulk solution. As the first step of adsorption, film diffusion predominates the overall uptake rate to some extent and even becomes the rate control step in some cases. The flux film diffusion can be expressed in linear form by multiplying its driving force and the phenomenological coefficient [33]

 (eq. 3)

Where:

Jf = the mass transfer flux

α= the volumetric surface area,

Cs = the adsorbate concentration at the exterior surface of adsorbent, and

kf = the film diffusion coefficient.

It is generally known that increasing the flow rate will decrease the film thickness and resistance, whereas larger film resistance can be caused by packing with smaller adsorbent pellets due to the extension of the exterior surface area.

(3) Intrapellet diffusion and reaction. As shown in Fig.3. 3, surface diffusion and pore diffusion proceed in parallel accompanying with Knudsen diffusion and the adsorption reactions. Of note, when the pore size is only slightly larger than the diameter of adsorbate ions or molecules, the Knudsen diffusion begins to play a significant role as shown in Fig.3b.

Generally speaking, the film diffusion driven solely by the concentration gradient can be expressed in a routine form (Eq. 3), and the intrapellet diffusion, which is more complex and diverse, is the keystone of modeling dynamic adsorption. Pore diffusion, surface diffusion and reaction are involved in intrapellet transfer simultaneously, and a set of equations could be set to consider all the possible mechanisms [33].

Moreover, consideration of the heterogeneity and Knudsen diffusion will tend to cause dramatic complexity and make the process very tedious. Hence, it is urgent to simplify such a process by making appropriate assumptions based on specific characteristics of the system, and several models were proposed based on different simplifications indeed [33]

Most mathematical models to predict a breakthrough curve have (or are acquired by) the same composition, i.e., (a) macroscopic mass conservation equation

(b) adsorption kinetic equation (sometimes including a set of equations) and

(c) equilibrium relationship.



Figure 3: Macroscopic schematic illustration of basic diffusion and adsorption steps inside the pore (a) Surface diffusion; (b) Pore diffusion; (c) Pore diffusion with significant Knudsen diffusion; (d) Combination of intrapellet diffusion and adsorption. 1: pore diffusion; 2: surface

diffusion; 3: adsorption; 4: desorption [33]

 **Single-component isotherms**

As we have illustrated, the general way to predict the breakthrough curve is to solve a set of partial differential equations which consist of a macroscopic mass conservation equation, uptake rate equation (sometimes including a set of equations), and isotherm equation. Obviously, as a prerequisite of modeling of the dynamic adsorption, the choice of the isotherm style will directly affect the effect of mathematic modeling.
Although several methods have been adopted to determine the isotherm, the most widely used one is the conventional static method proceeding in a closed system. Actually, due to the complexity of the structure of adsorbent and the interaction between each corpuscle, isotherms can present diverse shapes. Malek and Farooq (1996) suggested that there are three fundamental means to formulate an isotherm: dynamic equilibrium between adsorption and desorption, thermodynamic equilibrium between phases and species, and adsorption potential theory [35]. Although researchers have developed various isotherm models in the past decades, it is clear that none of them fit well with all cases, and thus, one has to determine the best suitable isotherm experimentally. Medved, I,and Cerny, R., (2011), reviewed the means to derive the isotherm by both batch method and adsorption-desorption method [36]. Here we do not intend to give a detailed discussion of various isotherms but only concisely introduce several widespread models.

**3.2.1. Langmuir isotherm**

The Langmuir isotherm assumes:

(1) the adsorption process takes place as monolayer adsorption (chemical adsorption); (2) the surface of adsorbent pellets or each adsorption site is homogeneous; and,

(3) the adsorption heat does not vary with the coverage.

In other words, in terms of the Langmuir isotherm, adsorption takes place when a free adsorbate molecule collides with an unoccupied adsorption site and each adsorbed molecule has the same percentage to desorption [37]. The model can be

written as:

 (eq.4)

Where:

 qe = the value of q at equilibrium,

qm = the maximum adsorptive capacity,

Ce= the concentration of adsorbate in liquid phase at equilibrium, and

b = the Langmuir constant.



Figure 3.4 Adsorption isotherms [38].

Certainly, we can obtain a linear form of the Langmuir model :

 ( eq.5)

Where:

 (eq. 6)

Where:

 ka = the adsorption rate coefficient of the Langmuir kinetic model, and

 kd = the desorption rate coefficient [39].

Despite the reversible adsorption nature of the Langmuir model, it sometimes fits irreversible adsorption well. Because of its simple form and well-fitting performance, the Langmuir isotherm has become one of the most popular models in adsorption studies.

 **Freundlich isotherm**

Another most widely used model is the Freundlich isotherm. Comparing with the Langmuir isotherm, the Freundlich isotherm does not have much limitation, i.e., it can deal with both homogeneous and heterogeneous surfaces, and both physical and chemical adsorption. Especially, this model frequently succeeds in depicting the adsorption behavior of organic compounds and reactive matters. The Freundlich isotherm is expressed as

 (eq. 7)

and its linear form is

 (eq. 8)

where K and n are the parameters to be determined.

Though the Freundlich isotherm is one of the earliest empirical correlation, it could be deduced from the assumption that Qa=Qa,0–af lnθ, where Qa is the differential heat of adsorption, θ is the coverage, Qa,0 is the value of Qa at θ=0, and af is a constant. According to (Haghseresht and Lu, 1998), the surface heterogeneity and type of adsorption can be roughly estimated by the Freundlich parameters [40].

