Adsorption of fluoride by porous adsorbents: Estimating pore diffusion coefficients from batch kinetic data

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ABSTRACT

A simple method is presented for extracting pore diffusion coefficients from batch adsorption kinetic data. The method employs the classic Langmuir kinetics model which is characterized by a single rate coefficient. An analytical solution in the form of a simple algebraic equation is available for this rate model. Fitting the algebraic equation to batch kinetic data to determine the rate coefficient is straightforward and can be conveniently accomplished using standard spreadsheet programs. The resultant rate coefficient can be converted to the pertinent pore diffusion coefficient via a separate algebraic expression. The proposed modeling approach provides accurate fits of experimental kinetic data taken from the literature and yields acceptable errors in the best estimates for pore diffusion coefficients. Specific examples discussed are the adsorption of fluoride by bone char and laterite adsorbents.

Keywords: Adsorption, Fluoride, Langmuir kinetics, Parameter estimation, Pore diffusion

1. Introduction

Adsorption provides an efficient means of removing organic and inorganic contaminants from aqueous solutions [1-6]. The equilibrium and kinetic characteristics of a given adsorption system are usually determined from experimental data obtained from batch contactors. In the case of batch kinetic studies, simple surface reaction models are frequently used by investigators for data analysis. Notable examples include the pseudo first-order or Lagergren kinetic equation and the pseudo second-order kinetic equation. The popularity of these two kinetic equations is due, in part, to the simplicity of their mathematical forms which allow the equations to be linearized for parameter estimation by means of linear regression. The two pseudo reaction rate equations have however encountered criticisms on several fronts. For example, the speciousness of a linearized form of the pseudo second-order equation for parameter estimation has been discussed at some length by a number of investigators [7-9]. Methodological biases and flaws exist in the comparison of the modeling abilities of these two kinetic equations [10-12]. From a theoretical viewpoint, they should be considered as being purely phenomenological with no sound phys-

icochemical basis [13]. The physical significance of their rate coefficients has been called into question [14-16]. Also, they are merely curve fitting tools and should not be used to identify the actual uptake mechanism [17, 18]. Two recent reviews [19, 20] as well as a recent textbook on adsorption [21] have summarized the various shortcomings of the two pseudo reaction rate equations.

For porous adsorbent particles the rate of adsorption is often controlled by intraparticle diffusion [22, 23]. Thus, a more instructive approach in the modeling of adsorption kinetics is to use physically reasonable rate models based on the kinetics of mass transfer processes. Rate models accounting for an external film mass transfer resistance and one or more intraparticle diffusion mechanisms allow a realistic mathematical description of the kinetics of many adsorption systems. Because intraparticle diffusion coefficients are an intrinsic property of a given adsorption system, they are independent of the mode of operation. For this reason, diffusion coefficients determined from a batch contactor may be used to model the dynamic behavior of a fixed bed adsorber. In general, two distinct intraparticle transport models, pore diffusion and surface/solid diffusion, are commonly used to describe the kinetics of contaminant adsorption by porous particles. Both dif-

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fusion models have been used by investigators to fit batch kinetic data with equal accuracy. More sophisticated models with pore and surface diffusion acting in parallel have also been studied by some practitioners [24-26]. From a practical standpoint, it is more convenient to use solid-phase diffusion models based on a single intraparticle diffusion mechanism to model adsorption kinetics because they are computationally simpler.

The present paper deals with an important aspect of pore diffusion: determination of pore diffusion coefficients from experimental data. Batch contactors provide a simple and convenient way to acquire kinetic data. By fitting a pore diffusion model to such data, the pore diffusion coefficient of the model can be determined. However, for nonlinear systems the data fitting process is often complicated by the need to solve the model equations numerically [27, 28]. As an alternative, the present article explores the feasibility of using a simple kinetic model to extract pore diffusivities from batch kinetic data without resorting to numerical methods. The approximation is based on the use of the classic Langmuir kinetics model – which reduces to the Langmuir isotherm model at large values of time – to describe the rate of uptake. Although the Langmuir kinetics model is based on a surface reaction mechanism, its rate coefficient, unlike those of the pseudo first-order and pseudo second-order kinetic equations, can be converted to the pertinent pore diffusion coefficient [29-31].

