CHAPTER VIII
CONTINUOUS FLOW STUDIES OF BASIC DYE BIOSORPTION

Most separation and purification processes that use sorption technologies involve continuous flow operations (Borba et al., 2006). In continuous systems, the saturated zone gradually extends throughout the column where the sorbate is adsorbed. To study the adsorption behavior of the basic dye in a fixed bed column, important factors such as flow rate and bed depth of the column were investigated. The mathematical analysis of the system was conducted to predict the column behavior.

8.1 Effect of bed depth

The different bed depths of 4, 6, and 8 cm were studied where the sorption breakthrough curves at the controlled flow rate of 1.2 ml min^{-1} cm^{-2} and at a constant influent concentration of 100 mg l^{-1} are shown in Fig. 8.1. The area under the breakthrough curve (A_c; mg ml^{-1}) obtained by integrating the plot between the sorbed concentration (C_s; mg l^{-1}) versus t (min) can be used to find the total sorbed dye quantity. In this study, this integrated boundary was defined to be from the start of the experiment (t=0) to the exhaustion point (t=t_x), and the total sorbed dye (w_d; mg) in the column for a given feed concentration and flow rate can then be calculated from:

$$w_d = \frac{QA_c}{1000} = \frac{Q}{1000}\int_{t=0}^{t=t_x} C_s \mathrm{d}t \qquad (8.1)$$

w_d can be used to calculate the total removal percentage from:

$$\text{Total Removal (\%)} = \frac{w_d}{m_{total}} \times 100 \qquad (8.2)$$

where m_{total} can be calculated from:

$$m_{total} = \frac{C_o Q t_x}{1000} \qquad (8.3)$$

The bed capacity of the column (q_{column}) was defined as the total amount of dye sorbed (w_d) per gram of algal sorbent (M):

$$q_{column} = \frac{w_d}{M} \qquad (8.4)$$

Both dye uptake quantity (mg) and exhaustion time increased with increasing bed depth, as more binding sites were available for the sorption. The bed capacities, q_{column}, were similar for cases with varying bed depth. For a constant flow rate of 1.2 ml min^{-1} cm^{-2}, bed capacities were 57.16 mg g^{-1} for the bed depth of 4 cm, and 56.92 and 54.26 mg g^{-1} for the bed depth of 6 and 8 cm, respectively (Table 8.1). However, the dye removal percentage was affected by the bed depth, e.g. the removal percentages acquired from this work were 75, 78 and 80% for the bed depths of 4, 6, and 8 at a constant flow rate of 1.2 ml min^{-1} cm^{-2}, respectively. This increase in the efficiency with bed depth was due to the nature of the operation of the column where the service time ended when the exhausting concentration reached a certain threshold value, often the effluent standard. Therefore the sorbent in the longer column could be employed more effectively than those in shorter columns. The effect of bed depth on the breakthrough curves is shown in Fig. 8.1. The influence of bed height on the sorption efficiency could be indicated using the mass transfer zone index (*Z/D*) which was defined here as the ratio between the length of mass transfer zone (*Z*) to the total bed depth (*D*). The length of mass transfer zone (Z), also called as critical bed depth, can be calculated from the breakthrough curve as follows (Vijayaraghava et al., 2005):

$$Z = D\left(1 - \frac{t_b}{t_x}\right) \tag{8.5}$$

The mass transfer zone index reflected the reciprocal of the useful length of the column and therefore a higher index indicated a lesser effective column. For the results from this work, this index was equal to 0.57 for the bed depth of 4 cm, 0.58 for 6 cm, and 0.66 for the bed depth of 8 cm, at a constant flow rate of 1.2 ml min cm^{-2} as shown in Table 8.2.