 **Modeling of fixed-bed adsorption**

As one of the most prevalent techniques for separation and purification, fixed-bed adsorption has been widely applied for its high efficiency and easy operation. How to optimize the design and operation conditions of the fixed-bed adsorption is obviously an important issue to be focused on [40]. Given the fact that experimental determination of the adsorption performance under diverse conditions is usually expensive and time-consuming, development of mathematical models to predict fixed-bed adsorption is necessary.

An ideal model should be mathematically convenient, be able to give an exact estimation of the breakthrough behavior, and evaluate the effect of each variable on adsorption. A dynamic adsorption model usually consists of a macroscopic mass conservation equation, uptake rate equation(s) and isotherm. Considering the different components of the adsorption systems (solvents, adsorbate, adsorbent), variable operation conditions and specific demands of accuracy and calculative simplicity, it is an important but challenging task to propose a general use model, because most models derived from different assumptions are only suitable for a limited situation but fail to describe others.

 **General rate models**

Based on the assumption that the rate of intrapellet diffusion is described by Fick’s Law, some different expressions of general rate models were developed, such as the pore diffusion model (PDM), homogeneous surface diffusion model (HSDM), and pore and surface diffusion model (PSDM).PDM can be described as (Du et al., 2008)[41]. :

 (eq. 9)

with the initial and boundary conditions as :

 (eq. 10)

Where:

ρ = the bed density

 rp = the radius of adsorbentpellets

Dep = the effective pore diffusion coefficient and

 r = the distance to the centre of the pellet

The basic mathematic form of HSDM is [42] :

 (eq. 11)

with its initial and boundary conditions as :

 (eq. 12)

where Ds is the surface diffusion coefficient.

In addition, PSDM can be represented as (Liu et al., 2010)[43] :

 (eq. 13)

with its specific initial and boundary conditions of :



Due to the fact that  is usually much higher than , the latter term was neglected in most cases.

With distinct rate control step(s) of different systems, the appropriate type of the general rate models should be applied, including the film-pore diffusion model, film-surface diffusion model and film-pore/surface diffusion model.

Reasonably, the film diffusion can be neglected when the film mass transfer resistance is quite small (i.e., negligible concentration gradient in the film). However, additional experiments should be performed to ensure that film diffusion is not a rate control step. Note that among Eqs. (9) – (11), the term of the surface reaction rate is not involved in most cases because it is much faster than other diffusion steps. Sometimes the surface reaction should be considered when it significantly affects the total adsorption rate or even becomes the sole rate control step. Plazinski et al. (2009) made a comprehensive review of sorption kinetics including surface reaction mechanism [44]. When a proper liquid phase continuity equation (eq. (1) or (2)), film diffusion equation (eq. (3)), intrapellet diffusion equation, and isotherm equation are available, it is possible to generate the breakthrough curve by solving these partial differential equations. Note that several parameters in the general rate models can be determined both theoretically and experimentally.

Especially, to our knowledge, there is no reliable method to theoretically predict the tortuosity τ and surface diffusion coefficient Ds, which are indispensable when using the general rate models. Thus, for trustworthy prediction, it is inevitable to use the experimental method to determinate these parameters. To directly solve the general rate models is usually a time-consuming and computationally troubled work.

A review of surface diffusion is available elsewhere (Medved and Cerny, 2011), which might provide some ideas to modify the intrapellet diffusion models[36]. The prevalence of the conventional/modified general rate models is not only because they give good prediction of dynamic adsorption, but also involves a variety of parameters to determine the process variables. The variables could be optimized by keeping other parameters constant and comparing the breakthrough curves predicted by this model under different values of the target parameter “*X*”, for example, 0.5*X*, *X* and 2*X* (Note that adjusting a parameter may lead to variation in the phenomenological coefficient(s), and optimization based on modeling is not a precise method). However, the main limitation of these models is the complicated and time-consuming computation.

**Linear driving force (LDF) model**

The linear driving force (LDF) model proposed by (Glueckauf, 1955) formulates a lumped mass transfer coefficient to represent the intrapellet diffusion rate, as written in a linear form as[45] :

 (eq. 14)

Where:

 qa = the average concentration of the adsorbed adsorbate

qs = the loading of the adsorbate at the external surface of adsorbent, and

 ke = the lump intrapellet diffusion kinetic coefficient

The original LDF model regards that qs in equilibrium corresponds to the concentration of the bulk solution C. In other words, it neglected the concentration gradient in the interface region between the liquid phase and adsorbent, and ke is a function of intrapellet diffusivity.

When the mass transfer within the interface is involved, the film diffusion equation should be added into the LDF model, namely

 (eq. 15)

Combining Eqs (3.14) and (3.15) with the liquid phase mass conservation equation and proper isotherm, it is possible to predict the breakthrough curve. Hence, the LDF model can be used to estimate the coefficients ke and kf.

Similar to the general rate models, these parameters can be acquired by the theoretical and experimental ways. For the theoretical way, a widely accepted expression is written as [45]:

 (eq. 16)

When intrapellet diffusion is dominated by pore diffusion:

 (eq. 17)

While by surface diffusion:

 (eq. 18)

An empirical equation of the rate constant was developed previously [46]:

 (eq. 19)

where:

De = the effective intrapellet diffusion coefficient involving both surface diffusion and pore diffusion and f′(C) is related to the isotherm. Except for Ds and De, all the parameters are available by directly measuring or referring to the corresponding isotherms.