For batch adsorption systems, it is possible to derive from the Langmuir kinetics model an analytical expression in the form of an algebraic equation. Fitting the algebraic equation to batch kinetic data yields the rate coefficient of the Langmuir kinetics model, from which the corresponding pore diffusion coefficient may be computed. The data fitting process can be easily accomplished using standard spreadsheet programs. Using data taken from the environmental adsorption literature, the potential of this simple modeling approach was evaluated here on its ability to provide accurate pore diffusion coefficients of fluoride ions. Elevated levels of fluoride in drinking water are a major public health concern in many parts of the world. Adsorption has been recognized as an effective technique for the removal of fluoride from water sources [32-34].

2. Theory

2.1. Film-Pore Diffusion Model

In this model the transport of a solute within a spherical particle is described by pore diffusion and is given by the following equation and initial and boundary conditions [22, 23]:

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{D_p}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c}{\partial r} \right) \quad (1)$$

$$t = 0 \quad c = 0 \quad q = 0 \quad (1(a))$$

$$r = 0 \quad \frac{\partial c}{\partial r} = 0 \quad (1(b))$$

$$r = R_p \quad D_p \frac{\partial c}{\partial r} = k_f (C - c) \quad (1(c))$$

In these equations, c and C are respectively the pore fluid and bulk solution concentrations at time t , q is the adsorbed phase concentration at time t , ε_p is the particle porosity, ρ_p is the particle density, D_p is the pore diffusion coefficient, k_f is the external mass transfer coefficient, r is the particle radial coordinate, and R_p is the particle radius. Eq. (1(c)) describes mass transfer through a boundary film surrounding an individual particle.

The conservation equation and initial condition for a batch contactor are given as [22, 23]

$$\frac{dC}{dt} = -\frac{3k_f}{R_p} \frac{m}{V} (C - c|_{r=R_p}) = -\frac{m}{V} \frac{d\bar{q}}{dt} \quad (2)$$

$$t = 0 \quad C = C_o \quad (2(a))$$

where m is the mass of adsorbent, V is the volume of solution, $\bar{q}$ is the solute concentration in the adsorbent particle averaged over the particle volume, and C_o is the initial concentration. The relationship between adsorbed phase and pore fluid concentrations is defined by the following Langmuir isotherm model [35]:

$$q = \frac{q_m b c}{1 + b c} \quad (3)$$

where q_m and b are respectively the Langmuir saturation capacity and Langmuir constant. These equations are nonlinear and must, in general, be solved numerically.

2.2. Langmuir Kinetics Modeling Approach

According to the classic Langmuir kinetics model [36, 37], the interaction between a solute and an adsorption site is described by the following reaction rate equation:

$$\frac{d\bar{q}}{dt} = k_1 C (q_m - \bar{q}) - k_2 \bar{q} \quad (4)$$

where k_1 is a second-order forward rate coefficient and k_2 is a first-order reverse rate coefficient. At equilibrium the derivative $d\bar{q}/dt$ approaches zero and Eq. (4) reduces to the Langmuir isotherm model given by Eq. (3) with $b = k_1/k_2$. Eq. (4) may be rewritten as

$$\frac{d\bar{q}}{dt} = k_1 \left[C (q_m - \bar{q}) - \frac{\bar{q}}{b} \right] \quad (5)$$

Integration of Eqs. (2) and (5) yields the following analytical solution [38]:

$$\frac{C}{C_o} = 1 - \frac{(m/V)(\alpha - \beta)}{C_o} \left\{ \frac{1 - \exp[-(2\beta m/V)k_1 t]}{1 - [(\alpha - \beta)/(\alpha + \beta)] \exp[-(2\beta m/V)k_1 t]} \right\} \quad (6)$$

where

$$\alpha = \frac{1}{2} \left(C_o \frac{V}{m} + q_m + \frac{1}{b} \frac{V}{m} \right) \quad \beta = \sqrt{\alpha^2 - C_o q_m \frac{V}{m}} \quad (6(a))$$

