Chemical Engineering Journal 97 (2004) 233–239

Chemical Engineering Journal

www.elsevier.com/locate/cej

Improved fixed bed models for metal biosorption

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Accepted 9 May 2003

Abstract

This paper describes the application of two new mathematical models, derived from an existing model with two adjustable parameters, to simulate the breakthrough curves of metal biosorption in fixed bed columns. No new adjustable parameters are introduced into the modified models. The models offer a fast and accurate alternative to the conventional mass balance-based models which are much more complicated mathematically. The major characteristic of this empirical modeling approach is that it requires experimental breakthrough data for model calibration. Modeling results suggest that the new models are capable of describing symmetric and asymmetric experimental breakthrough curves selected from the biosorption literature. Compared to the original model, the modified models show significant improvements for modeling breakthrough curves obtained with columns packed with native biomass but yield only small improvements on deviations from breakthrough data obtained with a column packed with immobilized biomass.

Keywords: Adsorption; Biosorption; Breakthrough curve; Heavy metals; Packed bed

1. Introduction

In recent years increasing concern about the effect of toxic metals in the environment has resulted in more stringent environmental regulations for industrial operations that discharge metal-bearing effluents. The existing physical-chemical treatment technologies appear to be inadequate or prohibitively costly to reduce the metal concentrations in wastewater to acceptable regulatory standards. As a result, highly efficient and cost-effective treatment technologies are needed. Biosorption is one such emerging bioremediation tool that is gaining attention among environmental research communities.

Numerous studies on metal biosorption in batch systems have been reported in the literature. However, in the practical operation of full-scale biosorption processes, continuous-flow fixed bed columns are often preferred. In such systems the concentration profiles in the liquid and adsorbent phases vary in both space and time. As a result, design and optimization of fixed bed columns are difficult to carry out a priori without a quantitative modeling approach. From the perspective of process modeling, the dynamic behavior of a fixed bed column is described in terms of the effluent concentration-time profile, i.e. the breakthrough curve.

A typical breakthrough curve for a contaminant is shown in Fig. 1 as the ratio of the effluent concentration (C_e) to the influent concentration (C_i) versus time or throughput volume. The shape of this curve is determined by the shape of the equilibrium isotherm and is influenced by the individual transport processes in the column and in the adsorbent. The most efficient adsorption performance will be obtained when the shape of the breakthrough curve is as sharp as possible. Fig. 1 shows that for short times contaminant in the feed is taken up completely by the column. After a while contaminant breakthrough occurs and the effluent concentration increases with time. It is normal practice in single column operations to terminate the influent flow at the breakthrough time (t_{bt}) at which the contaminant reaches a specified concentration, C_{bt}. For multiple columns operated in series, loading of the columns continues until the saturation point (t_{st}) is reached at which the effluent concentration becomes equal to the feed concentration. The variation of the breakthrough point and saturation point with respect to operating variables such as the influent flow is therefore of great practical interest. The general position of the breakthrough curve along the time or effluent volume axis depends on the capacity of the column with respect to the amount of contaminant applied to the column. The breakthrough curve shown in Fig. 1 is symmetric at $C_e/C_i = 0.5$.

Although a body of work carried out using laboratory-scale biosorption columns exists in the literature [1–12], very few have provided mathematical models to describe the

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1385-8947/$ – see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/S1385-8947(03)00214-6

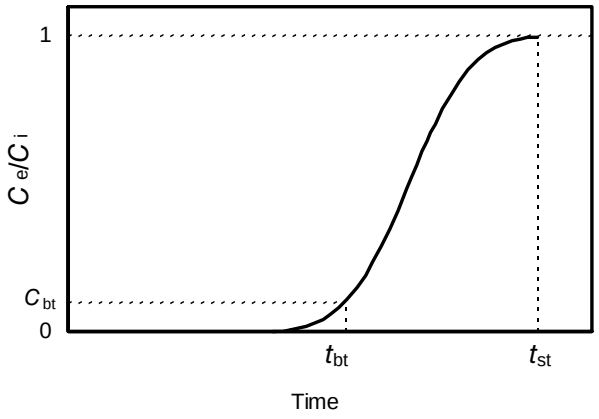

Fig. 1. A typical S-shaped breakthrough curve.