The service time of the continuous flow column can be considered as a function of the bed depth of the algal sorbent. The bed depth service time model (BDST) is a simple model which described this relationship (see Eq. (3.12)). The column service time was selected as the time when the effluent dye reaches the break point (t_b). The plot of service time, t_b, against bed depth, D, at a flow rate of 1.2 ml min^{-1} cm^{-2} was linear indicating the validity of the BDST model for the fixed-bed system (Fig. 8.2).

The slope of BDST plot is equal to N_o/C_oV'. The initial concentration C_o and the flow velocity (V') might be assumed to be reasonably constant during the column operation. The bed capacity, N_o, was used to predict the performance of the bed if there was a change in initial concentration C_o. The minimum bed depth D_{min} could also be found from the intercept at the x-axis of the BDST plot. For all flow rates demonstrated in this experiment, the bed depth of alga should not be lower than D_{min} values which were 3.44, 3.69, and 3.94 cm and the sorption capacities, N_o, were 53.1, 39.8, and 29.1 mg cm^{-3}, for the flow rates of 1.2, 2.4, and 3.6 ml $min^{-1}cm^{-2}$, respectively (Table 8.3).

8.2 Effect of flow rate

To investigate the effect of flow rate on the sorption of Astrazon® Blue FGRL by *C. lentillifera*, the influent dye concentration was held constant at 100 mg l^{-1}. The flow rates were manipulated at 1.2, 2.4, and 3.6 ml min^{-1} cm^{-2}. The sorption data were evaluated and the total amount of dye sorbed, bed capacity of the column and total dye removal percentage with respect to flow rate are presented in Table 8.1. The maximum dye removal percentage was 80% at the flow rate of 1.2 ml min^{-1} cm^{-2} and the bed depth of 8 cm. The average dye uptake capacity was found to be 42.85 mg g^{-1}. This number was lower than the maximum sorption capacity of the ground alga reported by Punjongharn et al., 2008 (68.0 mg g^{-1}). The lower average capacity obtained from continuous experiments than that from batch experiments was because the column was only operated to the exhaustion point (90% maximum capacity) and therefore the capacity of the sorbent was not fully utilized.

The experimental breakthrough curves as shown in Fig. 8.3 demonstrate that the breakthrough generally occurred more rapidly at faster flow rate. However, the effectiveness of the sorption columns seemed to be slightly lower with an increase in the flow rate. For instance, the column capacity of *C. lentillifera* obtained at the constant bed depth of 8 cm decreased from 54.26 to 29.24 mg g^{-1} when the flow rates increased from 1.2 to 3.6 ml min^{-1} cm^{-2}. This finding could also be explained using the concept of the mass transfer zone index. The length of mass transfer zone increased with the flow rate, and this reduced the effective length when compared with the height of the column. As a result, the mass transfer zone index increased with increasing flow rate (see Table 8.2). The influence of flow rate on the breakthrough curves is illustrated in Fig. 8.3.

The breakthrough data obtained from the column studies at different flow rates were also examined using the Thomas model (Thomas, 1944). The expression of the Thomas model for a sorption column is shown in Eqs. (3.13)-(3.14). The kinetic coefficient, k_{TH}, and the sorption capacity of the bed, q_{TH}, can be determined from the intercept and slope of the plot between $\ln(\frac{C}{C_0}-1)$ and V_{eff} at a given condition. The parameters, q_{TH} and k_{TH} as shown in Table 8.4 illustrated that, with an increasing flow rate, k_{TH} and q_{TH} decreased. The decreased of q_{TH} could be described by an increase in the length of mass transfer zone (as described in previous section).

Fig. 8.4 shows the plot of experimental and theoretical C_t/C_o against V_{eff} at a constant bed depth of 8 cm. The value of k_{TH} and q_{TH} obtained from the Thomas model were 0.018, 0.024, and 0.048 ml mg^{-1} min^{-1}, and 67.8, 60.0 and 45.1 mg g^{-1} for the flow rates of 1.2, 2.4, and 3.6 ml min^{-1} cm^{-2}, respectively.