For an experimental kinetic test, the parameters C_o , m , and V are known while the parameters α and β may be computed with known Langmuir isotherm parameters q_m and b , and so the rate coefficient k_1 is the only fitting parameter which may be obtained by matching Eq. (6) to the experiment's data. Note that Eq. (6) may be rearranged in the following manner to allow estimation of k_1 by means of linear regression:

$$\frac{1}{2} \frac{1}{\beta} \frac{V}{m} \ln \left[\frac{(C_o - C)/(\alpha + \beta) - m/V}{(C_o - C)/(\alpha - \beta) - m/V} \right] = k_1 t \quad (7)$$

A plot of the left-hand side of Eq. (7) versus t should be linear with slope k_1 [39].

In adsorption studies k_1 is often regarded as a "lumped" kinetic rate constant which includes all mass transfer resistances (film diffusion, surface diffusion, pore diffusion, and surface reaction resistance). Here, we restrict our interest to the film mass transfer and pore diffusion resistances which can be combined in the following manner [29-31]:

$$\frac{1}{k_1} = \frac{R_p^2 \rho_p q_m (R+1)}{30} \left(\frac{5}{k_f R_p} + \frac{1}{D_p} \right) \quad (8)$$

where,

$$R = \frac{1}{1 + bC_o} \quad (8(a))$$

Given k_1 , the film mass transfer coefficient k_f , and other relevant parameters, the pore diffusion coefficient D_p may be calculated from Eq. (8). An expression similar to Eq. (8) for k_1 which combines the film mass transfer and surface diffusion resistances are available in the literature [40].

2.3. Goodness-of-Fit Measure

The following coefficient of determination (COD) gives a good idea of the overall goodness-of-fit of the Langmuir kinetics model to measured data:

$$\text{COD} = \frac{\sum_{j=1}^w (z_j^{\text{mod}} - \bar{z}^{\text{exp}})^2}{\sum_{j=1}^w (z_j^{\text{mod}} - \bar{z}^{\text{exp}})^2 + \sum_{j=1}^w (z_j^{\text{mod}} - z_j^{\text{exp}})^2} \quad (9)$$

where z_j^{mod} is the model prediction for observation j , z_j^{exp} is the experimental data for observation j , and $\bar{z}^{\text{exp}}$ is the mean of experimental data. A COD score of unity indicates a perfect fit.

3. Results and Discussion

Intraparticle diffusion coefficients (pore and surface) serve as important input parameters to solid-phase mass transfer models which

are often used in fixed bed adsorber design and analysis. In addition, these diffusion coefficients may be used to compare the kinetic properties of different adsorbents. For a given contaminant removal process, it is important to select an adsorbent which exhibits not only optimal adsorption capacity but also fast uptake kinetics. As such, the subject matter of this work is of considerable practical interest.

Three literature batch data sets obtained for the uptake of fluoride by porous adsorbents have been used in this work to evaluate the performance of the proposed Langmuir kinetics modeling approach. In the selected literature reports the pore diffusion coefficient for each data set has been obtained by fitting either a numerical film-pore diffusion model or a numerical shrinking core model to the kinetic data.

An attractive feature of the Langmuir kinetics model is its ability to account for the effects of isotherm nonlinearity. As noted previously, at equilibrium the Langmuir kinetics model reduces to the Langmuir isotherm model, so the effects of isotherm nonlinearity are inherently included within the rate model. Since many experimental adsorption isotherms follow the Langmuir isotherm model, the Langmuir kinetics model can thus be used to describe the kinetics as well as the equilibrium characteristics of these systems. For rate models with a nonlinear isotherm, a numerical solution is in general required. The Langmuir kinetics model is an exception in this respect since it can be solved analytically. However, the Langmuir kinetics model cannot extract pore diffusion coefficients directly from experimental data; they are instead computed from Eq. (8).