observed breakthrough behavior. An excellent summary of theoretical models for predicting breakthrough curves of fixed bed columns packed with spherical adsorbents has been given by Ruthven [13], and several of these models adapted for the design of activated carbon fixed-bed adsorbers for wastewater treatment are well covered in the recent book of Cooney [14]. In the general case a mechanistic model considers axial dispersion in the direction of the liquid flow, film diffusion resistance, intraparticle diffusion resistance which may include both pore and surface diffusion, and sorption kinetics at the adsorbent surface. Because of the nonlinearity associated with the equilibrium expressions, a full solution of the resulting set of partial differential equations requires complicated numerical solution. In addition, to obtain a priori prediction of the breakthrough curve independent experiments and/or reliable engineering correlations are required to estimate the numerous equilibrium, transport, and sorption kinetic parameters.

In the area of fixed bed biosorption modeling, Abdel-Jabbar et al. [15] employed a rigorous model that considers axial dispersion, external film resistance, and intraparticle diffusion to describe copper biosorption in a column packed with moss. Because of the mathematical complexity and difficulty in determining some of the parameters employed in this type of rigorous models, simplified modeling approaches have been used by a number of investigators. The most commonly used simplification avoids the complexity of solving the partial differential equation for intraparticle diffusion by using the approximation of a linear driving force model. Another common simplification involves the assumption of local equilibrium which eliminates the need to consider the kinetics of adsorption. For example, Trujillo et al. [16] used a simplified fixed bed model that considers plug flow of the liquid phase and a linearized mass transfer rate expression to model breakthrough curves obtained with a column packed with immobilized sphagnum peat moss. The biosorption of copper [17,18] as well as a multimetal mixture [19] on seaweed biomass was modeled by means of a fixed bed model that considers axial dispersion and linearized mass transfer expressions. Hatzikioseyian et al. [20] applied a simplified fixed bed model based on the concept of rapid local equilibrium to simulate experimental breakthrough curves selected from the biosorption literature. Mass transfer resistances in the liquid and solid phases and other rate processes were lumped into an apparent overall dispersion coefficient. In general, the above approaches require a numerical solution in cases where the equilibrium isotherm is nonlinear. None of the studies have dealt with a priori prediction of the breakthrough curves as the model parameters were determined by fitting the model to experimental breakthrough curves. Such multiparameter fitting of experimental breakthrough curves may reduce the physical significance of the mechanistic parameters.

If the goal is to model the breakthrough behavior of a biosorption column with a high degree of accuracy, the use of simpler and more tractable models that avoid the need for numerical solution appears more suitable and logical and could have immediate practical benefits. Several such models have been applied to biosorption columns. The well-known Bed-Depth–Service–Time analysis derived from the Bohart–Adams model has been used by a number of researchers to model the breakthrough behavior of biosorption columns [21–26]. A dose–response model [27] and a simple two parameter model [28,29] have recently been tested for their ability to describe biosorption breakthrough curves. In general, these semiempirical models are easier to use and more efficient from a computational point of view compared to the use of full mechanistic models which are much more complicated mathematically. Although each of these approaches has shown sufficiently accurate results, deviations between simulations and experimental breakthrough data have been observed in some cases. The purpose of the present paper is to present two new mathematical models, derived from an existing two parameter model, for the modeling of the breakthrough behavior of biosorption columns. Literature breakthrough data obtained with columns packed with native and immobilized biomass are used to test the models.

2. Mathematical modeling of breakthrough curves

A simple two parameter model for the modeling of breakthrough curves described by Belter et al. [30] takes the form

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \mathrm{erf}\left[\frac{t - t_0}{\sqrt{2}\sigma t_0}\right]\right) \quad (1)$$

where erf[x] is the error function of x, t is the column residence time, t_0 is the time at which the effluent concentration is half the influent concentration, and σ represents the standard deviation which is a measure of the slope of the breakthrough curve. The likely mechanism influencing the shape of the breakthrough curve may be deduced from the relationships between σ^2 and the superficial velocity (v) and column length (L), as shown in Table 1 [30].

Table 1
Characteristics of the standard deviation σ for breakthrough curves [30]

Controlling mechanism	σ^2
Equilibrium	$\propto 1/L$
Kinetics of adsorption	$\propto v/L$
Mass transfer	$\propto v^{1/2}/L$
Dispersion	$\propto v/L$
Diffusion	$\propto 1/Lv$

The model parameters t_0 and σ can be estimated by fitting Eq. (1) to experimental breakthrough data. Since major process variables such as influent flow rate, column length, and adsorbent particle size are not incorporated in Eq. (1), it is necessary to empirically correlate the two model parameters with these variables in order to use Eq. (1) to simulate the dynamics of a biosorption column operated under varying experimental conditions.

