Kinetics of Adsorption at Solid/Solution Interfaces Controlled by Intraparticle Diffusion: A Theoretical Analysis

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The utility of Weber−Morris and Lagergren linear representations for describing the kinetics of sorption at solid/solution interfaces controlled by intraparticle diffusion is discussed. The effects of different sorbent particle sizes and nonlinear adsorption isotherm equations (including the nonlinearity caused by surface energetic heterogeneity) and the changing sorbate concentration in the bulk phase have been taken into account. The conclusion can be drawn that both Lagergren and Weber−Morris plots seem to be general linear representations inherent in the intraparticle diffusion model and can be used for most adsorption systems. However, for quantitative analysis of kinetic data, more sophisticated methods need to be applied. Moreover, reliable conclusions can be drawn about a given system only by combined analysis of kinetic and equilibrium data.

Introduction

According to some generally expressed views, a sorption process can be described by the following four consecutive stages:[1] (1) transport of sorbate in the bulk solution; (2) diffusion across the film surrounding the sorbent particles (subsurface region diffusion); (3) migration of sorbate within the pores of the sorbent (intraparticle diffusion); and (4) adsorption/desorption on the solid surface viewed as a kind of chemical reaction. All these processes may be involved in controlling the adsorption rate. However, it is usually assumed that one of these steps is the slowest and controls the rate of sorption.[1,2] In our previous papers we have developed a theoretical model describing the rate of adsorption at solid/solution interfaces and based on the new fundamental statistical rate theory (SRT) approach.[3−8] One of the main assumptions inherent in this model is that the overall adsorption kinetics is controlled mainly by the rate of surface reaction.[9−11] Recently, we have also shown how the SRT approach can be combined with diffusional models to describe adsorption kinetics. Both the intraparticle diffusion model expressed by the Crank equation[4−6] and the model of diffusion across the liquid film surrounding the sorbent particles[7] were considered by us. Now we are going to focus on the intraparticle diffusion kinetic step.

The problem of sorption kinetics controlled by the rate of sorbate transport within the porous particle has been widely considered in papers on both solid/gas[12−19] and solid/solution[20−32] adsorption systems. However, there are some aspects that may need further study. Namely, in most of the experimental works reporting on adsorption kinetics, some simple linear representations, like the Weber−Morris plot[33] or the pseudo-first-order (Lagergren) plot,[34] are used as a main tool for analyzing the measured data.[35−39] Moreover, the results of applying the simple Weber−Morris plot method are often treated as a check whether the intraparticle diffusion is the rate-determining step. Both mentioned representations originate from the intraparticle diffusion model and can be derived by assuming some idealized

conditions, such as constant sorbate concentration in the bulk phase or the linear form of the adsorption isotherm equation. These assumptions can hardly be accepted in most real adsorption systems.

The main aim of this work is to investigate the influence of the most important physicochemical and technical conditions on the adsorption kinetics governed by the rate of intraparticle diffusion.

Theory

The process of sorbate intraparticle diffusion and adsorption onto the porous particle surface can be generally described by the following mass balance equation using the radial coordinate r:[30,40,41]

$$\frac{\partial c}{\partial t} = \frac{D}{T}\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) - \frac{\rho}{\varepsilon_P}\frac{\partial N}{\partial t} \tag{1}$$

where t is the time, ρ is the particle density, ε_P is the particle porosity, D is the molecular diffusion coefficient of sorbate in liquid solution, and T is the dimensionless tortuosity factor. The local concentrations of the sorbate within a particle in the solution, c, and in the adsorbed phase, N, are related to their equilibrium relationship. This local equilibrium assumption can be expressed as

$$N = \varphi(c) \tag{2}$$

where $\varphi(c)$ is a general adsorption isotherm equation. The boundary condition following from the symmetry of the spherical particle is

$$\left(\frac{\partial c}{\partial r}\right)_{r=0} = 0 \tag{3}$$

It is usually assumed that, in the outside boundary layer of the sphere, mass transfer is directly proportional to the difference in concentration of the solute in the bulk solution, c_b, and that

