

A simple and rapid approach to modeling chromium breakthrough in fixed bed adsorber

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Abstract. A simple mathematical model for predicting fixed bed adsorption dynamics is described. The model is characterized by a linear adsorption isotherm and a linear driving force expression for mass transfer. Its analytic solution can be approximated with an algebraic equation in closed form which is easily evaluated by spreadsheet computation. To demonstrate one application of the fixed bed model, a previously published adsorption system is used as a case study in this work. The adsorption system examined here describes chromium breakthrough in a fixed bed adsorber packed with imidazole functionalized adsorbent particles and is characterized by a nonlinear adsorption isotherm. However, the equilibrium behavior of the fixed bed adsorber is in essence governed by a linear adsorption isotherm due to the use of a low influent chromium concentration. It is shown that chromium breakthrough is predicted reasonably well by the fixed bed model. The model's parameters can be easily extracted from independent batch experiments. The proposed modeling approach is very simple and rapid, and only Excel is used for computation.

Keywords: fixed bed; breakthrough curve; modeling; linear isotherm; linear driving force

1. Introduction

Adsorption provides an efficient means of removing organic and inorganic contaminants (Alizadeh and Zeidi 2017, Çifçi 2016, Gonsalvesh *et al.* 2017, Kalpaklı 2015) as well as recovering valuable resources (Galhoum *et al.* 2017) from waste streams. Several process configurations such as batch, fixed bed, expanded bed, fluidized bed, and moving bed may be used to process aqueous waste streams, each with its own advantages and limitations. Among them, fixed bed adsorbers offer definite advantages in simplicity and ease of operation and are widely used in full-scale applications.

A variety of mathematical models have been developed for the design and optimization of fixed bed adsorbers (Jang and Lee 2016, Jung *et al.* 2017). For porous adsorbents, a single intraparticle diffusional resistance (surface or pore) coupled with an external mass transfer resistance provides a realistic description of the rate of adsorption. To reduce model complexity and computational time in fixed bed modeling, the intraparticle diffusion formulation is often replaced by the classic linear driving force (LDF) rate expression developed by Glueckauf (1955). When the adsorption

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isotherm is nonlinear, a numerical solution of the fixed bed model is generally required, necessitating the use of specialized software packages (Davila-Guzman *et al.* 2016, Gama *et al.* 2017, Inglezakis and Fyrillas 2017, Knox *et al.* 2016, Landry and Boyer 2017, Luo *et al.* 2016).

Analytic solutions are an attractive alternative to numerical solutions since they can be more easily implemented in spreadsheet programs. For systems with a linear adsorption isotherm, analytic solutions have been derived to describe their breakthrough behavior however complex the mass transfer model selected is. These solutions, summarized in the monograph by Ruthven (1984), are however in the form of fairly complex equations. For spreadsheet computation, one may use simplified versions of these analytic solutions.

In this work, the breakthrough behavior of a previously published nonlinear adsorption system has been modeled using an analytic solution of a fixed bed model that incorporates a linear adsorption isotherm and a solid film LDF rate expression. The adsorption system considered here describes the uptake of chromium by an imidazole functionalized adsorbent in both batch and fixed bed contactors (Park and Tavlarides 2008). Although the batch equilibrium data collected over a large concentration range exhibit a nonlinear trend, the data in the low concentration range can be approximated with a linear adsorption isotherm. The use of a low influent chromium concentration in the fixed bed experiment of Park and Tavlarides (2008) allows the fixed bed adsorber to be treated as a linear adsorption system.