As will be discussed later, in general Eq. (1) is capable of modeling symmetric breakthrough curves but some deviations between model simulations and experimental breakthrough curves have been observed in cases where the curves are of asymmetric shape. To enhance the ability of Eq. (1) to model asymmetric breakthrough curves, it is modified as follows:

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{(t - t_0)\exp(\sigma(t/t_0))}{\sqrt{2}\sigma t_0}\right]\right) \quad (2)$$

$$\frac{C_e}{C_i} = \frac{1}{2}\left(1 + \text{erf}\left[\frac{(t - t_0)\exp(-\sigma(t/t_0))}{\sqrt{2}\sigma t_0}\right]\right) \quad (3)$$

Note that the modified equations do not require any additional parameters.

3. Results and discussion

The presentation in this article was motivated by the work of Brady et al. [28] who tested the ability of Eq. (1) to model biosorption breakthrough curves. Our purpose is to supplement their work by modifying the mathematical form of Eq. (1) to enhance its curve-fitting capability. Our objective will be accomplished through a comparison of Eq. (1), the original model, and Eqs. (2) and (3), the new models, using experimental breakthrough data selected from the biosorption literature. A nonlinear least-squares regression program based on a combination of Gauss-Newton and Levenberg–Marquardt methods is used to fit Eqs. (1)–(3) to experimental breakthrough data. The criterion for measuring the accuracy of Eqs. (1)–(3) is the absolute error (E):

$$E = \frac{1}{n}\sum_{i=1}^{n}|e_i - s_i| \quad (4)$$

where e and s denote experimental and calculated C_e/C_i values, respectively, and n is the number of data points.

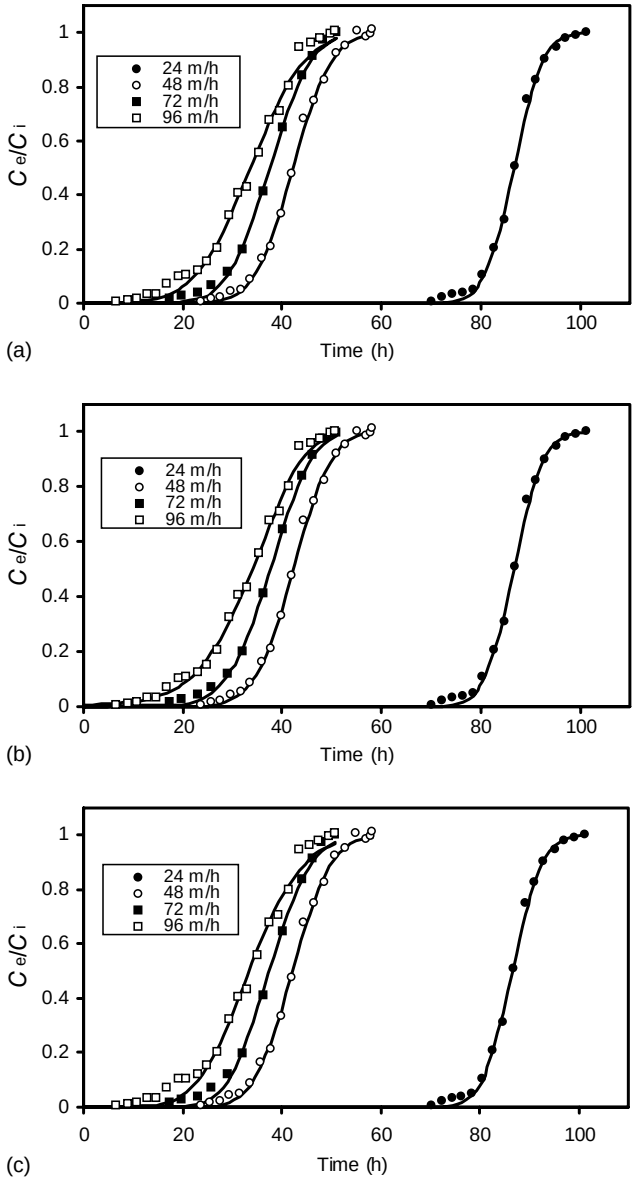

Fig. 2. Breakthrough curves for cadmium on 70.5 cm × 0.4 cm column packed with *A. nodosum* biomass [21]. Symbols, experimental; lines, from Eq. (1) (a), Eq. (2) (b), and Eq. (3) (c).