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on the surface of the particle, $c(r = R_0)$. Thus, the boundary condition can be expressed by the following relationship:[23,30]

$$\frac{D\varepsilon_P}{T}\left(\frac{\partial c}{\partial r}\right)_{r=R_0} = k_S[c_b - c(r = R_0)] \tag{4}$$

in which R_0 is the radius of the spherical particle and k_S is the external mass transfer coefficient. The initial condition for eq 1 corresponding to the experimental conditions (adsorption process) is

$$c(0 \le r \le R_0) = 0 \tag{5}$$

at $t = 0$. When the boundary layer mass transfer is much faster than the intraparticle diffusion (i.e., $k_S \to \infty$) the boundary condition (eq 4) reduces to its simpler form:

$$c(r = R_0) = c_b \tag{6}$$

The applicability of eq 6 depends on the technical conditions under which the kinetic experiment is carried out. The value of the mass transfer coefficient k_S is the function of agitation rate mainly. When the liquid phase is agitated, mass transport from the bulk solution to the external surface is usually fast, and at high agitation rates, k_S reaches a constant maximum value.[30] Thus, the process expressed by eq 4 is not usually considered as being the rate-limiting step in the sorption process. For the purpose of our further consideration we will accept the boundary condition in eq 6.

The average amount adsorbed onto the particle surface, $\bar{N}$, can be found by averaging the amount adsorbed in a given point of the particle over the volume of the particle:[40,41]

$$\bar{N}(t) = \frac{3}{R_0} \int_0^{R_0} r^2 N(r, t)\, dr \tag{7}$$

while the equilibrium adsorbed amount can be defined as $\bar{N}_e = \bar{N}(t \to \infty)$.

As a starting point we will accept eq 1 with the following additional conditions: (i) all sorbent particles have a uniform radius equal to R_0; (ii) the sorbate concentration in the bulk phase is time-independent and equals the initial concentration c_{in} (infinite volume of bulk phase); and (iii) the local equilibrium between the sorbate in solution and the adsorbed phase can be expressed by Henry's isotherm equation. All these assumptions will be further modified in order to check their significance and influence on sorption kinetics.

Equation 1, combined with the assumptions mentioned above, can be solved analytically. Its solution has been given by Crank:[40]

$$\frac{\bar{N}(t)}{\bar{N}_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_a \pi^2 n^2}{R_0^2} t\right) \tag{8}$$

in which D_a is called the effective (apparent) intraparticle diffusion coefficient. It can be defined as follows:[30]

$$D_a = \frac{D}{T(1 + \rho K_H/\varepsilon_P)} \tag{9}$$

where K_H is the Henry constant. When some nonlinear adsorption isotherm equations are accepted, eq 1 has to be solved numerically. All numerical solutions presented here were

obtained by use of the in-built PDE solver package 'NDSolve' in *Mathematica* 5.2 software.

For the purpose of clarity we will introduce the so-called "reduced time", t/t_f, where t_f is the time at which the value of $\bar{N}(t)/\bar{N}_e$ ratio reaches the value f. Moreover, introducing the reduced time allows for a smaller number of parameters. This is because some of them are only time-scaling factors; thus, their values are meaningless when time in the form t/t_f is used. All the kinetic isotherms will be presented in their reduced forms by using the two popular linear representations: the Weber−Morris plot [i.e., as $\bar{N}(t)/\bar{N}_e$ versus $(t/t_f)^{1/2}$] and the modified Lagergren plot {i.e., as $\ln [\bar{N}_e - \bar{N}(t)] - \bar{N}_e$ versus t/t_f}. The choice of these two representations has its source in the fact that the most popular diffusional equation (eq 8) for short adsorption times ($t \to 0$) reduces to the linear dependence of $\bar{N}(t)$ on the square root of time, whereas for long adsorption times ($t \to \infty$), when the system is close to equilibrium, eq 8 becomes the popular Lagergren (pseudo-first-order) equation. This issue has been discussed in detail in our previous papers.[4,6] Furthermore, application of the Lagergren plot for the analysis of measured kinetic data is essentially equivalent to application of the more popular Boyd plot method.[42] This issue is discussed below. We have modified the traditional Lagergren representation {i.e., $\ln [\bar{N}_e - \bar{N}(t)]$ versus time} in order to obtain better clarity of the plots.