8.3 Concluding remark

This biomass was proven to exhibit an outstanding sorption capacity of the dye. The useful parameters for the future design of the sorption column such as the BDST parameters and the Thomas model parameters were also determined. The finding from this work provided initial information for future development of the larger scale sorption columns for actual wastewater treatment systems. The use of this alga for such applications should not only be effective, but also be economically attractive as the alga was available as an unwanted excess agricultural material. However, the use of biomass in the treatment process might be limited by the biodegradability of the alga. For dried *Caulerpa lentillifera*, its life-time is around 5-7 days after immerged in dye solution. Hence, new algal sorbent has to be replaced every week if applied in the real treatment system.

Table 8.1 Effects of flow rate and bed depth on total amount of dye sorbed, bed capacity of the column and total dye removal percentage

Flow rate ($ml\ min^{-1}\ cm^{-2}$)	Bed depth (cm)	w_d (mg)	q_{column} ($mg\ g^{-1}$)	Total dye removal (%)
1.2	4	114.3	57.16	75
2.4	4	89.95	41.62	64
3.6	4	62.35	30.54	43
1.2	6	227.7	56.95	78
2.4	6	172.1	43.03	66
3.6	6	121.0	30.25	46
1.2	8	542.6	54.26	80
2.4	8	429.6	42.96	72
3.6	8	297.5	29.24	53

Table 8.2 Length of effective zone under various column lengths and flow rates

Flow rate ($ml\ min^{-1}\ cm^{-2}$)	Bed depth (cm)	Z (cm)	Z/D (-)
1.2	4	2.28	0.57
2.4	4	2.32	0.55
3.6	4	2.64	0.44
1.2	6	3.31	0.58
2.4	6	3.49	0.53
3.6	6	3.79	0.45
1.2	8	3.54	0.66
2.4	8	3.58	0.63
3.6	8	3.85	0.48

Table 8.3 Parameters calculated from the BDST model

Flow rate ($ml\ min^{-1}\ cm^{-1}$)	D_{min} (cm)	K_{BDST} ($l\ mg^{-1}\ min^{-1}$)	N_o ($mg\ cm^{-3}$)	R^2
1.2	3.44	0.013	53.1	0.9350
2.4	3.69	0.036	39.8	0.9499
3.6	3.94	0.069	29.1	0.8995

Table 8.4 Parameters predicted from the Thomas model at different flow rates and bed depths

Flow rate (ml min^{-1} cm^{-2})	Bed depth (cm)	q_{TH} (mg g^{-1})	k_{TH} (ml min^{-1} mg^{-1})	R^2
1.2	4	56.7	0.059	0.9863
2.4	4	41.7	0.11	0.9883
3.6	4	30.7	0.18	0.9866
1.2	6	60.4	0.023	0.9655
2.4	6	56.7	0.035	0.9541
3.6	6	38.3	0.038	0.9058
1.2	8	67.8	0.019	0.8095
2.4	8	60.0	0.024	0.9776
3.6	8	45.1	0.048	0.8891