Note that  is not constant if the isotherm is nonlinear (i.e., does not obey Henry’s Law). Hence, to obtain the value of De, an average value has to be applied to represent f′(C). As for Ds, it can be reckoned by combining eqs. (18) and (19):

 (eq. 20)

and then calculate De by :

 (eq. 21)

The calculated kinetic parameters sometimes fit well with the experimental data, but conspicuous deviation may appear in other cases. For instance, the theoretical value is often much higher than the experimental result when the dissolved organic matter (DOM) is adsorbed. In that case, the theoretical method could just approximately reckon the adsorption performance, and the parameters have to be determined by the experimental breakthrough curves. Another expression of the LDF model is available by incorporating eqs. (3.14) and (3.15):

 (eq. 22)

Where:

 ko = the overall kinetic constant combining both the film diffusivity and the intrapellet diffusivity. Additionally, surface reaction was also involved in LDF in some cases [47]. Computational software is often required to derive the numerical solution of the LDF model, especially when the isotherm is in the nonlinear form. Nevertheless, as compared to the general rate models, the LDF model could reduce the computational time significantly and its accuracy was generally acceptable. Hence, the LDF model has become one of the most widely used models now. For some recent developments of the LDF model one could refer to the work by Gholami and Talaie (2010) [48].

**Clark model**

As is well known, granular active carbon (GAC) is one of the most popular adsorbents with micropore structure. US EPA even initiated a series of field studies to evaluate the performance of GAC and acquired sufficient data. Based on the data from US EPA, Clark (1987) developed a model to predict the performance of GAC-organic compounds adsorption system. The Clark model was deduced based on the following equations and assumption [49].

1. Liquid phase continuity equation is :

 (eq. 23)

1. The shape of the mass-transfer zone is constant and all the adsorbates are removed at the end of the column

 (eq. 24)

1. The isotherm fits the Freundlich type:

  (eq. 25)

1. Expression of the adsorption rate is :

 (eq. 26)

Where:

J = the mass-transfer rate per unit reactor volume

A = the column cross-section area

QA = the volumetric flow rate per unit of cross-section area,

 ua = the mass velocity of the adsorbent to maintain the mass-transfer zone stationary, ΔC = the incremental change of concentration, and

 Δz = the differential reactor height.

The final expression of Clark model is :

 (eq. 27)

 (eq. 28)

 (eq. 29)

Where:

 Cb = the breakthrough concentration

 tb = the service time, and

Cin =the constant influent value on the carbon bed.

The following procedures should be completed prior to using the model [49].

(1) Determine n by the batch experiment

(2) Rearrange Eq. (28) into :

 (eq.30)

(3) The slope and intercept of the plot of ln[(CF/C)1/n−1] vs. t allow one to solve r’ and B, respectively.

(4) Generate the whole breakthrough curve.

It is clear that the mass conservation equation in the column is different from those discussed above. We find that eq. (26) actually disregards the accumulation of adsorbate concentration. In other words, it does not reflect the time difference between C and C+ΔC. If taking a controlled volume V (the volume passing through any cross-section per unit time) into consideration and postulating the uniformity of the control volume and negligible molecular diffusion, we obtain [49]:

 (eq. 31)

When Δt→0, then:

 (eq. 32)

Additionally:

 (eq. 33)

Cancelling Vdt of eq. (3.32) and combining eq. (3.33) we have:

 (eq. 34)

The same conclusion can also be made when assuming:



However, the Clark model has successfully predicted a variety of systems and even those not following this assumption. As mentioned above, the dynamic adsorption is such a complicated process that it is almost impossible to give a complete description of each variable. Actually, even the “most theoretically rigorous” general rate models are still simplified from the real situations, such as the distribution of adsorbent pellets with different size in the column, the wall effect, the mass transfer caused by momentum transfer and heat transfer. Moreover, by mathematical fitting, each phenomenological coefficient could be adjusted to the optimal values, which would compensate for the inherent shortages of the model to some extent. Thus, it is still rational to suppose the Clark model has good performance under different conditions [49].

 **Thomas model**

The Thomas model is another one frequently applied to estimate the adsorptive capacity of adsorbent and predict breakthrough curves, assuming the second-order reversible reaction kinetics and the Langmuir isotherm [50]. Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small. [51].

The Thomas model is given by [24]:

 (35)

Where:

 kTh = the Thomas rate constant,

 m = the mass of adsorbent in the column.

With several couples of m and Q, kTh and qF values derived through a plot of

ln[(CF/C)−1] vs. t, further prediction and design is then available.

Eq. (3.35) can also be expressed as:

 (eq. 36)

Where:

k′=kThCF and t1= qF m/(QCF). The general version of eq. (36) is represented as :

 (eq. 37)

This equation is applied when ln[(CF/C)−1] vs. t is not in linear form.

By fitting the experimental data, the corresponding parameters bi can be calculated.

Generally, it is adequately accurate to employ the former three terms. It is worth noting that qF derived from the experiment is often conspicuously different from the value acquired by equilibrium calculation, and the bed adsorptive capacity is often determined from the dynamic adsorption [52].

 **Bohart-Adams model and bed depth service time (BDST) model**

Bohart and Adams (1920) came up with the Bohart-Adams (B-A) model when they proceeded with their work of analyzing the typical chlorine charcoal transmission curve [53]. They hypothesized that the uptake rate of chlorine is proportional to the concentration of the chlorine existing in the bulk fluid and the residual adsorptive capacity of charcoal, from which the following two equations are obtained:

 (eq. 38)

 (eq. 39)

where:

qr = the residual adsorptive capacity, and

 kB =the kinetic constant of the Bohart-Adams model.