The Boyd plot method is used mainly in order to determine the rate-controlling step in sorption processes. Examples of its application can be found elsewhere.[43−45] This method is based on plotting the kinetic data as Bt versus t, where Bt, according to the model proposed by Boyd et al.,[42] is defined as

$$Bt = \ln \frac{6}{\pi^2} - \ln (1 - F) \tag{10}$$

where

$$F = \frac{\bar{N}(t)}{\bar{N}_e} \tag{11}$$

Let us also note that the expression $\ln (6/\pi^2)$ is usually used as its numerical value, that is, as -0.4977. When eqs 10 and 11 are combined, one obtains the following relationship:

$$Bt = \ln \frac{6}{\pi^2} - \ln [1 - \bar{N}(t)/\bar{N}_e] = \ln \frac{6}{\pi^2} -$$
$$\ln [\bar{N}_e - \bar{N}(t)] + \ln \bar{N}_e \tag{12}$$

Now it is obvious that the above form of the Boyd plot is essentially identical with the Lagergren representation, that is, with the $\ln [\bar{N}_e - \bar{N}(t)]$ versus t plot. The differences are in the signs assigned to these representations and in the constant value of $\ln (6/\pi^2) + \ln \bar{N}_e$. The most important factor, the criterion of the linearity, remains unchanged.

Results of Calculations

1. Infinite Volume of Bulk Phase. *a. Effect of Different Particle Sizes.* Let us assume the following rectangular particle radius distribution function $\phi(R_0)$:

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$$\phi(R_0) = \begin{cases} \dfrac{1}{2\delta_R} & \text{for } \bar{R}_0 - \delta_R \leq R_0 \leq \bar{R}_0 + \delta_R \\ 0 & \text{elsewhere} \end{cases} \quad (13)$$

in which $\bar{R}_0$ is the mean value of the particle radius and $\bar{R}_0 + \delta_R$ and $\bar{R}_0 - \delta_R$ are its highest and lowest values, respectively. The value of δ_R parameter can vary from 0 to $\bar{R}_0$; in the case when $\delta_R = 0$ the distribution (eq 13) becomes the delta Dirac function and one faces the case of uniform particle size [then the sorption rate is expressed by the Crank equation (eq 8)]. The more general method includes the following average:

$$\frac{\bar{N}(t)}{\bar{N}_e} = 1 - \frac{6}{\pi^2} \int_{\bar{R}_0 - \delta_R}^{\bar{R}_0 + \delta_R} \phi(R_0) \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_a \pi^2 n^2}{R_0^2} t\right) dR_0 \quad (14)$$

with $\phi(R_0)$ expressed by eq 13.

We are going to investigate the following two issues: (i) the degree of particle size dispersion, when the mean value of particle radius, $\bar{R}_0$, is set as a constant while the value of δ_R varies from 0 to $\bar{R}_0$; and (ii) the mean particle size effect when the value of δ_R is set as a constant and the $\bar{R}_0$ value changes.

The results of our model investigations are presented in Figures 1 and 2. Let us also note that in this case the choice of D_a parameter value was meaningless due to applying the reduced time t/t_f. We have accepted the following values of the f parameter: $f = 0.995$ for Weber–Morris plots and $f = 0.95$ for Lagergren plots. The values of both $\bar{R}_0$ and δ_R parameters are assumed to be dimensionless. In most cases, accepting $f = 0.95$ to adequately represent the wide range of the kinetic data is sufficient. However, in the case of Morris–Weber plots, nonlinear deformation of the time scale occurs ($t \rightarrow t^{1/2}$). Thus, for the sake of optimal clarity $f = 0.995$ was accepted in order to widen the range of times, which in turn makes the effect of saturation [$\bar{N}(t)/\bar{N}_e \rightarrow 1$ at $t \rightarrow \infty$] visible.

