

CHAPTER FOUR

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FIXED-BED BIOSORPTION

MATHEMATICAL MODELING FOR FIXED BED BIOSORPTION

A principal objective of fixed-bed biosorption and ion exchangers is a determination of the breakthrough concentration, or good breakthrough stage or concentration level for a specific set of influent conditions. A predictive mathematical model that accurately describes the concentration history profile of the effluent may be extremely useful in this regard. Accurate input data, including mass transfer and isotherm parameters are essential for the successful development of predictive design models.

Although the general uptake behavior of organic solvents is well established to be ion exchange in nature (Yang and Colwell, 1999; Flanagan et al., 1999) and numerous models providing first principle description of the mechanisms underlying metal biosorption by seaweed biomass including ion exchange, electrostatic interaction and surface complexation phenomena have recently been developed (Schiewer, 1999; Kim et al., 1998), the practical application of these models are still very limited. This is because extremely background work is required for successful model calibration. It is therefore important to select a model which has sufficient accuracy to provide an

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A principal factor in the design of fixed bed adsorbers and ion exchangers is a determination of when the effluent will reach a predetermined breakthrough stage or concentration level for a specific set of influent conditions. A predictive mathematical model that accurately describes the concentration-history profile of the effluent may be extremely useful in this regard. Accurate input data, including mass transport and isotherm parameters are essential for the successful use of predictive design models.

Although the metal uptake behaviour of marine seaweed is well established to be ion exchange in nature (Yang and Volesky, 1999; Figueira *et al.*, 1999) and numerous models providing first principle description of the mechanisms underlying metal biosorption by seaweed biomass including ion exchange, electrostatic interactions and surface complexation phenomena have recently been developed (Schiewer, 1999; Kim *et al.*, 1998), the practical application of these models are still very limited. This is because extensive background work is required for successful model calibration. It is therefore important to select a model which has sufficient accuracy to provide an

adequate representation of a fixed bed operation yet at the same time, simple enough to allow an accurate estimation of its parameters.

4.1 Two Parameter Model

The two parameter model characterises the breakthrough curve in a fixed bed by two parameters: a characteristic time and a standard deviation,

$$\frac{C_e}{C_i} = \frac{1}{2} \left(1 + \operatorname{erf} \left[\frac{t - t_o}{\sqrt{2}\sigma_o} \right] \right) \quad (4.1)$$

where

t_o = time at which the exit concentration is half the feed concentration (h)

σ = standard deviation, a measure of the slope of the breakthrough curve

$\operatorname{erf}[x]$ = error function of x

C_e = effluent concentration (mg/L)

C_i = influent concentration (mg/L)

The values of these two parameters can be obtained from the breakthrough curve. For example, when $C_e = 0.5 C_i$, $t = t_o$. Once t_o is known, σ can be obtained. Equation (4.1) can be used not only to fit experimental data but also extended to operating conditions not obtained experimentally (Belter *et al.*, 1988, Brady *et al.*, 1999). Such estimates depends critically on the standard deviation σ_o . This deviation depends on the solution velocity and the column length as shown in Table 4.1.

Table 4.1: Typical characteristics of the standard deviation for breakthrough curves

Controlling step	The quantity σ^2 is proportional to	The variance $(\sigma_o)^2$ is proportional to
Equilibrium	$1/l$	l/v^2
Kinetics of adsorption	v/l	l/v
Mass transfer	$v^{0.5}/l$	$l/v^{1.5}$
Dispersion	v/l	l/v
Diffusion	$1/lv$	l/v^3

Note: l is column length while v is axial velocity

* Source: Belter *et al.*, (1988)

For fixed bed biosorption, Brady *et al.*, (1999) and Tobin *et al.*, (1995) represented t_0 and σ with constants in Equations 4.2 and 4.3 respectively.