Additionally:



Finally, the basic form of the B-A model was obtained:

 (eq. 40)

If exp (kBqmH/u) is much larger than 1, eq. (3.40) can be reduced and rearranged as:

 (eq. 41)

Eq. (3.41) is the so-called bed depth service time model [54]. Note that the B-A model (or bed depth service time (BDST) model) involves several important variables of adsorption system such as CF, u, qm, and H, and approximate estimation of the effect of each parameter from both models is achievable. As two widely used models in practice, the B-A and BDST models succeeded in predicting several breakthrough curves and optimizing the parameters, although it is relatively rough. Both the B-A and BDST models have seven parameters, among which CF and u can be determined before the dynamic adsorption experiment. For the B-A model, the height of the fixed bed (i.e., the height of packing adsorbent), H, is a constant and can be directly measured. Subsequently, different C and corresponding t are obtained through the dynamic adsorption experiment, and then a plot of ln(CF/C−1) vs. t should theoretically be a straight line. After linear regression, qm and kB can be calculated from the tangent slope and intercept, respectively. In terms of calculated qm and kB, prediction of adsorption performance at different process variables is available based on eq. (3.40). As for the application of the BDST model, similar to the B-A model, after determining the demand concentration of the effluent solution, qm and kB can be worked out by a straight line of t vs. H. Then, the adsorption efficiency, under various conditions can be predicted.

Actually, qm and kB are not constant when the variable(s) is changed, which may lead to unsatisfactory prediction. Especially, at 50% breakthrough, C/CF=0.5 and t=t1/2, and eq. (3.41) changes to:

 (eq. 42)

Hence, qm can be calculated by plotting t1/2 vs. H. By rearranging Eq. (41) into proper form or giving specific values to parameters, the BDST model is frequently employed as a powerful tool to find the optimal operation condition. More recently, Ko et al. (2000) came up with a method to optimize the BDST model, where the bed adsorptive capacity qm is substituted by a modified correlation [52]:

 (eq. 43)

Integrating into eq. (3.38) :

 (eq. 44)

ar is the rate parameter, m′=qm/(CFu), and b′=−[1/(kBCF)]ln[(CF/C)−1].

This method provides a way to approximately evaluate the significance of both film diffusion and intrapellet diffusion. The intrapellet mass transfer rate is proportional to the square-root of the residence time when the sorption process is controlled by intrapellet diffusion [55]:

 (eq. 45)

According to the correlation proposed [56]:

 (eq. 46)

Namely:

 (eq. 47)

Combining Eq. (3.45) and Eq. (3.47), one can obtain:

 (eq. 48)

Where:

pi, pf reflect the fractions of the overall uptake rate influenced by intrapellet diffusion and film diffusion, respectively. Thus,



Where p′ is determined by fitting the experimental data so that pi and pf are acquired subsequently.

 **Yoon-Nelson model**

The Yoon-Nelson model is extremely concise in form, supposing that the decrease in the probability of each adsorbate to be adsorbed is proportional to the probability of its adsorption and breakthrough on the adsorbent [57].

 It can be represented by :

 (eq. 49)

where KYN is the Yoon-Nelson rate constant.

By plotting ln[C/(CF−C)] vs. t, KYN and theoretical t1/2 are reckoned. The Yoon-Nelson model not only has a more simple form than other models, but also requires no detailed data concerning the characters of adsorbate and adsorbent, as well as the parameters of the fixed bed [58]. Also, as limited by its rough form, the Yoon-Nelson model is less valuable or convenient to obtain process variables and to predict adsorption under variety conditions.

**Wang model**

Wang et al. (2003) developed a mass transfer model to describe the breakthrough curve of solutions containing Co or Zn ions in the fixed bed on the basis of the following assumptions [59]:

(1) The adsorption process remains isothermal

(2) The mass transfer equation is written as

  (eq. 50)

Where:

 kw = the kinetic constant

 y = the fraction of the adsorbed metal ions, and

 x = the fraction of metal ions passing through the fixed bed, with x+y=1.

(3) The breakthrough curve is symmetrical and,

(4) There is negligible axial dispersion in the column.

Presuming y=yw at t=tw and integrating eq. (3.50), one can obtain:

 (eq. 51)

Let w=0.5, then yw=y1/2=x1/2, tw=t1/2. Combining the above parameters with eq. (51) :

 (eq. 52)

where x can be expressed as :

 (eq. 53)

Substituting eq. (53) into eq. (52), t should be in direct proportion to ln[(CF/C)−1]. A plot of ln[(CF/C) −1] vs. t produces the slope and intercept value as 1/kw and t1/2, respectively.

Then the entire breakthrough curve can be obtained based on Eq. (52). Meanwhile, similar to the Yoon-Nelson model, it cannot provide sufficient information of an adsorption system.

**Wolborska model**

 Wolborska and Pustelnik (1996) analyzed the adsorption of p-nitrophenol on activated carbon and found that the initial segment of the breakthrough curve is controlled by film diffusion with constant kinetic coefficient, and the concentration profile of the initial stage moves axially in the column at a constant velocity[60].

Moreover, the width of concentration profile in the column and the final breakthrough curve were nearly constant. Based on above observations, they developed a model to describe the breakthrough at low concentration region, which was written as:

 (eq. 54)

Where βL is the film diffusivity, which can be determined from the initial linear section of the breakthrough curve in the semi-logarithmic system through experiment or correlations.

**3.4.9. Modified dose-response model**

This model was initially developed for pharmacology studies and recently used to describe adsorption of metals in some cases, e.g. as in [61]. The modified dose-response model can be written as:

 (eq. 55)

After rearrangement, it could be written as:

 (eq. 56)

where α′ is the model parameter. Similar to other models, α′ and qF could be determined by plotting ln[C/(CF−C)] vs. ln(CF*Q*t).