2. Theory

For a plug flow fixed bed adsorption column with equilibrium governed by a linear adsorption isotherm and the rate of adsorption represented by a solid film LDF expression, the breakthrough curve for a step change in feed concentration at time zero is given by the solution of the following set of equations

$$\varepsilon \frac{\partial c}{\partial t} + \varepsilon v \frac{\partial c}{\partial z} + \rho(1 - \varepsilon) \frac{\partial q}{\partial t} = 0 \quad (1)$$

$$\frac{\partial q}{\partial t} = k(q^* - q) \quad (2)$$

$$q^* = Kc \quad (3)$$

$$t = 0: c = 0, q = 0; \quad z = 0: c = c_0; \quad z = L: \partial c / \partial z = 0 \quad (4)$$

In these equations, c is the liquid phase adsorbate concentration, c_0 is the initial adsorbate concentration, q is the solid phase adsorbate concentration, q^* is the solid phase adsorbate concentration in equilibrium with the bulk solution, k is the LDF mass transfer coefficient, K is the equilibrium constant, ρ is the adsorbent particle density, ε is the bed void fraction, v is the interstitial velocity, t is the time coordinate, z is the axial coordinate, and L is the bed length.

The solution to Eqs. (1)-(4), originally obtained for an analogous heat transfer case (Anzelius 1926), is

$$\frac{c}{c_0} = 1 - \int_0^n \exp(-\xi - n\tau) I_0(2\sqrt{n\tau\xi}) d\xi \quad (5)$$

with

$$n = \frac{(1-\varepsilon)k\rho KL}{\varepsilon v} ; \quad \tau = \frac{\varepsilon v}{(1-\varepsilon)\rho KL} \left(t - \frac{L}{v} \right) \quad (6)$$

where I_0 is the modified Bessel function of zeroth order, ξ is an integration variable, and n and τ are dimensionless bed length and time, respectively. The right-hand-side of Eq. (5) is the so-called J function (Hiester and Vermeulen 1952), which is a two-parameter function of n and $n\tau$.

$$J(n, n\tau) = 1 - \int_0^n \exp(-\xi - n\tau) I_0(2\sqrt{n\tau\xi}) d\xi \quad (7)$$

The numerical value of the J function is between zero and one. Since the J function is somewhat complex, its values have been presented in both tabular and graphical form. For spreadsheet computation, the following approximate expression (Thomas 1948) may be used

$$J(n, n\tau) \cong \frac{1}{2} \left[1 - \operatorname{erf}(\sqrt{n} - \sqrt{n\tau}) \right] + \frac{\exp\left[-(\sqrt{n} - \sqrt{n\tau})^2\right]}{2\sqrt{\pi} \left[\sqrt{n\tau} + \sqrt[4]{n \times n\tau} \right]} \quad (8)$$

Eq. (8) is accurate to <1% error for $n \times n\tau \geq 36$. Furthermore, at $n \times n\tau \geq 3600$, the last term of Eq. (8) can be dropped and the J function becomes

$$J(n, n\tau) \cong \frac{1}{2} \left[1 - \operatorname{erf}(\sqrt{n} - \sqrt{n\tau}) \right] \quad (9)$$

The entity $\operatorname{erf}(x)$ denotes the error function of x , where x is a dummy variable, and is given by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\lambda^2) d\lambda \quad (10)$$

$$\operatorname{erf}(-x) = -\operatorname{erf}(x) \quad (11)$$

where λ is an integration variable. The error function is included as a function in most spreadsheet programs. Eq. (5) can now be simplified to the following form

$$\frac{c}{c_0} = \frac{1}{2} \left[1 - \operatorname{erf}(\sqrt{n} - \sqrt{n\tau}) \right] \quad (12)$$

3. Results and discussion

Literature data of a chromium breakthrough experiment together with equilibrium and kinetic data obtained from batch experiments reported by Park and Tavlarides (2008) are used to assess the predictive ability of the fixed bed adsorber model presented above. For the column adsorption experiment, a laboratory-scale fixed bed adsorber with an internal diameter of 0.7 cm and a bed depth (L) of 2.5 cm was packed with 0.5 g of imidazole functionalized sol-gel adsorbent particles, giving a bed void fraction (ε) of 0.33. The properties of the adsorbent are: average particle size=153 μm and particle density (ρ)=986 g/L. The fixed bed breakthrough experiment was