$$t_0 = \frac{k_1}{Q} \quad (4.2)$$

$$\sigma^2 = \frac{k_2 Q}{L} \quad (4.3)$$

where

Q = flow-rate (mL/h)

L = column length (m)

k_1 = constant (mL)

k_2 = constant (mh/mL)

According to Equations (4.2) and (4.3), a linear relationship exists whereby the constants k_1 and k_2 can be obtained. This linear correlation was also mentioned by Brady *et al.* (1999) in his biosorption studies employing *Rhizopus arrhizus* and *Mucor meihei* as biosorbents in his fixed bed operation. The constant k_1 can be obtained from a series of breakthrough curves operated at constant feed concentration and bed depth

with different flow rates. Constant k_2 was obtained by minimizing the objective function F that represents the sum of the squares of the relative deviations between the model and the experimental data for different values of sigma, σ :

$$\text{Minimize } F = \sum_i (X_e - X_m)^2 \quad (4.4)$$

Once the minimized value of σ is obtained, constant k_2 can be evaluated with Equation (4.3). Since Equation (4.1) is actually a statistical model that attempts to predict a given breakthrough curve based on two constants, mass transfer limitations does not affect the values of the two constants as they are derived directly from the breakthrough curve. Hence, Equation (4.1) is independent of internal and external mass transfer limitations. The method presented here to obtain the best-fit values of σ differs from the method used by Brady *et al.* (1999) which is done simply by adjusting the most appropriate value of σ into Equation (4.1) and hence deriving a linear relationship. Such curve fitting method is inaccurate and will compound errors. In the present work, a commercially available mathematical software, MathCAD 2000 professional version was used to evaluate Equation (4.1) together with the corresponding equations. Equation (4.4) was solved using Microsoft Excel spreadsheet.

4.2 Materials and Methods

4.2.1 Materials

Algal biomass of *Sargassum baccularia* that were processed as described in Section 3.3.1 to 3.3.2 are now employed for fixed bed modeling. Analytical grade reagents (Fluka, Switzerland) were used in the experiments. The pH of the solutions was measured and adjusted by using a calibrated pH meter (Metrohm, Switzerland).

A chromatographic column with an I.D. (Internal Diameter) of 1.5 cm and column length of 20 cm together with a variable plunger (Pharmacia) was used for this study. Copper and EDTA solutions were pumped through the column by using a LC-6A liquid chromatography pump (Shimadzu, Japan) with a programmable flow rate. Effluent samples were collected at the column outlet through a programmable fraction collector (Model FC 204, Gilson).

Copper concentration collected by the fraction collector was analyzed by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) using a Baird ICP 2000 (Baird, Switzerland) instrument. Copper standard solutions were prepared by using ICP reagent grade obtained from Fluka (Switzerland).

4.2.2 Methods

Fixed bed studies were categorised into model calibration and model verification. All experiments were conducted at room temperature. For model calibration studies, the chromatographic column was packed with the biomass beads to a bed depth of 13 cm and a probe was inserted into the column to agitate the packed bed to ensure that no air bubbles were trapped. The variable plunger was then inserted slowly into the column. Before the experiments were carried out, the chromatographic column and liquid pump were purged off trapped air using a special syringe. This was to ensure that there was no internal circulation of fluid in the column, which might upset the experiments.

Feed concentration was set to 20 mg/L. Only three different flow rates were necessary for model calibration: 1, 1.5 and 2 mL/min. Effluent samples for ICP analysis were collected periodically in special test tubes using the Gilson programmable fraction collector. After the completion of each experiment, the biomass beads were removed and the column rinsed with approximately 500 mL of distilled water at 5 mL/min. Fresh biomass beads were then packed into the column again and the experiments resumed.

For model verification, two different bed depths at 11 cm and 13 cm were tested. Different operating conditions such as feed concentration, particle size, flow rate and bed depth were studied to determine the suitability of the model in predicting the breakthrough curves under different conditions. Each experiment is conducted with fresh biomass to ensure consistency in the experiments.