**CONCLUSIONS**

Fixed-bed or column adsorption is the most popular option in practical application of adsorption process, and due to the complexity of a column adsorption system and lack of solid theory, its mathematical modeling is obviously more difficult than batch adsorption. To choose or develop a suitable model, accuracy and convenience should be considered simultaneously. Currently, although some effort had been made to complete these models (especially the general rate models and LDF model), each model has its inherent shortages and requires further development.

The general rate models (and “general rate type” models) and LDF model generally fit well with the experimental data for most cases, but they are relatively time-consuming. Other models including the Bohart-Adams model, Yoon-Nelson model, Thomas model, Wang model, Wolborska model, and modified dose-response model could be applicable without isotherm information, but they are derived from specific situations and limited in space.

The Clark model is suitable to describe column adsorption obeying the Freundlich isotherm and do not show conspicuously better accuracy than the above models.

The constant pattern model is relatively convenient to apply and gives satisfactory prediction, but it cannot be readily employed for adsorption predominated by intrapellet diffusion.

In addition, experimental work is always required to determine the isotherm and dynamic model as well as the related parameters. Moreover, when the breakthrough curve deviates from the ideal S shape, prediction derived from any model usually cannot meet our demand.

**References**

1. Seader, J.D. and Henley, Ernest J. (2006). Separation Process Principles (2nd Edition ed.). John Wiley & Sonstahm. ISBN 0-471-46480-5.
2. Fogler, H. Scott (2006). Elements of Chemical Reaction Engineering (4th Edition ed.). Prentice Hall. ISBN 0-13-047394-4.
3. Perry, Robert H. and Green, Don W. (1984). Perry's Chemical Engineers' Handbook (6th Edition ed.). McGraw-Hill. ISBN 0-07-049479-7.
4. Ergun, Sabri. "Fluid flow through packed columns." Chem. Eng. Prog. 48 (1952).
5. J. Kozeny, "Ueber kapillare Leitung des Wassers im Boden." Sitzungsber Akad. Wiss., Wien, 136(2a): 271-306, 1927.
6. P.C. Carman, "Fluid flow through granular beds." Transactions, Institution of Chemical Engineers, London, 15: 150-166, 1937.
7. Barros, M.A.S.D., Zola, A.S, Tavares, C.R.G., Sousa-Aguiar, E.F. Chromium uptake from tricomponent solution in zeolite fixed bed, Adsorption, 12, 229-248, 2006.
8. Barros, M.A.S.D., Silva, E.A., Arroyo, P.A., Tavares, C.R.G., Schneider, R.M., Suszek, M., Sousa-Aguiar, E.F., Removal of Cr(III) in the fixed bed column and batch reactors using as adsorbent zeolite NaX, Chemical Engineering Science, 59, 5959 – 5966, 2004.
9. McCabe, W. L., Smith, J.C., and Harriot, P.”Unit Operations of Chemical Engineering”,McGraw-Hill International Ed., 6th ed., New York, USA, 2001.
10. Helferich, F.,Ion Exchange, Dover Publications Inc., New York, 1995.
11. Sánchez, A., Ballester, A., Blásquez, M.L., González, F., Muñoz, J., Hammaini, A.: Biosorption of copper and zinc by cymodocea nodosa. FEMS Microbiol. Rev. 23 527-536 (1999).
12. Myers, A. L.; Prausnitz, J. M.; Thermodynamics of mixed-gas adsorption; AIche Journal, 11, 1, 121-127, 1965.
13. Geankoplis, C.J., Transport Processes andUnit Operations, 3rd ed., PTR Prentice Hall, USA, 1993.
14. Walker, G.M., Weatherly, L.R. Adsorption of acid dyes on to granular activated carbon in fixed beds, Water Research, 31, 8, 2093–2101, 1997.
15. Gazola, F. C., Pereira, M.R., Barros, M.A.S.D, Silva, E.A, Arroyo, P.A. Removal ofCr3+ in fixed bed using zeolite NaY, Chemical Engineering Journal, 117, 253–261,2006.
16. Fogler, H.S., Elements of Chemical Reaction Engineering, 3rd ed., Prentice Hall, New Delhi- India, 2004.
17. Hill, C.G.,”An Introduction to Chemical Engineering Kinetics and Reactor Design,’ John Wiley & Sons, USA, 1977.
18. Barros, M,A,S,D, Zola, A,S., Arroyo, P.A., Sousa-Aguiar, E.F., Tavares, C.R.G. Binary Ion Exchange of Metal Ions in Y and X Zeolites, Brazilian Journal of Chemical Engineering, 20, 4, 413-421, 2003.
19. Valdman, E., Erijman, L., Pessoa, F.L.P. and Leite, S.G.F. Continuous Biosorption of Cu and Zn by Immobilized Waste Biomass Sargassum sp., Process Biochemistry, 36, 869-873, 2001.
20. Mohan, D. and Chander, S., Single Component and Multi-component Adsorption of Metal Ions by Activated Carbons, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 177, 2-3, 183-196, 2001.
21. KLamer, K, Van Krevelen, D. W., Studies on ion Exchange-I, Chem. Eng. Sci, 7, 4, 197-203, 1958.