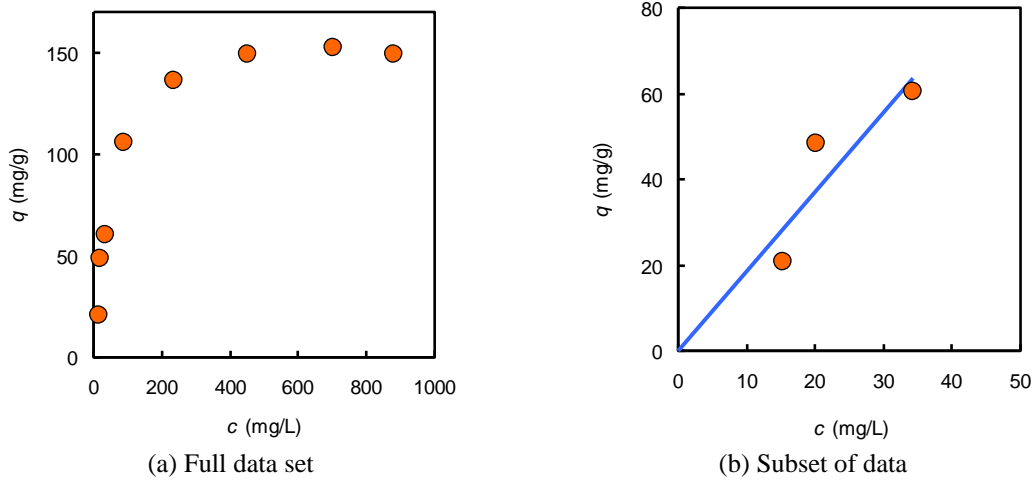


Fig. 1 Batch equilibrium data for chromium adsorption on imidazole functionalized sol-gel adsorbent at pH 2.5, data of Park and Tavlarides (2008)

conducted using an initial chromium concentration (c_0) of 50 mg/L at pH 2.6 and at a flow rate of $1.1 \text{ cm}^3/\text{min}$ (interstitial velocity (v)= $8.66 \text{ cm}/\text{min}$). According to Park and Tavlarides (2008), the initial chromium concentration of 50 mg/L falls within the concentration range of industrial wastewaters.

The equilibrium constant K of the linear adsorption isotherm (Eq. (3)) and the mass transfer coefficient k of the LDF rate expression (Eq. (2)) serve as key input parameters to the fixed bed adsorber model and they are extracted from independent batch experiments. Batch adsorption equilibrium data reported by Park and Tavlarides (2008) show that chromium uptake capacity decreases with increasing solution pH. Because the influent chromium concentration for the fixed bed experiment is 50 mg/L at pH 2.6, the relevant concentration range for estimating K from equilibrium data is the 0-50 mg/L range measured at the same pH. Fig. 1(a) shows batch equilibrium data measured at a similar pH of 2.5. It is apparent that the data exhibit a nonlinear equilibrium distribution relationship over a relatively large liquid phase concentration range (0-900 mg/L). The shape of the equilibrium relationship over the 0-50 mg/L range is shown in Fig. 1(b). Due to a lack of data, it is difficult to ascertain whether the three data points exhibit a linear equilibrium relationship. Nevertheless, the solid line in Fig. 1(b) indicates that the three data points can be approximated fairly well by a linear isotherm with a K value of 1.86 L/g.

Next, we extract the LDF mass transfer coefficient k from batch kinetic data reported by Park and Tavlarides (2008) for the same adsorption system. The mass conservation equation and initial condition for adsorption in batch mode is given by

$$V \frac{dc}{dt} + m \frac{dq}{dt} = 0 \quad (13)$$

$$t = 0: \quad c = c_0, \quad q = 0 \quad (14)$$

where V is the solution volume and m is the adsorbent mass. For linear adsorption, the following solution to Eqs. (13) and (14) and (2) and (3) has been given by Chu (2014)

$$\frac{c}{c_0} = \frac{1}{1 + \alpha} \left\{ \alpha + \exp \left[- \left(\frac{1 + \alpha}{\alpha} \right) kt \right] \right\} \quad (15)$$

where $\alpha = V/mK$. Note that Eq. (15) may be rearranged to allow estimation of k by means of linear regression

$$\frac{\alpha}{1 + \alpha} \left\{ \ln \left[(1 + \alpha) \frac{c}{c_0} - \alpha \right] \right\} = -kt \quad (16)$$

It is evident that a plot of the left-hand-side of Eq. (16) versus t should be linear with slope $-k$.