4.3 Results and Discussion

The performance of the immobilized algal biomass in a fixed bed is best depicted by the breakthrough curve which shows the copper concentration profile at the column outlet as a function of time or bed volume. By fitting predicted values from the models to compare with the experimental data, one can qualitatively and quantitatively compare the data.

4.3.1 Model Calibration

The immobilized biomass beads of *S. bacularia* were packed into a chromatographic column until a depth of 13 cm and copper concentration at 20 mg/L with flow rates of 1, 1.5 and 2 mL/min were tested. Figure 4.1 shows the copper loading breakthrough curves at various flow rates as a function of time with a typical S shape profile characterizing the breakthrough curve.

By evaluating Figure 4.1, a plot of t_o versus $1/Q$ for the three different flow rates will yield the constant k_1 as depicted in Figure 4.2. Using Equation 4.4, a plot of F versus different values of σ will yield a curve with a minimum value, where the minimised value denotes the optimum value of σ for that flow rate (Figure 4.3). In Figure 4.4, a plot of σ^2 versus Q/L will yield a linear curve. The gradient of the curve will yield the constant k_2 .

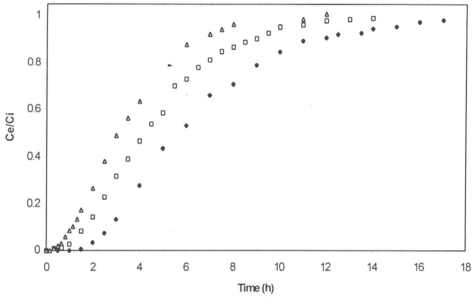


Figure 4.1: Column breakthrough curves for bed depth at 13 cm (\diamond , $Q = 1$ mL/min; \square , $Q = 1.5$ mL/min; \triangle , $Q = 2$ mL/min)

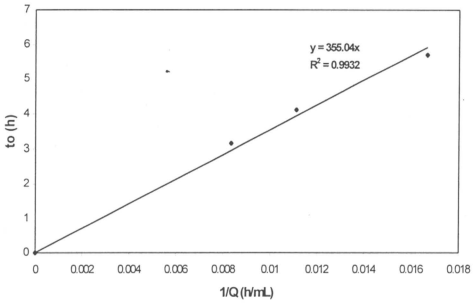


Figure 4.2: Plot of t_o against $1/Q$ for column length of 13 cm

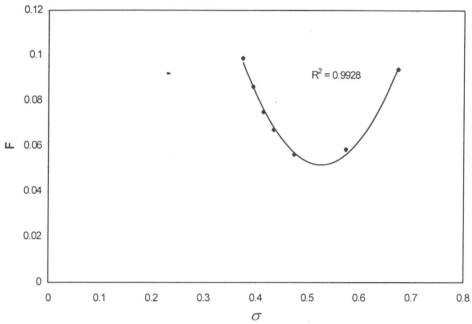


Figure 4.3: Plot of F against σ for column length of 13 cm at flow rate of 1 mL/min

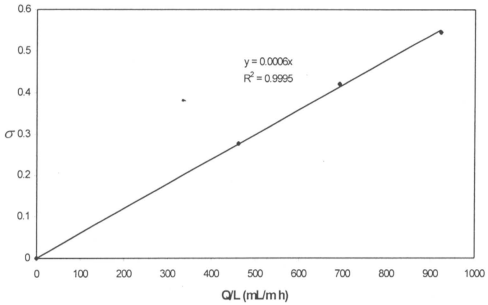


Figure 4.4: Plot of σ^2 against Q/L for column length of 13 cm at various flow rates

Table 4.2 summarises the constants for k_1 and k_2 , evaluated from Figures 4.2 and 4.4.