Fig. 1. Adsorption of fluoride by bone char showing comparison between the kinetic data of Nigri et al. [41] and theoretical curve computed from Eq. (6). COD = 0.986.

3.1. Case 1: Adsorption of Fluoride by Bone Char

Nigri et al. [41] measured the uptake of fluoride by a commercial bone char adsorbent as a function of time using Erlenmeyer flasks containing fluoride solutions and bone char which were placed on a thermostatic orbital shaker. The resultant kinetic data set is shown in Fig. 1. The authors extracted D_p from the Fig. 1 data by means of a pore diffusion model which was solved numerically. The numerical solution is based on the explicit finite difference

method of lines. The optimal value of D_p so obtained is $7.15 \times 10^{-6} \text{ cm}^2/\text{s}$. In their modeling approach, Nigri *et al.* [41] assumed negligible resistance to external film mass transfer. As a result, the pore diffusion model defined by Eq. (1) reduces to their pore diffusion model by omitting the external mass transfer mechanism.

In the Langmuir kinetics modeling approach, determination of D_p is based on two distinct steps: estimation of k_1 by fitting Eq. (6) to batch kinetic data followed by computation of D_p from Eq. (8) using the resultant k_1 value. To extract k_1 from the Fig. 1 data via Eq. (6), one requires values of the Langmuir isotherm parameters q_m and b and two system parameters C_o and m/V . These parameter values, given in the paper by Nigri *et al.* [41], are $q_m = 6.7 \text{ mg/g}$, $b = 800 \text{ cm}^3/\text{g}$, $C_o = 1 \times 10^{-2} \text{ g/cm}^3$, and $m/V = 2 \times 10^{-3} \text{ g/cm}^3$.

Since the Langmuir isotherm parameters serve as input parameters to Eq. (6), it is important to check whether the Fig. 1 kinetic data are consistent with prediction of the Langmuir isotherm model. This consistency will ensure a good fit of Eq. (6) to the data points of Fig. 1 collected at large values of time when apparent equilibrium was established. The equilibrium concentration at large values of time, C_e , for a batch adsorber that follows the Langmuir isotherm may be computed from the following expression:

$$C_e = \frac{\sqrt{h^2 + \frac{4C_o}{b}} - h}{2} \quad (10)$$

where

$$h = \frac{1}{b} + \frac{m}{V} q_m - C_o \quad (10(a))$$

The value of C_e for the batch kinetic experiment of Nigri *et al.* [41] computed from Eq. (10) is $1.9 \times 10^{-3} \text{ mg/cm}^3$, which agrees with the observed C_e value of approximately $1.8 \times 10^{-3} \text{ mg/cm}^3$ (indicated by the last data point of Fig. 1). Thus, it is evident that the Langmuir parameters q_m and b extracted from independent equilibrium experiments are able to describe the equilibrium state of the batch kinetic experiment with good accuracy.

Eq. (6) was fitted to the Fig. 1 data by a nonlinear regression procedure using the q_m , b , C_o , and m/V values given above, yielding $k_1 = 4.38 \times 10^{-3} \text{ cm}^3/\text{mg s}$ and a COD score of 0.986. As seen in Fig. 1, the entire data set is fitted well by Eq. (6). Having determined k_1 , it is straightforward to compute D_p from Eq. (8), which has several other input parameters. Values of q_m , b , and C_o are listed above while values of the adsorbent radius R_p and adsorbent density ρ_p , as reported by Nigri *et al.* [41], are respectively 0.07 cm (mean) and 0.96 g/cm³. The remaining parameter of Eq. (8), the external mass transfer coefficient k_f , is not available since Nigri *et al.* [41] assumed negligible external mass transfer in their modeling approach.