22. Barros, M.A.S.D., Zola, A.S., Arroyo, P.A., Sousa-Aguiar, E.F., Tavares, C.R.G.Equilibrium and dynamic ion exchange studies of Cr3+ on zeolites NaA and NaX, Acta Scientiarum, 24, 6, 1619-1625, 2009.
23. Bohart, G. S., Adams, E. Q., Some aspects of the behavior of charcoal with respect to chlorine,Journal of the American Chemical Society, 42, 523-544, 1920.
24. Thomas, H.C., Heterogeneous ion exchange in a flowing system, Journal of the American Chemical Society, 66, 1664–1666, 1944.
25. Hsuen, H. K., An improved linear driving force approximation for intraparticle adsorption, Chemical Engineering Science, 55,3475-3480, 2000.
26. Delgado, J.M.P.Q., A critical review of dispersion in packed bed, Heat Mass Transfer, 42, 279-310, 2006.
27. Ostroski, I.C., Mechanism of removal of Iron(III) and Zinc(II) ontoZeolite Na-Y, In Portuguese, Master Thesis, UEM - State University of Maringá, Brazil,Chemical Engineering Department , 2007.
28. Abu-Lail, L., Bergendahl, J.A., Thompson, R.W., 2012.Mathematical modeling of chloroform adsorption ontofixed-bed columns of highly siliceous granular zeolites.*Environmental Progress & Sustainable Energy*, **31**(4):591-596. [doi:10.1002/ep.10593]
29. Zhao, Y., Shen, Y.M., Bai, L., Ni, S.Q., 2012. Carbon dioxideadsorption on polyacrylamide-impregnated silica gel andbreakthrough modeling. *Applied Surface Science*, **261**:708-716. [doi:10.1016/j.apsusc.2012.08.085]
30. Cheknane, B., Baudu, M., Bouras, O., Zermane, F., 2012. Modeling of basic green 4 dynamic sorption onto granularorgano-inorgano pillared clays (GOICs) in column reactor.*Chemical Engineering Journal*, **209**:7-12. [doi:10.1016/j.cej.2012.07.118]
31. Crittenden, J.C., Hutzler, N.J., Geyer, D.G., Oravitz, J.L.,Friedman, G., 1986. Model development and parametersensitivity. *Water Resources Research*, **22**(3):271-284.[doi:10.1029/WR022i003p00271]
32. Helfferich, F.G., 1995. Ion Exchange, Dover Pubns.
33. Fournel, L., Mocho, P., Brown, R., le Cloirec, P., 2010. Modeling breakthrough curves of volatile organic compounds on activated carbon fibers. *Adsorption*, **16**(3):147-153.
34. Warchoł, J., Petrus, R., 2006. Modeling of heavy metal removal dynamics in clinoptilolite packed beds. *Microporous and Mesoporous Materials*, **93**(1-3):29-39. [doi:10.1016/j.micromeso.2006.01.021]
35. Malek, A., Farooq, S., 1996. Comparison of isotherm models for hydrocarbon adsorption on activated carbon. *AIChE Journal*, **42**(11):3191-3201. [doi:10.1002/aic.690421120]
36. Medved, I., Cerny, R., 2011. Surface diffusion in porous media:A critical review. *Microporous and Mesoporous Materials*, **142**(2-3):405-422.
37. Langmuir, I., 1916. The constitution and fundmental properties of solids and liquids. part I. Solids. *Journal of the American Chemical Society*, **38**(11):2221-2295. [doi:10.1021/ja02268a002]
38. Giles, C., MacEwan, T., Nakhwa, S.N., 1960. Studies inadsorption. Part XI. A system of classification of solutionadsorption isotherms, and its use in diagnosis ofadsorption mechanisms and in measurement of specificsurface areas of solids. *Journal of the Chemical Society*,(0):3973-3993. [doi:10.1039/jr9600003973]
39. Azizian, S., 2004. Kinetic models of sorption: a theoretical analysis. *Journal of Colloid and Interface Science*, **276**(1):47-5[doi:10.1016/j.jcis.2004.03.048]
40. Haghseresht, F., Lu, G., 1998. Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents.*Energy & Fuels*, **12**(6):1100-1107. [doi:10.1021/ef9801165]
41. Du, X., Yuan, Q., Li, Y., 2008. Mathematical analysis ofsolanesol adsorption on macroporous resins using thegeneral rate model. *Chemical Engineering & Technology*,**31**(9):1310-1318. [doi:10.1002/ceat.200800010]
42. Tien, C., 1994. Adsorption Calculations and Modeling.Butterworth-Heinemann Boston.
43. Liu, B., Zeng, L., Ren, Q., 2010. Simulation of levulinic acidadsorption in packed beds using parallel pore/surfacediffusion model. *Chemical Engineering & Technology*,**33**(7):1146-1152. [doi:10.1002/ceat.201000147]
44. Plazinski, W., Rudzinski, W., Plazinska, A., 2009. Theoreticalmodels of sorption kinetics including a surface reactionmechanism: a review. *Advances in Colloid and Interface Science*, **152**(1-2):2-1[doi:10.1016/j.cis.2009.07.009]
45. Glueckauf, E., 1955. Theory of chromatography. Part 10.—Formulæ for diffusion into spheres and their applicationto chromatography. *Transactions of the Faraday Society*,**51**(0):1540-1551. [doi:10.1039/tf9555101540]