Table 4.2: Two Parameter constants for column length of 13 cm		
Constants	Value	R^2
k_1	355.04 mL	0.9932
k_2	6×10^{-4} mh/ mL	0.9995

Correlation coefficient R^2 shown in Figures 4.2 and 4.4 represents the goodness of fit and linearity of our data. A value of 0.99 and higher indicates a strong linear correlation. This suggest that the Two Parameter model is suitable for this biosorption system and can be readily applied to fixed bed operations. Figure 4.5 is a plot of the theoretical and experimental data for bed depth of 13 cm with various flow rates. Visual inspection of these curves in Figure 4.5 suggest a good fit between the experimental and theoretical data.

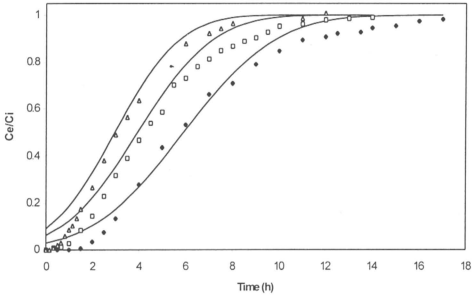


Figure 4.5: Theoretical and experimental breakthrough curves at various flow rates for $L = 13$ cm. Solid line represents model prediction. (\diamond , $Q = 1$ mL/min; \square , $Q = 1.5$ mL/min; \triangle , $Q = 2$ mL/min)

4.3.2 The Effect of Bed Depth

To study the effect of bed depth, the biomass beads were packed into a chromatographic column of 11 cm and 13 cm. The operating conditions are a flow rate of 1 mL/min and a feed concentration of 20 mg/L of copper ions. Figure 4.6 shows the copper loading breakthrough curves as a function of time.

By defining breake time as time when the effluent concentration of copper was under 10% of copper concentration in the feed (Ruthven, 1984), the lengthening of bed depth from 11 cm to 13 cm prolonged the breake time from approximately 3.5 hours to 5.1 hours. This is expected as the increase in bed depth means more biosorbents are available for the copper ions to be passively adsorbed. The breakthrough profile for the longer column is also more pronounced. According to Suzuki (1990), this broadening of the adsorption front as a result of bed lengthening is due to flow in void spaces between particles as a result of axial dispersion.

From Figure 4.6, we observe that the model is able to characterise the entire breakthrough profile with a typical sigmoidal or S shape, which is typical of all fixed bed operations. The solid line represents the model prediction for the longer column while the dashed line for the shorter one. The 2 Parameter model was able to fit the experimental data at the early stages of the fixed bed operation. For column length of 11 cm, deviation occurred after 9 hours of operation. Similarly for 13 cm, deviation started after 10 hours of continuous operation. A possible explanation for the poor agreement between both data lies in the inadequacy of the estimated constants to describe the biosorption of copper in a particular concentration region.

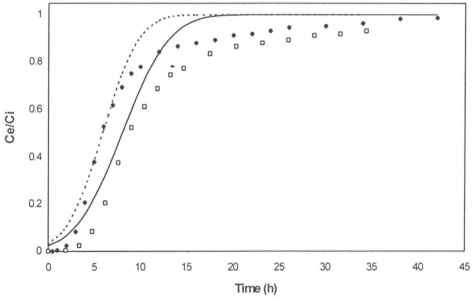


Figure 4.6: Breakthrough curves for immobilized *S. bacularia* at various bed depths. Solid line represents model prediction at 13 cm while dotted line at 11 cm. (\diamond , $L = 11$ cm; \square , $L = 13$ cm)

4.3.3 The Effect of Flow Rate

To study the effect of flow rate, fresh biomass beads were packed into a 13 cm chromatographic column and operated at 1 and 2 mL/min with a feed concentration of 20 mg/L. The breakthrough profile is depicted in Figure 4.7. When flow rate was increased two fold from 1 to 2 mL/min, the breakthrough profile steered to the left with a breaktime of approximately 1.7 hours. At higher flow rate, the copper ions were eluted out faster due to insufficient time to equilibrate onto the active sites of the immobilized biomass surface, resulting in the under utilization of the mass transfer zone for adsorption.