For a given batch kinetic experiment, the parameters V and m are known and the equilibrium constant K can be obtained from batch equilibrium data, as discussed above. The LDF mass transfer coefficient k is thus the only fitting parameter in Eq. (15) which may be obtained by matching the equation to the concentration versus time data of the batch test. Fig. 2 shows batch kinetic data of Park and Tavlarides (2008) obtained with the following experimental conditions: $c_0=50$ mg/L, $V=0.25$ L, $m=0.5$ g, and pH=4.5. Note that the pH value of the batch kinetic test is noticeably higher than that of the fixed bed case, which is pH 2.6. In the absence of kinetic data measured at the same pH value of the fixed bed case, we will fit Eq. (15) to this set of kinetic data measured at pH 4.5 in order to obtain an approximate value for k . Consequently, the K value reported above, which has been obtained from the equilibrium data measured at pH 2.5 (Fig. 1(b)), cannot be used as input parameter to Eq. (15). A new K value must be extracted from equilibrium data measured at pH 4.5. Figs. 3(a) and 3(b) show respectively the full set of equilibrium data measured at pH 4.5 and a subset of the data over the 0-50 mg/L concentration range. The equilibrium distribution relationship is again nonlinear over the 0-900 mg/L concentration range. The equilibrium trend over the 0-50 mg/L concentration range is approximated with a linear adsorption isotherm, yielding a K value of 1.09 L/g, as indicated by the solid line in Fig. 3(b).

Using the K value obtained from Fig. 3(b) and the known values of V and m , the parameter α in Eq. (15) can now be computed. We fit Eq. (15) to the Fig. 2 kinetic data using the Solver function of Excel, obtaining a best-fit value of 0.20 min^{-1} for k . From Fig. 2, it is apparent that the fit is not accurate. It can be seen that Eq. (15) is not able to track the shape of the experimental concentration decay profile, predicting noticeably higher c/c_0 values. In other words, Eq. (15) underestimates the extent of chromium uptake at large values of time when apparent equilibrium is established. The extent of chromium uptake at equilibrium is governed by the value of K . The discrepancy is most likely due to errors associated with K . A lack of data points in the 0-50 mg/L concentration range makes it somewhat difficult to get an accurate estimate of K (see Fig. 3(b)). Nonetheless, the k value so obtained is still adequate for preliminary modeling, as discussed below.

A single chromium breakthrough curve is presented in the Park and Tavlarides (2008) article. In Fig. 4 the experimental breakthrough curve is compared with prediction calculated from the approximate expression given by Eq. (12). Excel is used for the computation. Values of the parameters required by the dimensionless bed length and time parameters n and τ (see Eq. (6)) are summarized in Table 1. Note that no adjustable parameters are used to generate the prediction shown in Fig. 4. As can be seen in Fig. 4, a sharp experimental breakthrough curve is obtained, indicating that mass transfer is not a significant limit to performance. The experimental breakthrough behavior is predicted reasonably well by Eq. (12). In particular, Eq. (12) is able to