b. Effect of Nonlinear Isotherm Equation. The case when Henry's equation matches the experimental equilibrium adsorption data is rather rarely observed. The more common case is when the measured data can be correlated well by other equations, such as Langmuir, Langmuir–Freundlich, Freundlich, Redlich–Peterson or Toth isotherms.[46-49] Then eq 1 has to be solved numerically by accepting a certain isotherm, as in eq 2. The $\partial N/\partial t$ term in eq 1 can be then calculated by using the following relationship:
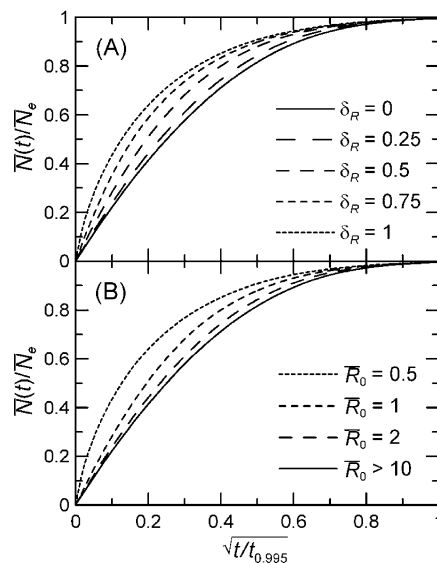
$$\frac{\partial N}{\partial t} = \frac{\partial N}{\partial c} \frac{\partial c}{\partial t} \quad (15)$$

Let us consider the simplest case of the Langmuir isotherm equation, describing adsorption onto a homogeneous surface:

$$N = \frac{N_m K_L c}{1 + K_L c} \quad (16)$$

in which K_L is the Langmuir constant and N_m is the monolayer capacity, that is, the maximum amount that can be adsorbed onto the surface. Then, eq 15 takes the following form:

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial c}\left(\frac{N_m K_L c}{1 + K_L c}\right)\frac{\partial c}{\partial t} = \frac{N_m K_L}{(1 + K_L c)^2}\frac{\partial c}{\partial t} \quad (17)$$

Figure 1. Influence of particle size distribution. Weber–Morris representations of the kinetic isotherms were calculated from eq 14. (A) The accepted value of the mean radius $\bar{R}_0$ was equal to unity; (B) the accepted value of δ_R was 0.5.
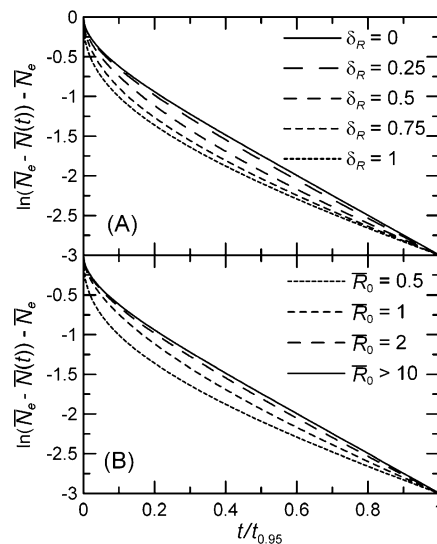
Figure 2. Lagergren plots of the kinetic isotherms presented in Figure 1. Other details are as described for Figure 1.

The obvious fact is that the value of K_L affects the linearity of the Langmuir isotherm. When the K_L value is very small, then eq 16 becomes Henry's equation. This is the case when a kinetic equation (eq 8) can be applied. When the value of K_L increases, eqs 16 and 17 combined with eq 1 have to be used.

Let us also note that in this case the parameter D/T acts as a time-scaling factor and one does not have to assign any value to it when the reduced time t/t_f is used. However, now the value of ρ/ε_P becomes important. It can vary in a wide range, depending on the type and internal structure of the adsorbent. Thus, in the present model investigation one has to take into account both isotherm deviation from linearity and the porosity/density ratio characteristic for a given sorbent.