At higher flow rate, the model was in better agreement in comparison to the one at 1 mL/min. However, at the start of the operation, the model yielded a value of 0.088 for C_e/C_i while the experimental data was still zero. Brady *et al.* (1999) also encountered similar problems. These problems may stem from the value obtained from k_1 . For a given flow rate, if the value of t_0 is high, i.e. the time for effluent concentration to be half of the feed concentration is longer, the value for k_1 would also be higher. This would enviably result in a breakthrough curve that is more pronounced and stretched, eliminating the initial value error. Several examples by Brady *et al.* (1999) points to this.

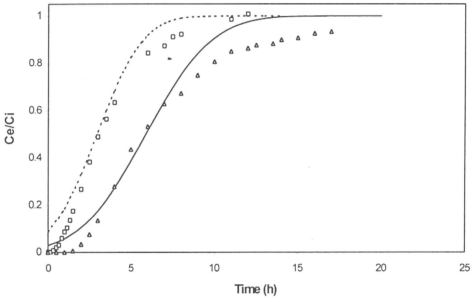


Figure 4.7: Breakthrough curves for immobilized *S. bacularia* at various flow rates. Solid line represents model prediction at 1 mL/min cm while dotted line at 2 mL/min. (Δ , $Q = 1$ mL/min; \square , $Q = 2$ mL/min)

4.3.4 The Effect of Feed Concentration

To study the effect of copper concentration, the biomass beads were packed into a 13 cm column and a flow rate of 1 mL/min was selected. The feed concentration was varied between 20 and 40 mg/L of copper ions with their breakthrough profiles shown in Figure 4.8. When the feed concentration was increased to 40 mg/L, the resultant breakthrough profile had a steep curve with a rapid ascension followed by a plateau when the effluent concentration reached the feed concentration. This is due to the rapid saturation of the mass transfer zone by copper ions. The curve steered to the left with a breaktime at approximately 1 hour.

While agreement between the theoretical and experimental data is favourable at higher feed concentration, the model overestimated the fixed bed operation between 9 to 17 hours. At 20 mg/L, the model already reached feed concentration after 20 hours of operation but experimental breakthrough curve approached it slowly. The poor fit maybe the result of the estimated constants not being able to characterise the experimental curve well enough.

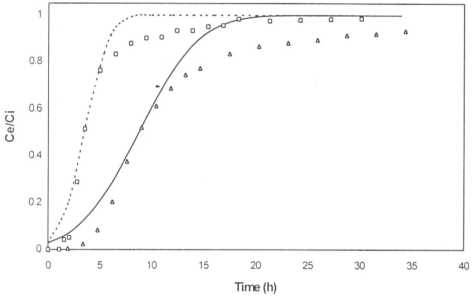


Figure 4.8: Breakthrough curves for immobilized *S. bacularia* at various feed concentration. Solid line represents model prediction at 20 mg/L while dotted line at 40 mg/L. (Δ , = 20 mg/L; \square , = 40 mg/L)

4.3.5 The Effect of Particle Size

Particle size also plays a crucial role in influencing the adsorption of copper ions onto the surface of the immobilized biomass. To investigate the effects of particle size in a fixed bed operation, the immobilized beads were packed to a bed depth of 13 cm. A feed concentration of 20 mg/L with a flow rate of 1 mL/min was employed. Particle sizes of 0.35 cm and 1.5 cm were selected for this study.

The respective breakthrough curves are shown in Figure 4.9. An increase in particle size from 0.35 cm to 1.5 cm significantly altered the adsorption profile. For the larger particle size, breakthrough occurred earlier at approximately 3.6 hours while breakthrough for the smaller particle size occurred at 5.8 hours. It is apparent that the saturation capacity for particle size of 1.5 cm is smaller than 0.35 cm. For a given bed depth, the larger the particle size the smaller the surface area available for adsorption because lesser number of beads were able to be packed into the column.