46. Worch, E., 2008. Fixed-bed adsorption in drinking watertreatment: a critical review on models and parameter estimation.*Journal of Water Supply Research and Technology—AQUA*, **57**(3):171-183. [doi:10.2166/aqua.2008.100]
47. Szukiewicz, M.K., 2002. An approximate model for diffusionand reaction in a porous pellet. *Chemical EngineeringScience*, **57**(8):1451-1457. [doi:10.1016/S0009-2509(02)00055-6]
48. Gholami, M., Talaie, M., 2010. Investigation of simplifyingassumptions in mathematical modeling of natural gasdehydration using adsorption process and introduction ofa new accurate LDF model. *Industrial & EngineeringChemistry Research*, **49**(2):838-846. [doi:10.1021/ie901183q]
49. Clark, R.M., 1987. Evaluating the cost and performance offield-scale granular activated carbon systems. *EnvironmentalScience & Technology*, **21**(6):573-580. [doi:10.1021/es00160a008]
50. Ghasemi, M., Keshtkar, A.R., Dabbagh, R., Jaber Safdari, S.,2011. Biosorption of uranium (VI) from aqueous solutions by Ca-pretreated Cystoseira indicaalga: breakthrough curves studies and modeling. *Journa of Hazardous Materials*, **189**(1-2):141-149 [doi:10.1016/j.jhazmat.2011.02.011]
51. Aksu, Z., Gönen, F., 2004. Biosorption of phenol byimmobilized activated sludge in a continuous packed bed:prediction of breakthrough curves. *Process Biochemistry*,**39**(5):599-613. [doi:10.1016/S0032-9592(03)00132-8]
52. Ko, D.C.K., Porter, J.F., McKay, G., 2000. Optimised correlations for the fixed-bed adsorption of metal ions on bone char. *Chemical Engineering Science*, **55**(23):5819-5829. [doi:10.1016/S0009-2509(00)00416-4]
53. Bohart, G. S., Adams, E. Q. (1920). Some aspects of thebehaviour of charcoal with respect to chlorine. J. Am. Chem.Soc., **42**, 523-529.
54. Hutchins, R., 1973. New method simplifies design of activated carbon systems. *Chemical Engineering*, **80**(19):133-138.
55. McKay, G., 1979. Basic dye adsorption on activated carbon.*Water, Air, & Soil Pollution*, **12**(3):307-317. [doi:10. 1007/BF01047018]
56. Wilson, E., Geankoplis, C., 1966. Liquid mass transfer at verylow Reynolds numbers in packed beds. *Industrial & Engineering Chemistry Fundamentals*, **5**(1):9-14. [doi:10. 1021/i160017a002]
57. Yoon, Y.H., James, H.N., 1984. Application of gas adsorptionkinetics I. A theoretical model for respirator cartridgeservice life. *The American Industrial Hygiene AssociationJournal*, **45**(8):509-516. [doi:10.1080/15298668491400197]
58. Hamdaoui, O., 2006. Dynamic sorption of methylene blue bycedar sawdust and crushed brick in fixed bed columns.*Journal of Hazardous Materials*, **138**(2):293-303.[doi:10.1016/j.jhazmat.2006.04.061]
59. Wang, Y.H., Lin, S.H., Juang, R.S., 2003. Removal of heavy metal ions from aqueous solutions using various low-costadsorbents. *Journal of Hazardous Materials*, **102**(2-3):291-302. [doi:10.1016/S0304-3894(03)00218-8]
60. Wolborska, A., Pustelnik, P., 1996. A simplified method fordetermination of the break-through time of an adsorbentlayer. *Water Research*, **30**(11):2643-2650. [doi:10.1016/S0043-1354(96)00166-2]
61. Araneda, C., Basualto, C., Sapag, J., Tapia, C., Cotoras, D.,Valenzuela, F., 2011. Uptake of copper (II) ions fromacidic aqueous solutions using a continuous column packed with microcapsules containing a β-hydroxyoximic compound. *Chemical Engineering Research & Design*,**89**(12):2761-2769. [doi:10.1016/j.cherd.2011.05.008]
62. Rao JR, Viraraghavan T. Biosorption of phenol from a aqueoussolution by *Aspergillus niger* biomass. Bioresour Technol 2002;85:165–71.
63. Aksu Z, Akpinar D. Modelling of simultaneous biosorption of phenoland nickel(II) onto dried aerobic activated sludge. Sep Pur Technol 2000;21:87–99.
64. Texier AC, Andres Y, Faur-Brasquet C, LeCloirec P. Fixed-bed studyfor lanthanide (La, Eu, YB) ions removal from aqueous solutionsby immobilized *Pseudomonas aeruginosa*: experimental data and modelization. Process Biochem 2002;47:333–42.
65. Aksu Z, Gönen F, Demircan Z. Biosorption of chromium(VI) ions by Mowital®B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon. Process Biochem 2002;38:175–86.
66. N. Akhtar, J. Iqbal, M. Iqbal, Removal and recovery of nickel (II) fromaqueous solution by loofa sponge-immobilized biomass of *Chlorelasorokiniana*: characterization studies, J. Hazard. Mater. B108 (2004) 85–94.
67. B. Volesky, Biosorption of Heavy Metals, CRC Press, Boston/Boca Raton, FL, 1990.
68. E.W. Wilde, J.R. Benemann, Bioremoval of heavy metals by use of microalgae, Biotechnol. Adv. 11 (1993) 781–812.
69. E. Sandau, P. Sandau, O. Pulz, Heavy metal sorption by microalgae, Acta Biotechnol. 16 (1996) 227–235.