Figure 3A shows the influence of K_L value on the linearity of Langmuir isotherm plots, while in Figures 4 and 5 one can observe the kinetic isotherm plots calculated from eqs 1, 16, and 17. The equilibrium sorbate concentration in the
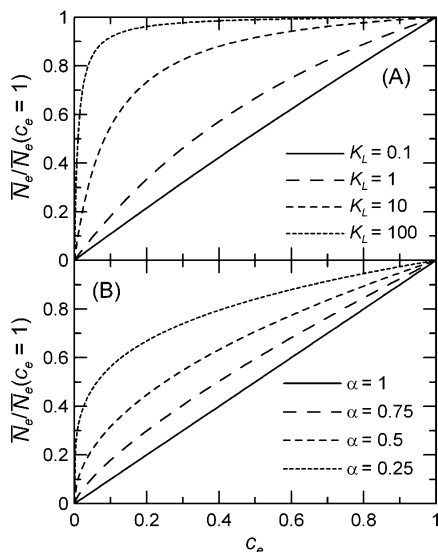
Figure 3. Influence of (A) K_L (Langmuir isotherm equation) and (B) α (Freundlich isotherm equation) on the equilibrium of adsorption. All the isotherms were plotted in their reduced forms for better clarity.
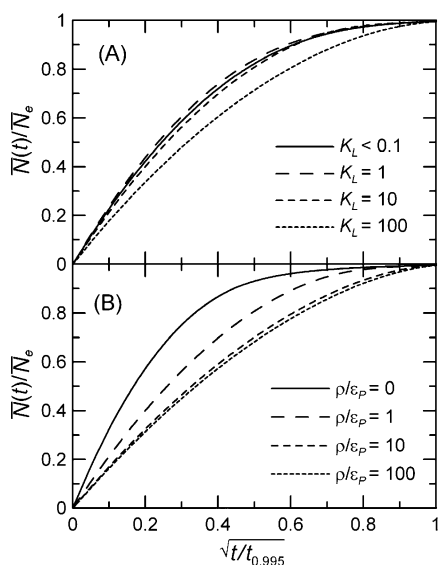

Figure 4. Influence of nonlinear equilibrium isotherm equation. Weber−Morris representations of kinetic isotherms were calculated from eqs 1, 16, and 17. Accepted values of ρ/ε_P and K_L were equal to unity in panels A and B, respectively. The assumed value for monolayer capacity was $N_m = 1$.

bulk phase has been denoted there as c_e. The range of c_e values (from 0 to 1) has been chosen due to the fact that the value of solute concentration in the pores of sorbent particle can change from 0 (initial concentration) to $c_{in} = 1$ (the constant value of sorbate concentration in the bulk phase accepted by us).

When the surface heterogeneity has to be considered, a variety of adsorption isotherm equations can be proposed. In order to reduce the number of parameters, we decided to apply the following Freundlich isotherm equation:

$$N = K_F c^\alpha \qquad (18)$$

in which K_F and α are some constants. For physical reasons the value of α parameter can vary from 0 to 1; that is, a decreasing value of α denotes increasing surface heterogene-
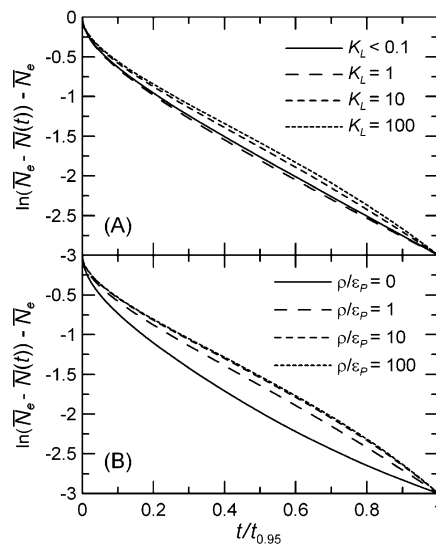
Figure 5. Lagergren plots of kinetic isotherms presented in Figure 4. Other details are as described for Figure 4.
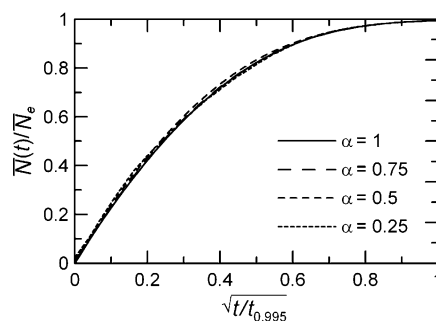
Figure 6. Influence of surface energetic heterogeneity. Weber−Morris representations of the kinetic isotherms were calculated from eqs 1, 18, and 19.