There was a good agreement between the predicted data and the experimental data. For particle size at 1.5 cm, the model predicted higher effluent concentration between 10 and 20 hours of operation. A closer inspection of the curve for the 1.5 cm particle suggested that an experimental error may have occurred between that particular time interval. The values obtained were smaller than expected. For the smaller particle size of 0.35 cm, the column is only 82% saturated after 20 hours of operation although the model is almost reaching feed concentration. This deviation points to the shortcoming of the model in that the constants could not fully characterise the breakthrough curve at this interval.

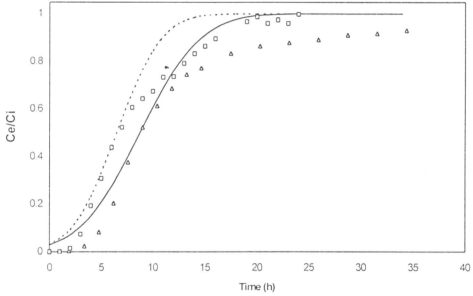


Figure 4.9: Breakthrough curves for immobilized *S. bacularia* at various particle size. Solid line represents model prediction at 0.35 cm while dotted line for 1.5 cm. (Δ , $d = 0.35$ cm; \square , $d = 1.5$ cm)

Model parameters used in predicting the theoretical breakthrough curves are listed in Table 4.3.

Table 4.3: Model parameters

	Operating Conditions	Two Parameter Constants	
		k_1 (mL)	k_2 (mh/mL)
Bed Depth	L = 11 cm	482.25	5×10^{-4}
	L = 13 cm	355.04	6×10^{-4}
Flow Rate	Q = 1 mL/min	355.04	6×10^{-4}
	Q = 2 mL/min	355.04	6×10^{-4}
Feed Concentration	[Cu ²⁺] = 20 mg/L	355.04	6×10^{-4}
	[Cu ²⁺] = 40 mg/L	225.60	6×10^{-4}
Particle Size	d = 0.35 cm	355.04	6×10^{-4}
	d = 1.50 cm	375.60	6×10^{-4}

Conclusion

Fixed bed biosorption studies with immobilized biomass of *S. bacularia* were characterised in this chapter. Various operating conditions were studied and a mathematical model with an analytical solution was employed to study the resulting breakthrough curves.

The constants k_1 and k_2 obtained from the model calibration revealed that a linear relationship exists between t_o and $1/Q$ and between σ^2 and Q/L . The linearity of the data implies that the mathematical model can be suitably employed to predict the breakthrough curves of immobilized *S. bacularia* in a fixed bed column.

The breakthrough profile of immobilized *S. bacularia* in a fixed bed is sigmoidal. When operating conditions such as flow rate, particle size and feed concentration were increased, breake time occurred earlier. The reduction in bed depth also yielded similar results.

The Two Parameter model performed favourably for most conditions tested and was able to characterise the entire breakthrough curve. In few cases, the values between experimental and estimated model do not agree well. This is because the predicted curves depend highly on k_1 and k_2 . While a strong linear correlation exists as depicted in Figures 4.2 and 4.4, the modelled breakthrough curves did not fit experimental data well. The constant k_1 depends on t_o while k_2 depends on σ^2 . For t_o with values less than 15 hours, Equation (4.1) would compute higher values reaching saturation earlier. Since σ^2 is a measure of the slope of the curve, low values in the region of 10^{-4} would

invariably result in initial values even when $t = 0$. Some of these examples are seen in Figures 4.7 and 4.9.

However, the ease of calibration coupled with an elegant analytical solution that reduces computational errors makes the Two Parameter model an ideal choice for the prediction of breakthrough curves inspite of some minor limitations. The Two Parameter model is still a useful tool for the design and scale up of fixed bed reactors for the treatment of heavy metal waste.