3.1. Biosorption of cadmium by Ascopyllum nodosum

Biosorption of cadmium by the marine alga *A. nodosum* in a fixed bed column has been reported by Volesky and Prasetyo [21]. The laboratory-scale column used was 70.5 cm long with 0.4 cm internal diameter. Continuous cadmium sequestration from an influent solution of 10 mg/l cadmium was measured at four different superficial velocities in the range 24–96 m/h. The resulting breakthrough curves, shown in Fig. 2 (symbols), are used in this work to test Eqs. (1)–(3). Breakthrough curves calculated from Eqs. (1)–(3) are also included in Fig. 2 (lines) and these are discussed later. As expected, Fig. 2 shows that the breakthrough curves shifted towards the origin with increasing velocity. When the velocity

was increased from 24 to 96 m/h the time required for complete column saturation decreased from 100 h to about 50 h. The breakthrough pattern varies from the sigmoidal shape at $v = 24$ m/h to curves of asymmetric shape at higher velocities. In particular, a shallow breakthrough curve is obtained at the highest velocity tested ($v = 96$ m/h). In addition, the curve has a broad leading edge, indicating poor utilization of the column capacity. The use of high flow rates reduces the time that cadmium in the solution is in contact with the biomass, thus allowing less time for biosorption to occur, leading to an early breakthrough of cadmium. However, the use of low flow rates will result in long overall processing times which may not be desirable in practice when large volumes of metal-bearing wastewater have to be processed.

The model parameters t_0 and σ for the biosorption of cadmium on *A. nodosum* are found by matching Eqs. (1)–(3) to the experimental data shown in Fig. 2. Breakthrough curves calculated using these best fit values for t_0 and σ are shown as lines in Fig. 2, in comparison with the experimental data. Overall, the experimental data are well represented by Eqs. (1)–(3) over a wide range of influent flow rate. A summary of the errors calculated from Eq. (4) is given in Table 2. As seen in Table 2, Eq. (2) yields major improvements over Eq. (1), the original model. It reduces the average error, averaged over the four data sets, by about 19%. However, the modeling results based on the other modified model, Eq. (3), are less satisfactory than those based on the original model. Table 2 also indicates that for all three equations deviations from experimental data are the highest at $v = 96$ m/h. It may be seen from Fig. 2 that all three equations overestimate the sharpness of the leading and trailing edges of the experimental breakthrough curve at this flow rate.

Table 2
Errors calculated from Eq. (4) for comparisons of model simulations and experimental breakthrough data for the biosorption of cadmium by *A. nodosum* (Fig. 2) [21]

Velocity (m/h)	*E*		
	Eq. (1)	Eq. (2)	Eq. (3)
24	0.013	0.013	0.013
48	0.012	0.011	0.014
72	0.016	0.011	0.018
96	0.024	0.017	0.029
	Average *E*		
	0.016	0.013	0.019

Fig. 3 displays the relationships between t_0 and σ of Eq. (1) and the superficial velocity. The parameter t_0 is inversely proportional to v (Fig. 3a) while the best linear correlation is obtained when σ^2 is plotted against v/L (Fig. 3b). According to Table 1, this indicates that the controlling mechanism for this biosorption system is either the kinetics of adsorption or axial dispersion. The linear plots of Fig. 3a and b may be used to estimate t_0 and σ for simulating the breakthrough behavior under flow conditions other than those used to obtain the correlations. However, the drawback of these empirical correlations is that they are calibrated only on the available breakthrough data, without detailed knowledge of the underlying principles. Additionally, t_0 and σ will vary with other process variables such as the dimensions of the column. These empirical correlations may therefore