ity.[49] Figure 3B shows the influence of α parameter value on the linearity of Langmuir isotherm plots. Both the Langmuir and Freundlich equations are nonlinear isotherm equations, however, the main difference between them is that the Langmuir equation (eq 16) reduces to the Henry's isotherm equation when the sorbate concentration is low. The $\partial N/\partial t$ derivative is, thus, described by

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial c}(K_F c^\alpha)\frac{\partial c}{\partial t} = K_F \alpha c^{\alpha-1}\frac{\partial c}{\partial t} \qquad (19)$$

The above derivative (eq 19) can be combined with eqs 1 and 18 to calculate kinetic isotherms. Selected results are shown in Figures 6 and 7.

2. Finite Volume of Bulk Phase. *a. Effect of Different Particle Sizes.* When the sorption process takes place in a vessel having a limited volume V, the sorbate concentration decreases with time in the progress of adsorption. Then the actual, time-dependent value of c_b has to be calculated from the following mass-balance relationship:

$$V[c_{in} - c_b(t)] = \bar{N}(t) \qquad (20)$$

The above expression assumes that the amount of sorbate localized in the pores of sorbent is negligibly small compared to both adsorbed amount and that remaining in the bulk solution. When such an assumption is not reasonable (especially for the
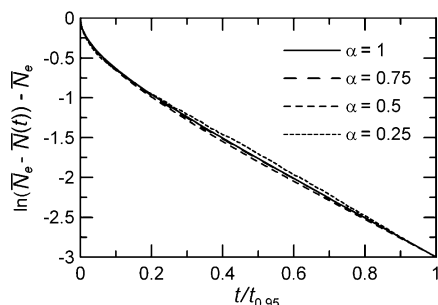
Figure 7. Lagergren plots of kinetic isotherms presented in Figure 6. Other details are as described for Figure 6.

extremely high values of the solid/solution ratio), more sophisticated expressions have to be applied.[30]

For the adsorption system described by the Henry isotherm equation and including sorbent particles with a uniform radius, the following kinetic equation was given by Crank:[40]

$$\frac{\bar{N}(t)}{\bar{N}_e} = 1 - \sum_{n=1}^{\infty} \frac{6\beta(\beta+1)}{9 + 9\beta + q_n^2\beta^2} \exp\left(-\frac{D_a q_n^2}{R_0^2}t\right)$$

(21)

in which the apparent diffusion coefficient D_a is defined by eq 9 and the β coefficient represents the so-called "adsorbent load factor", defined by using the value of equilibrium sorbate concentration in the bulk solution (c_e):

$$\beta = \frac{c_e}{c_{in} - c_e}$$

(22)

It can be noted that β may be also defined by using the value of Henry's constant;[41] however, eq 22 is the more general definition. The q_n values are nth nonzero positive roots of

$$\tan q_n = \frac{3q_n}{3 + \beta q_n^2}$$

(23)

The influence of particle size distribution was studied by using eq 13 and the following average:

$$\frac{\bar{N}(t)}{\bar{N}_e} = 1 - \int_{\bar{R}_0-\delta_R}^{\bar{R}_0+\delta_R} \phi(R_0) \sum_{n=1}^{\infty} \frac{6\beta(\beta+1)}{9 + 9\beta + q_n^2\beta^2} \times$$
$$\exp\left(-\frac{D_a q_n^2}{R_0^2}t\right) dR_0 \quad (24)$$

Accepted values of the δ_R and $\bar{R}_0$ parameters as well as the calculation procedures were identical to those described in section 1a. Selected results of calculations are shown in Figures 8 and 9.