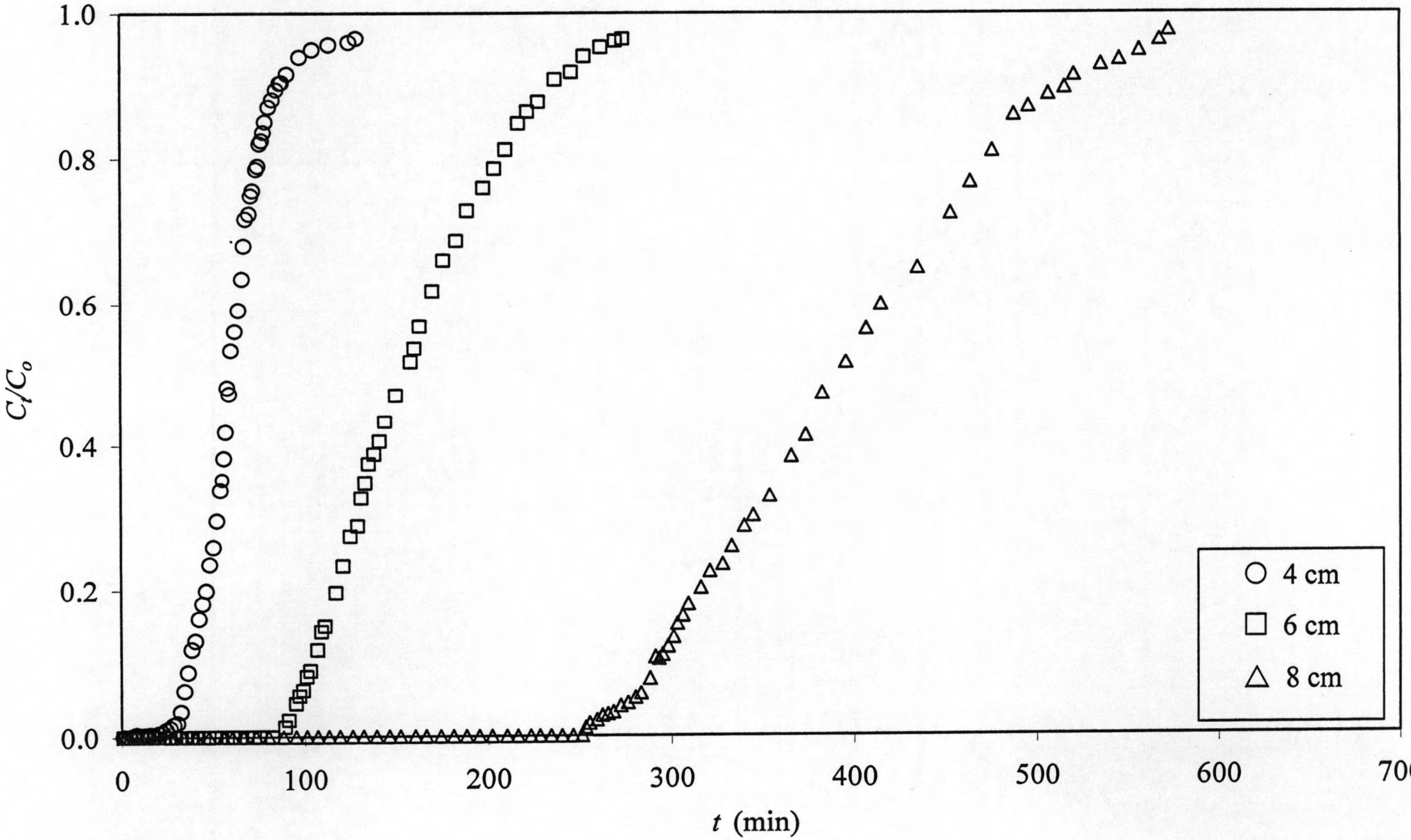

Fig. 8.1 Breakthrough curves for the uptake of Astrazon® Blue FGRL onto *C. lentillfera* at different bed depths (flow rate = 1.2 ml min^{-1} cm^{-2}, initial dye concentration = 100 mg l^{-1}, pH= 7)