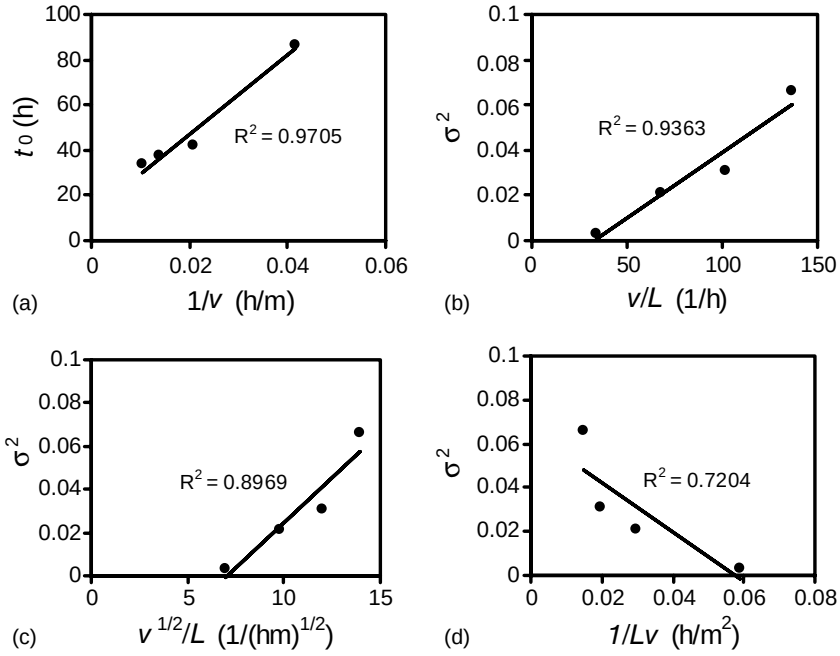

Fig. 3. (a) Variation of t_0 with the inverse of the superficial velocity. (b)–(d) σ^2 plotted against the superficial velocity according to the relationships given in Table 1.

be inadequate and inaccurate for extrapolation because they lack physical significance. As a general rule, the effects of all major operating variables on t_0 and σ should be investigated for each biosorption system. As pointed out previously, such empirical dependence on operating variables of the values of model parameters has also been observed in studies that employed simplified mechanistic models. Consequently, the modeling approach based on simplified mechanistic models suffers from the same drawback.

3.2. Biosorption of copper by immobilized Rhizopus arrhizus and native Mucor miehei

Brady et al. [28] reported breakthrough curves for copper biosorption on two fungal biomass; polyvinyl formal-immobilized *R. arrhizus* and native *M. miehei*. These two biosorption systems are also used in this work to test Eqs. (1)–(3). For the immobilized biosorption system, biomass beads of 0.5–1.0 mm in diameter were packed into a laboratory-scale column 7 cm in length with 1.4 cm diameter. Aqueous solutions containing 150 mmol/l copper at pH 4 were pumped in an upward direction through the column at flow rates ranging from 3.4 to 11.6 ml/min. Representative experimental breakthrough curves at four flow rates are shown in Fig. 4 (symbols), along with modeling results (lines). The breakthrough patterns for copper biosorption on immobilized *R. arrhizus* are different from those for cadmium biosorption on *A. nodosum* (see Fig. 2). An increase in the rate of influent flow appears to increase the sharpness of the breakthrough curves. The curves exhibit a sharp leading edge and a very broad trailing edge, especially at high influent flow rates. The broadness of the trailing edge is most likely due to slow intraparticle diffusion within the pores of the immobilized biomass beads. Copper ions must first diffuse into the porous beads before sequestration of the metal ions by the fungal biomass could take place. According to Cooney [31], the 'tailing' of a breakthrough curve (i.e. a slow approach of C_e/C_i towards 1) is commonly observed in liquid phase sorption where intraparticle diffusion is the rate-limiting transport process.

Eqs. (1)–(3) are fitted to the experimental breakthrough data of Fig. 4 by simultaneously determining optimum values of t_0 and σ as a function of influent flow rate. Calculated curves are in reasonably good agreement with experimental data, as shown in Fig. 4. However, systematic discrepancies are found in all cases; the latter stage of the breakthrough curves is found to trail behind the models. Nevertheless, it appears that the broad trailing edge of the breakthrough curves can be adequately described by Eq. (3). Comparisons of the errors listed in Table 3 indicate that Eq. (3) is the best performing model. However, the improvements of Eq. (3) over Eq. (1), the original model, are small; the average error is reduced by about 8%. Furthermore, Eq. (1) outperforms Eq. (2), the other modified model.