Let us note that for high values of β parameter, eq 21 reduces to eq 8. Thus, it can be expected that the behavior of the sorption system predicted by eq 24 will be similar to that predicted by eq 14 when $\beta \to \infty$. This fact has been confirmed by the results of our calculations and led us to accept the value of β that corresponds to the case when most of the sorbate is removed
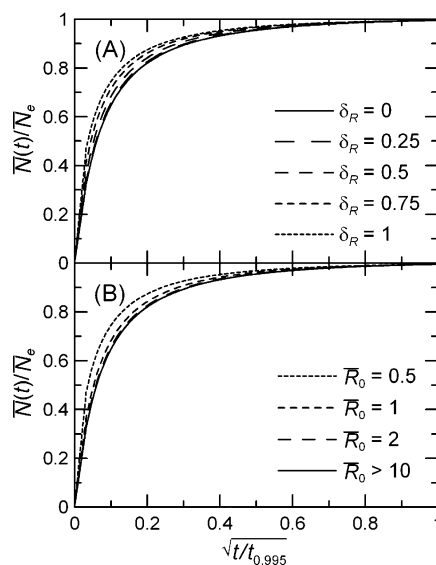
Figure 8. Influence of particle size distribution. Weber–Morris representations of the kinetic isotherms were calculated from eq 24. (A) Accepted value of the mean radius $\bar{R}_0$ was equal to unity; (B) accepted value of δ_R was 0.5. The accepted value of β was 0.1.
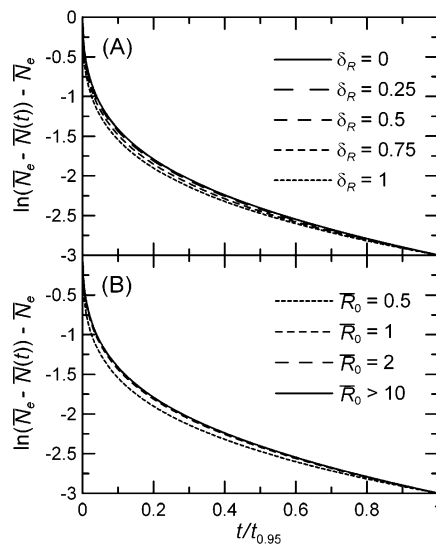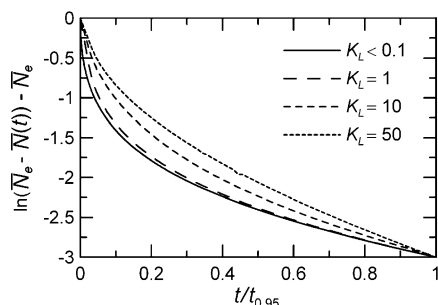

Figure 9. Lagergren plots of kinetic isotherms presented in Figure 8. Other details as as described for Figure 8.
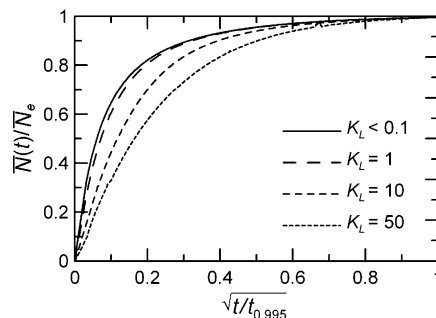
Figure 10. Influence of the nonlinear equilibrium isotherm equation. Weber–Morris representations of the kinetic isotherms were calculated from eqs 1, 16, 17, and 20. Assumed values of parameters were $N_m = 1$, $\rho/\varepsilon_P = 1$, and $\beta = 0.1$.

from the solution during the experiment. Figures 8–11 present the kinetic isotherms calculated for $\beta = 0.1$.

b. Effect of Nonlinear Isotherm Equation. Here the case of the nonlinear isotherm equation combined with the effect of

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Figure 11. Lagergren plots of kinetic isotherms presented in Figure 10. Other details are as described for Figure 10.

decreasing sorbate concentration (eq 20) is considered. Equation 21 can no longer be accepted and the desired kinetic isotherm can be obtained by solving eq 1 numerically with the boundary condition (eq 6) combined with the mass balance (eq 20). The β coefficient can be again used as a measure of solid/solution ratio accepted in a given system. We set its value again as $\beta = 0.1$. Our considerations were limited only to the cases of Langmuir (eq 16) and Freundlich (eq 18) isotherm equations.

Figures 10 and 11 show the selected results of calculations performed by accepting the Langmuir equation (eq 17) as the equilibrium adsorption isotherm (introducing surface heterogeneity leads to the results similar to those presented in Figures 6 and 7, so they are not shown).