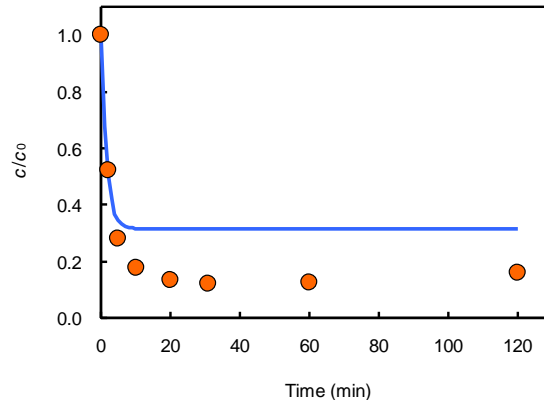


Fig. 2 Batch kinetic data for chromium adsorption on imidazole functionalized sol-gel adsorbent at pH 4.5, data of Park and Tavlarides (2008)

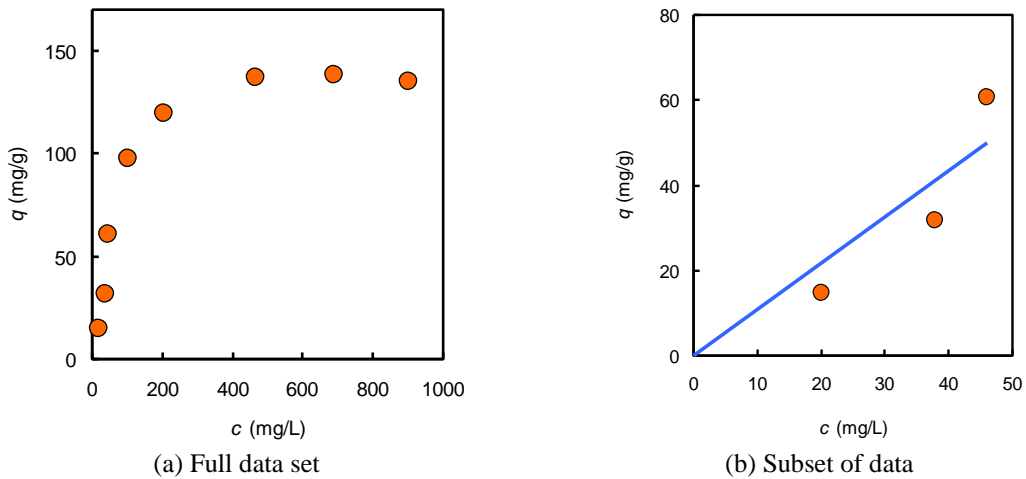


Fig. 3 Batch equilibrium data for chromium adsorption on imidazole functionalized sol-gel adsorbent at pH 4.5, data of Park and Tavlarides (2008)

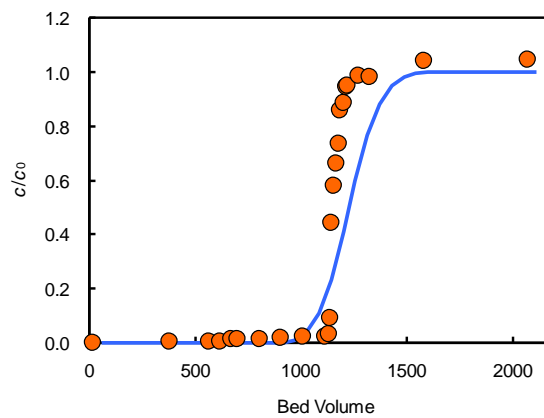


Fig. 4 Comparison of experimental breakthrough data and prediction obtained from Eq. (12), data of Park and Tavlarides (2008)

Table 1 Parameters for calculation of breakthrough curve

Parameter	Value	Units
Bed depth (L)	2.5	cm
Bed void fraction (ε)	0.33	–
Adsorbent density (ρ)	986	g/L
Interstitial velocity (v)	8.66	cm/min
Equilibrium constant (K)	1.86	L/g
LDF coefficient (k)	0.20	min ⁻¹

predict the initial portion of the breakthrough curve. This result has practical importance because the onset of a breakthrough curve determines the breakthrough time for a specified breakthrough concentration. The good agreement around the early breakthrough levels validates the assumption of linear adsorption for the fixed bed adsorber. Because the position of the predicted breakthrough curve is primarily governed by the equilibrium constant K , the good agreement also indicates that the use of a linear adsorption isotherm to fit the batch equilibrium data in the 0-50 mg/L concentration range appears reasonable (see Fig. 1(b)).