Because the initial uptake of solute is controlled only by the external mass transfer resistance, k_f may be estimated from experimental values of C/C_o obtained during the initial uptake period. The fluid phase concentration change during the initial period is given by [42, 43]:

$$\frac{C}{C_o} = 1 - \frac{3k_f m}{R_p \rho_p V} t \quad (11)$$

The preceding equation implies that a plot of C/C_o against t for small times gives a straight line with slope $(3m/R_p \rho_p V)k_f$. Therefore, k_f can be calculated from such a slope. We calculated k_f as $1.01 \times 10^{-3} \text{ cm/s}$ by fitting Eq. (11) to the first two data points of Fig. 1.

Knowing all the relevant parameters, the pore diffusion coefficient can be computed from Eq. (8): $D_p = 8.03 \times 10^{-6} \text{ cm}^2/\text{s}$. This D_p value obtained by the Langmuir kinetics modeling approach and the D_p value determined by Nigri *et al.* [41] differ only by 12%, as shown in Table 1. The good agreement confirms the validity of the proposed modeling approach.

Table 1. Comparison between D_p Values Obtained by the Langmuir Kinetics Modeling Approach and Literature D_p Values

Adsorption system	D_p (cm ² /s)		Error (%)
	Literature	This work	
Fluoride-bone char [41]	7.15×10^{-6}	8.03×10^{-6}	12
Fluoride-bone char [44]	3.31×10^{-6}	3.04×10^{-6}	8
Fluoride-laterite [45]	2.3×10^{-6}	1.81×10^{-6}	21

Fig. 2. Adsorption of fluoride by bone char showing comparison between the kinetic data of Leyva-Ramos *et al.* [44] and theoretical curve computed from Eq. (6). COD = 0.961.

3.2. Case 2: Adsorption of Fluoride by Bone Char

The uptake of fluoride by a commercial bone char adsorbent has also been investigated by Leyva-Ramos *et al.* [44] who employed a rotating basket batch adsorber to obtain kinetic data for a series of experimental runs with varying system and operational conditions. We will focus on a particular kinetic experiment (run 13 in Fig. 6 of their paper). The adsorbent size of this run is similar to that of case 1. The authors fitted the film-pore diffusion model given by Eq. (1) to the chosen kinetic data set, shown in Fig. 2, obtaining $D_p = 3.31 \times 10^{-6} \text{ cm}^2/\text{s}$. The partial and ordinary differential equations of the film-pore diffusion model (Eqs. (1) and (2))

were numerically solved by using a specialized software package. The external mass transfer coefficient k_f – required by the fitting procedure as one of the model inputs – was estimated from data points in the small time region which yielded $k_f = 3.07 \times 10^{-3}$ cm/s. Other relevant system and operational parameters are as follows: $C_o = 5.66 \times 10^{-3}$ g/cm³, $m/V = 1 \times 10^{-3}$ g/cm³, $R_p = 0.065$ cm, and $\rho_p = 0.96$ g/cm³. Note that the ρ_p value is taken from case 1 since it is not given in the paper by Leyva-Ramos et al. [44].

As in case 1, one should verify the ability of the Langmuir isotherm to predict the apparent equilibrium state of the kinetic data set of Fig. 2 before fitting Eq. (6) to the kinetic data. The final data point of Fig. 2 gives an experimental C_e value of approximately 2.4×10^{-3} mg/cm³. According to Leyva-Ramos et al. [44], the Langmuir isotherm parameters q_m and b extracted from batch equilibrium data are 5.89 mg/g and 450 cm³/g, respectively. The theoretical C_e value calculated from Eq. (10) using these two isotherm parameters is 2.5×10^{-3} mg/cm³, confirming the validity of the Langmuir isotherm parameters. Knowing C_o , m/V , q_m , and b , the unknown rate coefficient k_1 can be obtained by fitting Eq. (6) to the Fig. 2 data. The best-fit value of k_1 is 2.19×10^{-3} cm³/mg s. A comparison between experimental and calculated curves is shown in Fig. 2 from which it may be seen that the Langmuir kinetics model provides a satisfactory fit of the experimental data (COD = 0.961).