The data of Brady et al. [28] on copper biosorption on native *M. miehei* are used. A series of columns of diame-

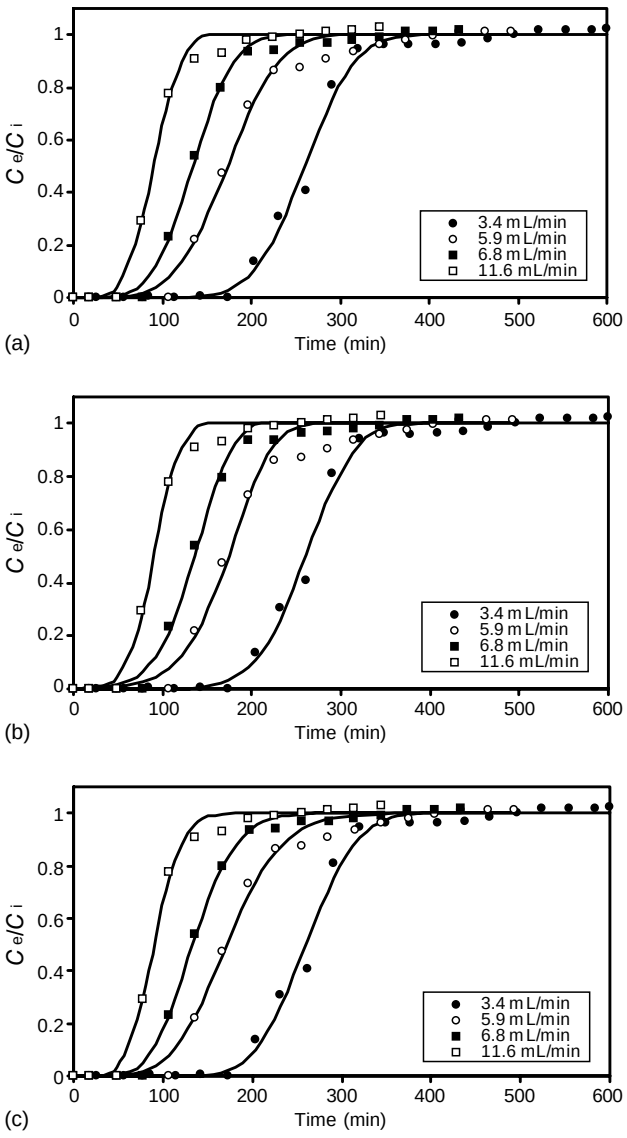

Fig. 4. Breakthrough curves for copper on 7 cm × 1.4 cm column packed with immobilized *R. arrhizus* biomass [28]. Symbols, experimental; lines, from Eq. (1) (a), Eq. (2) (b), and Eq. (3) (c).

Table 3
Errors calculated from Eq. (4) for comparisons of model simulations and experimental breakthrough data for the biosorption of copper by immobilized *R. arrhizus* (Fig. 4) [28]

Flow rate (ml/h)	*E*		
	Eq. (1)	Eq. (2)	Eq. (3)
3.4	0.024	0.024	0.024
5.9	0.030	0.035	0.026
6.8	0.021	0.028	0.016
11.6	0.022	0.024	0.020
	Average *E*		
	0.024	0.028	0.022