70. K.H. Chong, B. Volesky, Description of two-metal biosorption equilibria by Langmuir type models, Biotechnol. Bioeng. 47 (1995) 451–460.
71. S. Schiewer, B. Volesky, Modelling multi-metal ion exchange in biosorption Environ. Sci. Technol. 30 (1996) 2921–2927.
72. M.T. Veit, C.R.G. Tavares, E.A. Silva, Influence of pH and pre-treatedbiomass *Sargassum filipendula* in organic leaching, in: Anais do II Congresso Brasileiro de Termodinˆamica Aplicada, 2004
73. E.A. Silva, E.S. Cossich, C.R.G. Tavares, L. Cardozo, R. Guirardello,Modeling of copper (II) biosorption by marine alga *Sargassum* sp. infixed bed column, Process Biochem. 38 (2002) 791–799.
74. D. Kratochvil, B. Volesky, Advanceds in biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300
75. E.A. Silva, C.R.G. Tavares, M.A.S.D. Barros, P.A. Arroyo, R.M. Schneider,M. Suszek, Modeling and experimental Cr+3 uptake using NaXzeolite, in: Sixth Italian Conference on Chemical and Process Engineering 2003, Pisa, Italy, Chem. Eng. Trans. 3 (2003) 303–308.
76. G. McKay, M.J. Bino, Fixed bed adsorption for the removal of pollutants from water, Environ. Pollut. 66 (1990) 33–53.
77. D.C.K. Ko, J.F. Poter, G. Mackay, Optimised correlations for the fixedbed adsorption of metal ions on bone char, Chem. Eng. Sci. 55 (2000) 5819–5829.
78. S.M. Robinson, W.D. Arnold, C.H. Byers, Mass-transfer mechanismsfor zeolite ion exchange in wastewater treatment, Environ. Energy Eng.40 (1994) 2045–2053.
79. G.S. Bohart, E.Q. Adams, Some aspects of the behavior of charcoal with respect to chlorine, J. Am. Chem. Soc. 42 (1920) 523–544.
80. H.C. Thomas, Heterogeneous ion exchange in a flowing system, J. Am. Chem. Soc. 66 (1944) 1664–1666.
81. M. Otero, M. Zabkova, A.E. Rodrigues, Comparative study of adsorption of phenol and salicylic acid from aqueous solution onto nonionic polymeric resins, Sep. Purif. Technol. 45 (2005) 86–95.
82. M.A.S.D. Barros, E.A. Silva, P.A. Arroyo, C.R.G. Tavares, R.M. Schneider, M. Suszek, E.F. Sousa-Aguiar, Removal of Cr(III) in the fixed bed column and batch reactors using as adsorbent zeolite NaX, Chem. Eng. Sci. 59 (2004) 5959–5966.
83. S. Brosillon, M.H. Manero, J.N. Foussard, Mass transfer in VOC adsorption on zeolite: experimental and theoretical breakthrough curves, Environ. Sci. Technol. 35 (2001) 3571–3575
84. E.M. Trujillo, T.H. Jeffers, C. Ferguson, H.Q. Stevenson, Mathematically modeling the removal of heavy metals from a wastewater using immobilized biomass, Environ. Sci. Technol. 25 (1991) 1559–1565.
85. F.X. Stuart, D.T. Camp, Comparison of kinetic and diffusional models for packed bed adsorption, I. C. Fundam. 6 (1967) 156–158.
86. J.S.C. Hsieh, R.M. Turian, C. Tien, Multicomponent liquid phase adsorption in fixed bed, AIChE J. 23 (1977) 263–275.
87. M.V. Ernest Jr., R.D. Whitley, Z. Ma, N.H.L. Wang, Effects of mass action equilibria on fixed bed multicomponent ion exchange dynamics, Ind. Eng. Chem. Res. 36 (1997) 212–226.
88. Mehta S K, Gaur J P, 2005. Use of algae for removing heavymetal ions from wastewater: progress and prospects[J]. Crit Rev Biotechnol, 25: 113–152.
89. Zemke-WhiteWL, Ohno M, 1999.World seaweed utilization: an end-of-century summary[J]. J Appl Phycol, 11: 369–376.
90. Xian X, Qiu H Y, Cai Z Z *et al*., 2006. The research on theadsorption e\_ect on metal ions by immobilized marine algae[J]. Acta Oceanologica Sinica, 25: 153–158.
91. Cossich E S, da Silva E A, Tavares C R G *et al*., 2004. Biosorption of chromium(III) by biomass of seaweed *Sargassum* sp. In a fixed-bed column[J]. Adsorption, 10: 129–138.
92. Chen K C, Lin Y F, 1994. Immobilization of microorganisms with phosphorylated polyvinyl alcohol (PVA) gel[J]. Enzyme Microb Technol, 16: 79–83.
93. Cooney D O, 1999. Adsorption design for wastewater treatment[ M]. Boca Raton: Lewis Publishers.
94. Ruthven D M, 1984. Principles of adsorption and adsorption processes[M]. New York: Wiley
95. G. Rich, K. Cherry, Cited in Hazardous Waste Treatment Technology, Pudvan Publishing Co., New York, 1987.
96. A.K. Bhattacharya, C. Venkobachar, J. Environ. Eng.—ASCE 110 (1984) 110–122.
97. C. Huang, C.P. Huang, Water Res. 30 (1996) 1985–1990.
98. J.M. Brady, J.M. Tobin, J.C. Roux, J. Chem. Technol. Biotechnol. 74 (1999) 71–77.
99. V.C. Taty Costodes, H. Fauduet, C. Porte, A. Delacroix, Proceedingsof the 12th European Conference and Technology Exhibition on Biomass for Energy Industry and Climate Protection, Amsterdam, The Netherlands, 17–21 June, 2002
100. V.C. Taty Costodes, H. Fauduet, C. Porte, A. Delacroix, J. Hazard.Mater. 105 (2003) 121–142.
101. A.V. Pethkar, K.M. Paknikar, J. Biotechnol. 55 (1998) 121–136.