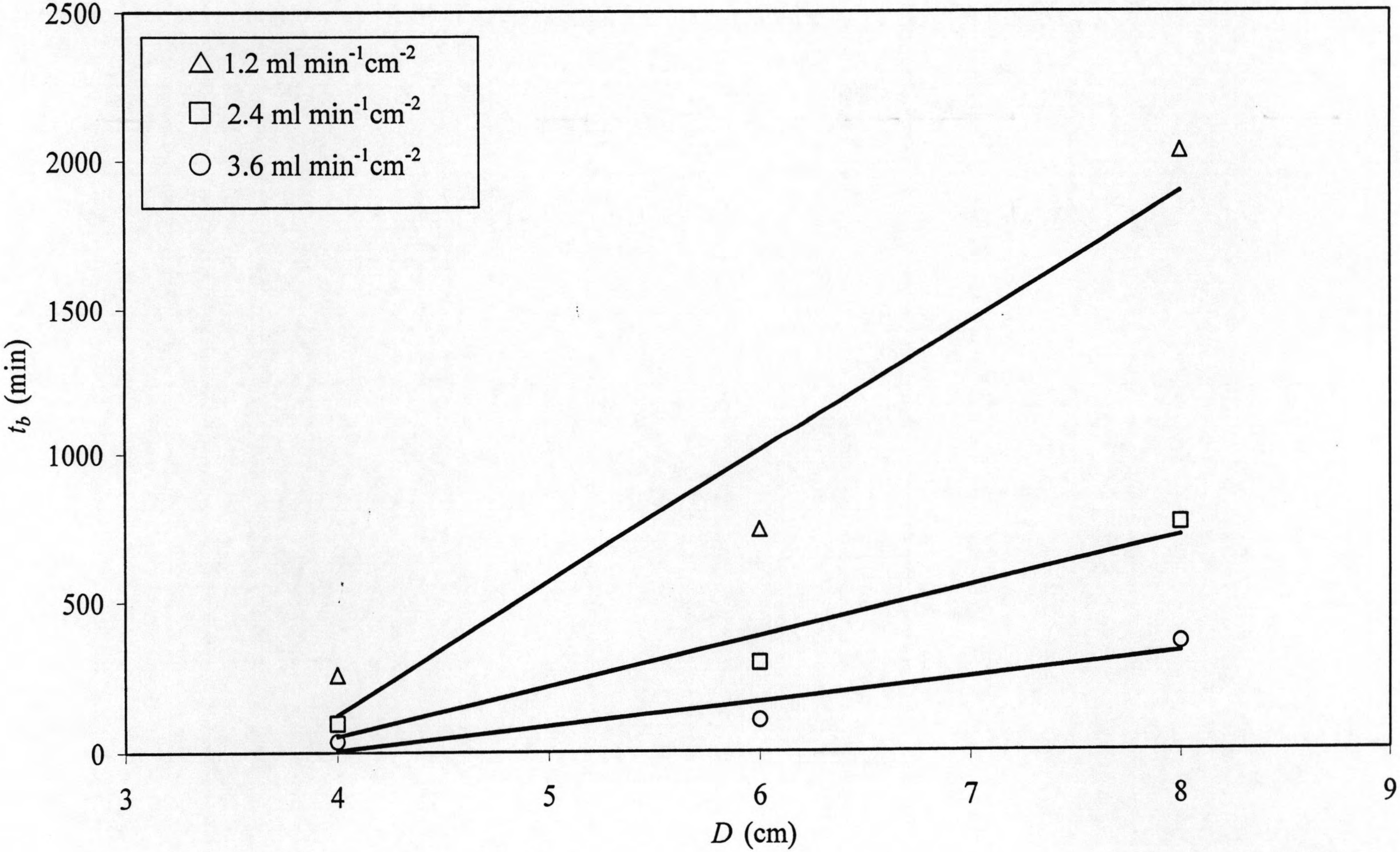

Fig. 8.2 BDST model plot for Astrazon® Blue FGRL biosorption by *C. lentillifera* (initial dye concentration = 100 mg l^{-1}, pH= 7)