We calculated k_f as 6.17×10^{-4} cm/s by fitting Eq. (11) to the first two data points of Fig. 2. Note that our k_f value is noticeably smaller than the k_f value obtained by Leyva-Ramos et al. [44]. The difference may be due to the use of different initial data points to extract k_f from the small time region. We were not able to extract accurate initial data points from the original figure because it contains several cluttered data points in the small time region. Also, as noted above we have used an assumed value for the adsorbent density ρ_p in the calculation of k_f from Eq. (11). Knowing k_1 , k_f , q_m , b , C_o , R_p , and ρ_p , the pore diffusion coefficient D_p can be computed from Eq. (8) as 3.04×10^{-6} cm²/s. The D_p value obtained here is in excellent agreement with that determined by Leyva-Ramos et al. [44], showing a deviation of 8% (see Table 1).

It is interesting to note that the literature D_p value for case 1 (7.15×10^{-6} cm²/s) is about two times larger than the literature D_p value for case 2 (3.31×10^{-6} cm²/s). This difference is somewhat unexpected given that the textural properties of the two commercial bone char adsorbents are quite similar, as shown in Table 2. In principle, adsorbents with similar textural properties should exhibit similar pore diffusivities.

Table 2. Textural Properties of Two Commercial Bone Char Adsorbents

Reference	Nigri et al. [41]	Leyva-Ramos et al. [44]
Raw material	Cow bone	Cow bone
Manufacturer	BONECHAR, Brazil	APELSA, Mexico
Particle size (mm)	1.1-1.7 (mean = 1.4)	1.29
Surface area (m ² /g)	138.8	104
Particle density (g/cm ³)	0.96	–
Total pore volume (cm ³ /g)	0.308	0.30
Average pore diameter (nm)	8.86	11.1

3.3. Case 3: Adsorption of Fluoride by Laterite

Batch experiments were conducted by Maiti et al. [45] to obtain kinetic data of fluoride adsorption in a chemically treated laterite adsorbent. Three kinetic data sets obtained at different temperatures are available in their paper. The kinetic data set measured at 15 °C is presented here for analysis (Fig. 3). The experimental conditions are $C_o = 1 \times 10^{-2}$ g/cm³ and $m/V = 5 \times 10^{-4}$ g/cm³. The properties of the adsorbent are $R_p = 0.01$ cm and $\rho_p = 1.08$ g/cm³. The authors adopted a shrinking core model to describe pore diffusion and external mass transfer. The advantage of this model is that it can be formulated in terms of ordinary differential equations, avoiding the need to solve the partial differential equation given by Eq. (1). The shrinking core model was numerically solved and fitted to the kinetic data of Fig. 3, yielding $D_p = 2.3 \times 10^{-6}$ cm²/s and $k_f = 8.3 \times 10^{-2}$ cm/s.

By fitting Eq. (3) to independent equilibrium data, Maiti et al. [45] obtained $q_m = 36.31$ mg/g and $b = 230$ cm³/mg. This maximum adsorption capacity is about five to six times larger than the q_m values of the two bone char adsorbents analyzed in the previous two cases. Using known values of C_o , m/V , q_m , and b , Eq. (6) was fitted to the Fig. 3 data to determine k_1 . The resultant k_1 is 6.54×10^{-3} cm³/mg s. As seen in Fig. 3, the calculated curve of the Langmuir kinetics model with a COD score of 0.957 is capable of fitting the data reasonably well. The external mass transfer coefficient k_f was again determined by fitting Eq. (11) to the first two data points of Fig. 3. Knowing k_1 , k_f , q_m , b , C_o , R_p , and ρ_p , the pore diffusion coefficient D_p can be calculated from Eq. (8) as 1.81×10^{-6} cm²/s. The D_p value obtained by our approach is consistent with that obtained by Maiti et al. [45]; they differ by 21% (see Table 1). It should be noted that the shrinking core model used by Maiti et al. [45] to estimate their D_p value is based on a number of assumptions and simplifications. As a result, their D_p value could differ from the D_p value of the formal film-pore diffusion model given by Eq. (1), to which our D_p should be compared.