An alternative to Eq. (12), developed by Klinkenberg (1948), is available in the literature. The approximate expression of Klinkenberg is written as

$$\frac{c}{c_0} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\sqrt{n\tau} - \sqrt{n} + \frac{1}{8\sqrt{n\tau}} + \frac{1}{8\sqrt{n}} \right) \right] \quad (17)$$

It is obvious that Eq. (17) is very similar to Eq. (12). The Klinkenberg equation has been used by Chatterjee and Schiewer (2014), Chu (2014), and Gutiérrez Ortiz *et al.* (2014) to model the column breakthrough characteristics of adsorption systems characterized by nonlinear isotherms. The use of relatively low feed concentrations in the fixed bed experiments of Chatterjee and Schiewer (2014) and Chu (2014) allowed adsorption in the fixed bed adsorbers to take place under linear conditions. Both studies report satisfactory fixed bed modeling results obtained from the Klinkenberg equation. By contrast, in the work of Gutiérrez Ortiz *et al.* (2014) some fixed bed experiments employed relatively high feed concentrations, allowing the nonlinear isotherm to govern the fixed bed adsorber behavior. The study of Gutiérrez Ortiz *et al.* (2014) reports significant discrepancies between breakthrough profiles calculated from the Klinkenberg equation and experimental breakthrough curves, especially around the early breakthrough levels.

As can be seen from Fig. 4, Eq. (12) fails to give precise prediction on a point-by-point basis; the predicted and experimental curves diverge towards the saturation point with Eq. (12) underestimating the tailing portion of the experimental curve. The discrepancy may be attributed to the fact that a somewhat imprecise estimate of the LDF mass transfer coefficient k (see Fig. 2) has been used as input parameter to the fixed bed model. The parameter k governs the shape of the predicted breakthrough curve. Another possible reason for the deviation is that the k value extracted from the batch kinetic test contains contributions from external film mass transfer. The LDF coefficient k can be regarded as an overall lumped parameter containing the effects of both external and internal transport resistances. The external film transport resistance depends on the hydrodynamics of the moving fluids and so is influenced by the mode of operation. Accordingly, one should not use Eq. (12) with a k value extracted from a batch adsorber in which the external

film transport resistance dominates the adsorption rate to predict fixed bed dynamics. On the other hand, the intraparticle diffusional resistance is an intrinsic property of a given adsorption system and is independent of the mode of operation. For this reason, Eq. (12) with a k value obtained from a batch adsorber with the adsorption rate dominated by the internal transport resistance is likely to be able to track the shape of breakthrough curves of a fixed bed adsorber with the adsorption rate dominated by the same mass transfer resistance.

We have used Eq. (12) to calculate the breakthrough curve shown in Fig. 4, which is valid for $n \times n \tau > 3600$. Using the parameter values listed in Table 1, we obtain $n = 216$ from Eq. (6). Therefore, the criterion of $n \times n \tau > 3600$ requires that τ be > 0.08 . This means that t must be > 86 min, according to Eq. (6). This value of t translates to 99 bed volumes. From Fig. 4, we can see that the breakthrough curve begins to emerge at around 900 bed volumes; the criterion for use of Eq. (12) is met.

4. Conclusions

The simple fixed bed model described in this work, which is valid for linear adsorption, has been shown to provide satisfactory prediction of chromium breakthrough in a fixed bed adsorber characterized by a nonlinear adsorption isotherm. Due to the use of a low influent chromium concentration, the equilibrium behavior of the fixed bed adsorber is in essence governed by a linear adsorption isotherm. The model's parameters can be estimated from independent batch equilibrium and kinetic data. The approximate analytic expression of the fixed bed model is very straightforward, easy to apply, and provides acceptable quantitative results. For rapid calculations of fixed bed breakthrough curves under the condition of linear adsorption, the approximate expression may be used quite effectively.

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