Conclusions

Both the Boyd and Lagergren plot methods are equivalent and can be used interchangeably. However, their applicabilities are limited in most cases to the range of kinetic isotherms when the adsorption system is close to equilibrium. More details related to this observation can be found elsewhere.[4−6]

When the constant sorbate concentration in the bulk phase is maintained, both Weber−Morris and Lagergren linear representations can be used, even for systems described by the nonlinear equilibrium adsorption isotherm equation (this is true for both Langmuir and Freundlich equilibrium isotherm equations). Then the specific properties of a given sorbent (expressed as the density/porosity ratio) also become an important factor. The following two observations are worth noting:

The presence of surface energetic heterogeneity does not seem to play an important role. It may be caused by the fact that introducing even an extremely high heterogeneity (i.e., accepting $\alpha = 0.25$) leads to an approximately similar degree of deviation from the linear character of equilibrium adsorption isotherm to that noted for the Langmuir isotherm and $K_L = 10$ (compare panels A and B of Figure 3).

When the value of K_L coefficient is increased, the linear range of the kinetic isotherm (plotted in the Weber−Morris representation) decreases at first and then increases when $K_L > 2$ (see Figure 4A).

When we assume that the sorbate concentration is changing with time (i.e., the volume of the bulk phase has a finite value), then increasing the value of K_L coefficient leads to improved linearity (i.e., to increased range) of both Weber−Morris and Lagergren plots. Accepting the surface energetic heterogeneity does not affect significantly the linearity of these plots.

Similar observations have also been made when the classical Langmuirian kinetics model[50,51] or, mentioned earlier, the SRT approach,[3,4] is accepted. It has been proved that both these approaches predict the behavior characteristic of the Lagergren equation, especially when constant or nearly constant sorbate

concentration in the bulk solution is assumed. Combining that result with the present ones suggests that this kind of behavior may be of a general nature for sorption systems.

The presence of the dispersion among the sorbent particles diameters influences the linearity of the Weber−Morris and Lagergren plots only slightly. This observation is valid for the systems with both infinite and finite volumes of bulk phase. The linearity is not obtainable only in the case of Weber−Morris plots when the substantial part of the sorbent particle has a very small diameter (i.e., sorbent particles are "dust"). However, then other (faster) kinetic mechanisms might be involved in the process. Then the kinetic equations describing the rate of sorption can be different for the particles of different sizes. When one assumes existence of two fractions of particles, the overall sorption process can be described by the following "modified" Weber−Morris plot:

$$\bar{N}(t) = \sigma \bar{N}_e + X\sqrt{t} \qquad (25)$$

where σ if the fraction of sorbent particles being "dust" for which the rate of sorption is assumed to be very fast and X is a constant. The mathematical form of eq 25 can be justified as follows: let us assume that the sorption process can be divided into two independent but simultaneously occurring, kinetic steps 1 and 2. When the rate of step 1 is very fast when compared to the rate of step 2, it can be neglected and the appropriate kinetic term can be replaced by the term representing the equilibrium state to which this process would evolve. The only difference is then the initial condition for step 2 represented now, in an approximate way, by $\bar{N}_{(2)}(t = 0) = \sigma \bar{N}_e$. When step 2 is intraparticle diffusion, expressed by the classical Morris−Weber linear equation, the overall kinetics of the process is given by eq 25.

Another important observation is that systems with finite volume of bulk phase have restricted ranges of linearity for both Weber−Morris and Lagergren plots when they are compared to the idealized systems with constant sorbate concentration in the bulk phase.

On the basis of all cases studied here, the conclusion can be drawn that both Lagergren and Weber−Morris plots seem to be general linear representations inherent in the intraparticle diffusion model for most of the adsorption systems.

Although the type of equilibrium adsorption isotherm does not affect significantly the linearity of Weber−Morris and Lagergren plots, it should be strongly emphasized that these two simple representations are only local approximations of the "actual" kinetic isotherms, which can be obtained by solving eq 1 combined with an appropriate equilibrium isotherm equation. Thus, any reliable conclusions can be drawn only by combined analysis of kinetic and equilibrium data.

References and Notes

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