Fig. 3 reveals that the fluoride-laterite adsorption system needed about 10 h to reach apparent equilibrium. By contrast, the contact time needed by the two fluoride-bone char adsorption systems

Fig. 3. Adsorption of fluoride by laterite showing comparison between the kinetic data of Maiti et al. [45] and theoretical curve computed from Eq. (6). COD = 0.957.

to reach apparent equilibrium was more than 50 h, as may be seen in Figs. 1 and 2. This marked difference is due to the fact that the particle size of the laterite adsorbent (0.2 mm) is very much smaller than those of the bone char adsorbents (Table 2). This particle size effect implies that the intraparticle diffusion mechanism played a dominant role in the overall adsorption rates of fluoride in these porous adsorbents.

3.4. Errors in Fitted D_p Values

On the whole the parameter estimation method presented in this work has proven to be satisfactory, providing a simple and convenient way to extract D_p from batch kinetic data without resorting to numerical methods. The fitted D_p values differ from literature values by 8-21% (Table 1). These deviations are in line with errors reported in other similar studies. Differences in the range 3-23% have been reported by Chu [40] who used the Langmuir kinetics modeling approach to extract surface diffusion coefficients from batch kinetic data. Yao and Chen [46] developed a simplified method based on algebraic equations for estimating surface diffusion coefficients from batch kinetic data and reported errors in the range 11-24%. For the uptake of fluoride by bone char in batch adsorbers, Leyva-Ramos *et al.* [44] demonstrated that concentration decay curves predicted with best-fit D_p values are very similar to those predicted with non-optimal D_p values that differ from the best-fit values by 10-17% (see Fig. 4 of their paper). The magnitude of the errors in D_p reported here is therefore deemed tolerable.

4. Conclusions

From our evaluation of the Langmuir kinetics modeling approach considered here, we conclude that it affords a simple and convenient way to extract pore diffusion coefficients from batch kinetic data and, with limited computational effort, gives acceptable quantitative results. For the three case studies dealing with the uptake of fluoride by bone char and laterite adsorbents, the fitted pore diffusion coefficients are in good agreement with literature results. The Langmuir kinetics modeling approach requires accurate Langmuir isotherm parameters as well as external mass transfer coefficients which serve as important input parameters. The major drawback of this simple method is that it is restricted to adsorption systems in which the adsorption equilibrium behavior follows the Langmuir isotherm. Additional studies using adsorption systems dealing with other water contaminants such as heavy metals and dyes will be required to expand the evaluation presented here and to confirm the utility of the simple method as a rapid and reliable modeling tool for estimating pore diffusion coefficients from batch kinetic data.

Nomenclature

b	Langmuir constant (cm^3/mg)
c	Solute concentration in pore fluid (mg/cm^3)
C	Solute concentration in bulk fluid (mg/cm^3)
C_e	Equilibrium concentration (mg/cm^3)

C_o	Initial value of C (mg/cm^3)
D_p	Pore diffusion coefficient (cm^2/s)
h	Parameter defined by Eq. (10(a))
k_1	Langmuir second order forward rate coefficient ($\text{cm}^3/\text{mg s}$)
k_2	Langmuir first order reverse rate coefficient ($1/\text{s}$)
k_f	External film mass transfer coefficient (cm/s)
m	Mass of particles (g)
q	Solute concentration in particle (mg/g)
q_m	Langmuir saturation capacity (mg/g)
$\bar{q}$	Particle-average solute concentration (mg/g)
r	Particle radial coordinate (cm)
R	Separation factor defined by Eq. (8(a))
R_p	Particle radius (cm)
t	Time (s)
V	Bulk solution volume (cm^3)
z_j^{exp}	Experimental data (C/C_o) for observation j
z_j^{mod}	Model prediction (C/C_o) for observation j
$\bar{z}^{exp}$	Mean of experimental data (C/C_o)

Greek Letters

α	Parameter defined by Eq. (6(a)) (mg/g)
β	Parameter defined by Eq. (6(a)) (mg/g)
ε_p	Porosity of particle
ρ_p	Density of particle (g/cm^3)

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