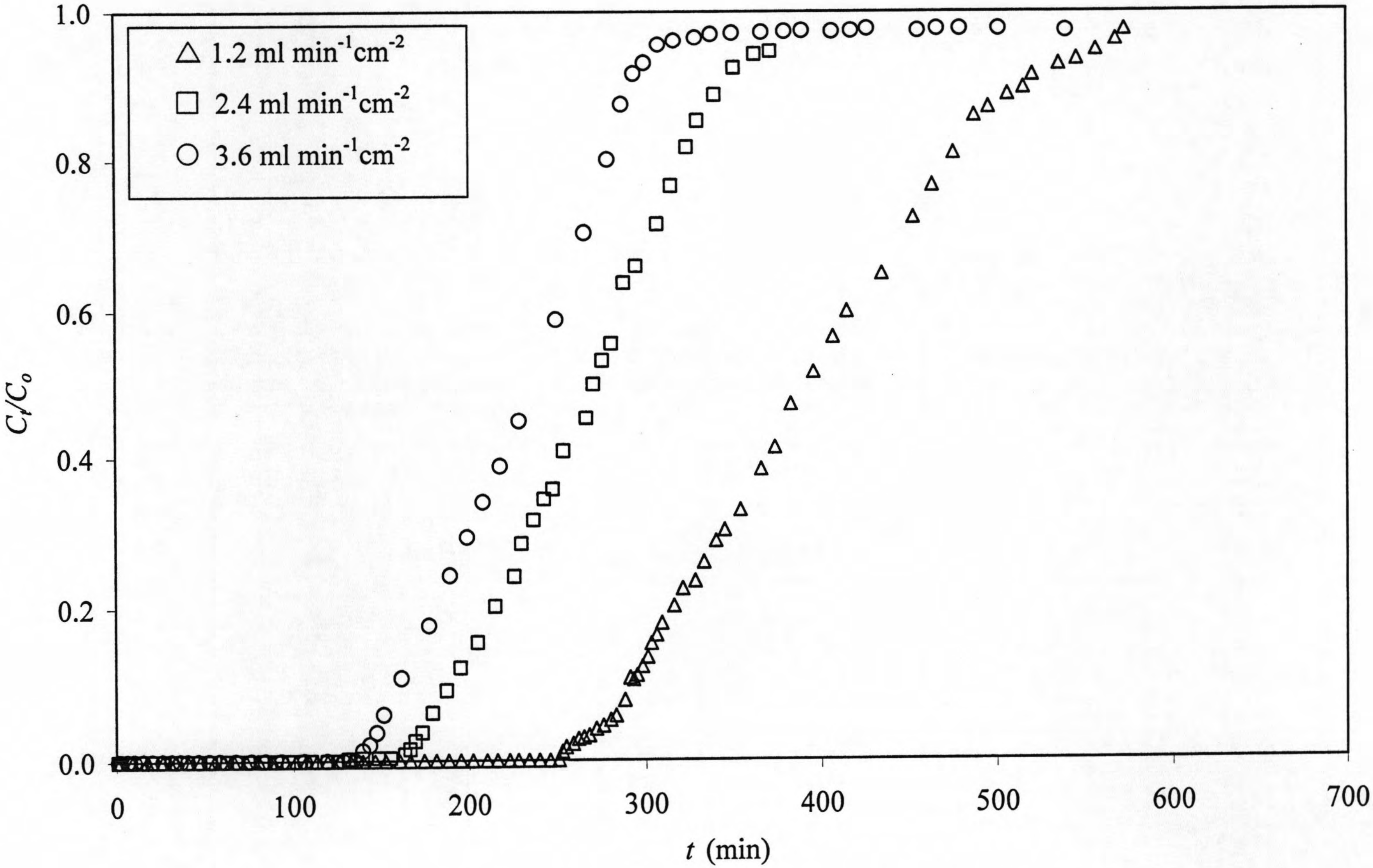

Fig. 8.3 Effect of wastewater flow rate on the biosorption by *C. lentillifera* (bed depth = 8 cm, initial dye concentration = 100 mg l^{-1}, pH= 7)