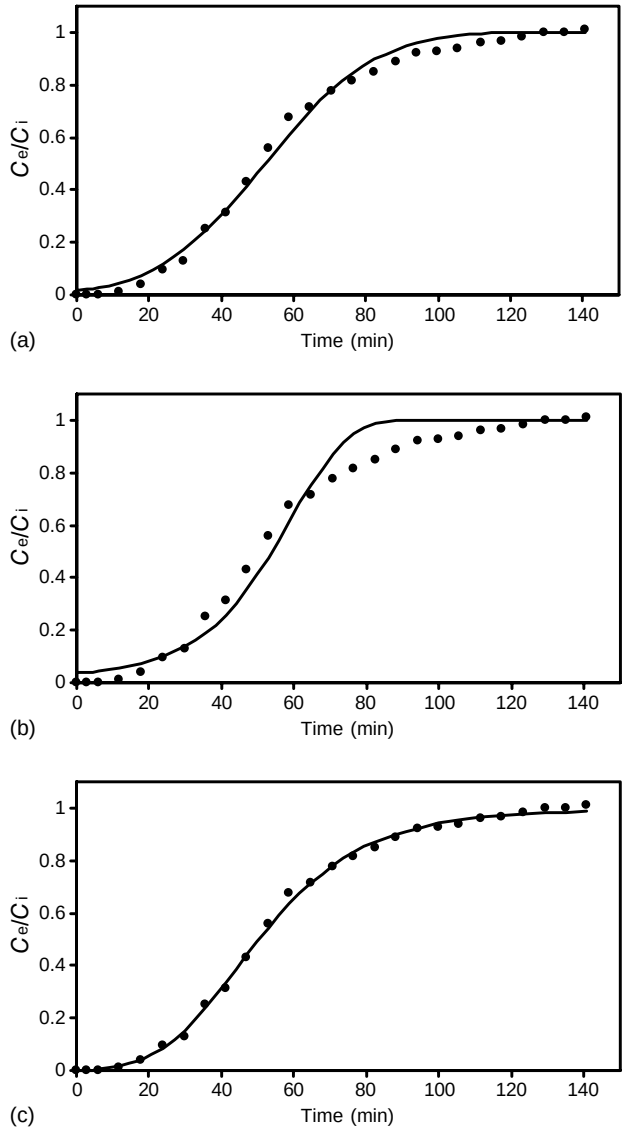

Fig. 5. Breakthrough curves for copper on 5.4 cm × 1.0 cm column packed with native *M. meihei* biomass [28]. Symbols, experimental; lines, from Eq. (1) (a), Eq. (2) (b), and Eq. (3) (c).

ter in the range 10–26 mm were packed with the biomass to various column heights. The columns were tested with an influent solution containing 1000 mmol/l copper at a flow rate of 5 ml/min. Fig. 5 displays a representative experimental breakthrough curve obtained with a column of 5.4 cm in length and 1.0 cm diameter (symbols). Here too, the copper breakthrough curve has an asymmetric shape with a rapid initial rise, followed by a very gradual approach to the feed concentration. This type of breakthrough behavior indicates the existence of either mass transfer limitation or flow non-idealities (e.g. preferential channeling at the column walls). Modeling results show that significant deviations exist between breakthrough curves calculated from Eqs. (1) and (2) and experimental data, as shown in Fig. 5a and b. Eqs. (1) and (2) overestimate the sharpness of the leading and trailing edges of the breakthrough curve, resulting in $E = 0.027$ and 0.053, respectively. In addition, both equations predict a nonzero effluent concentration at $t = 0$ which contradicts real conditions. By contrast, Fig. 5c shows that the breakthrough curve computed from Eq. (3) is in excellent agreement with experimental data ($E = 0.012$). Compared to Eq. (1), Eq. (3) reduces the error by more than half. The improvement of Eq. (3) over Eq. (1) is obvious in this case.

On the basis of the modeling results presented here, it can be concluded that biosorption systems exhibiting breakthrough curves of asymmetric nature can be simulated effectively with the modified models. The new models have been validated against experimental breakthrough data selected from the biosorption literature. It is interesting to compare the curve-fitting capability of the two models. The modeling results show that Eq. (2) is capable of simulating breakthrough curves with a broad leading edge (see Fig. 2b) while Eq. (3) can be used to describe breakthrough curves with a broad trailing edge (see Figs. 4c and 5c). Such close agreement between the simulated and experimental breakthrough curves validates the simplistic modeling approach and suggests that the salient features of the dynamics of biosorption columns have been captured by the mathematical form of the model equations. Since accuracy of a model is generally a function of the number of adjustable parameters in the model, it is worthwhile pointing out that the original model and the two modified models have the same adjustable parameters. Although we have restricted our investigation to biosorption systems, it is reasonable to suggest that any fixed bed adsorption system could be modeled by such an approach. However, the modified models cannot be used as a predictive tool to determine breakthrough a priori because evaluation of the model parameters requires fitting the models to experimental breakthrough data. Sound correlations of the model parameters with operating variables are needed before the models can be used for design and scale-up studies.

4. Conclusions

In this study we have proposed two new mathematical models for the modeling of biosorption column dynamics. The models are based on an existing two parameter model. The modification of the original model does not introduce any new parameters. The modified models require far fewer mathematical manipulations than the conventional mass balance-based models. The modeling results of the new models are clearly better than those of the original model. The two models, although of an empirical nature, are capable of describing symmetric and asymmetric breakthrough curves obtained with continuous-flow columns packed with native seaweed or fungal biomass as well as with fungal biomass immobilized in a polymeric matrix. It is expected that the modified models will be more

widely used for simulating fixed bed biosorption columns. However, using these simple models to design or optimize fixed bed biosorption columns requires knowledge of the effect of process variables on the two model parameters, t_0 and σ.

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