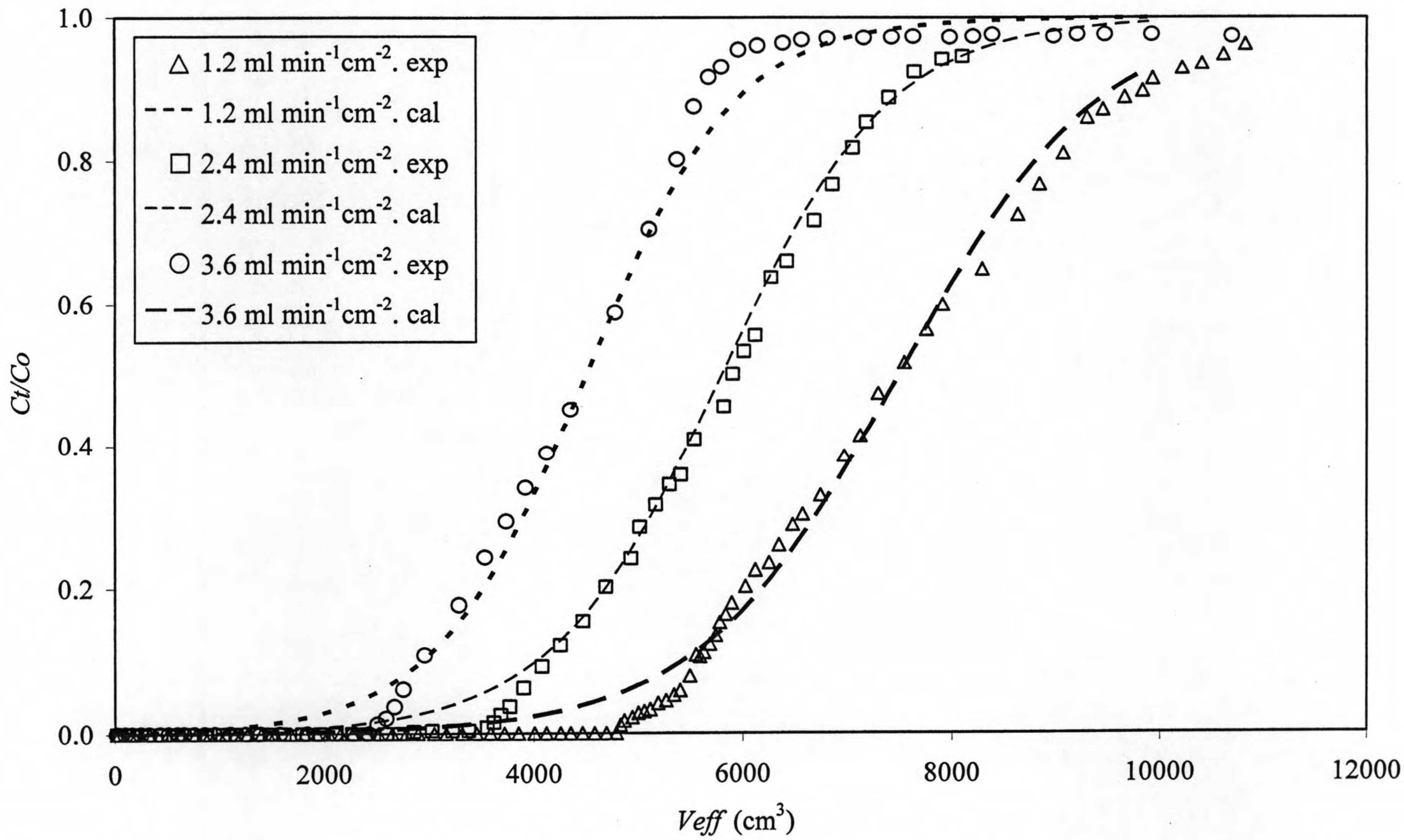

Fig. 8.4 Thomas model prediction for the biosorption of Astrazon® Blue FGRL onto *C. lentillifera* at different flow rates (bed depth = 8 cm, initial dye concentration = 100 mg l^{-1}, pH= 7), exp= experimental data; cal=calculated from the Thomas model