CHAPTER VI

BATCH REMOVAL OF BASIC DYES BY

CAULERPA LENTILLIFERA

A great deal of the biosorption studies were performed in batch systems. These processes are conceptually simple where a suitable biosorbent (both untreated and pretreated) is contacted with aqueous solution containing organic pollutant molecules or ions. The contacting process is allowed to proceed for a sufficient time for the biomass to sequester these molecules and to reach equilibrium. Then the biomass is separated from the liquid phase and the pollutant-containing biomass is either regenerated or disposed of in an environmentally acceptable manner (Aksu, 2005).

Astrazon® Blue FGRL (AB) was chosen as a modeled basic dye. Both sorption equilibrium and kinetics were studied. In order to provide thermodynamics information, the effects of temperature were also investigated. Along with batch sorption studies, desorption of such dye was also investigated.

6.1 Sorption efficiency

The sorption efficiency in the batch experiment was found to be higher than 90% when using the algal mass of more than 0.5 g in the range of dye concentrations from 20-80 mg l^{-1} (Fig. 6.1). On the other hand, the adsorbed dye quantity per gram of adsorbent, q, decreased with an increase in the adsorbent dosage. However, the values of q would change when the adsorbent dose and initial concentration change. Hence, the study of sorption equilibrium was conducted in order to investigate the maximum sorption capacity of this alga

6.2 Sorption equilibrium

In order to examine the sorption equilibrium of Astrazon® Blue FGRL, the sorption experiments were set up with various amounts of dried alga (0.1, 0.2, 0.5, 0.7, 0.9) and at various experimental temperatures (18, 27, 40, 50, 70°C). The sorption isotherms illustrated in Fig. 6.2 shows raw data from the experiment at 5 levels of temperature

whilst Figs. 6.3 and 6.4 illustrate the plots according to Langmuir's and Freundlich's isotherm criteria, respectively. From Fig. 6.3, straight lines could be well observed between $1/q_e$ and $1/C_e$ indicating that the experimental data followed Langmuir's isotherm. The maximum sorption capacities (q_m) and the Langmuir constants (b) were also calculated from these plots. It was found that the Langmuir parameters, i.e. q_m and b, increased with temperature. High temperatures increased the kinetic energy of the dye, and hence, enhanced the mobility of the dye ions. This led to a higher chance of the dye being adsorbed onto the adsorbent and an increase in its sorption capacity. This agreed well with the findings of Lee et al. (1996). However, an excessively high temperature (70°C) might not be appropriate for the sorption of Astrazon® Blue FGRL as it could destroy or change the integrity of the alga and reduce the active sorption sites. In this case, q_m was dropped from 49.26 mg g^{-1} at 50°C to 46.73 mg g^{-1} at 70°C.

The sorption of Astrazon® Blue FGRL by *C. lentillifera* at various sorbent size and experimental pH were reported by Punjongharn et al., 2008. Among the 3 sizes of alga: S (0.1-0.84 mm), M (between 0.84-2.0 mm), and L sizes (larger than 2.0 mm), the S size gave the highest adsorption capacity followed by M and L sizes, respectively. The q_m of S, M and L-size were 68.0, 70.4, and 80.7 mg g^{-1}, respectively. It was clear that the ground alga gave higher maximum sorption capacity than the unground alga. For the effect of pH, the conditions at pH of 6 and at uncontrolled pH seemed to give the highest adsorption capacity, and in most cases, the adsorption capacity decreased with a drop in pH.

The linearity of the plot displayed in Fig. 6.4 suggested the applicability of the Freundlich model. The Freundlich constants, i.e., $1/n$ and K_F were calculated from the slope and interception of the Freundlich plots, respectively. It should be noted that the exponential constants, $1/n$, were almost unity, which meant that the dye was favorably adsorbed onto the dried alga. These calculated parameters are summarized in Table 6.1. As both the Langmuir and Freundlich models could explain the sorption, the sorption in the range of concentration employed in this work should still be in the monolayer region. This tend was also found in the sorption of methylene blue onto dead macro fungi (Maurya et al., 2006), methylene blue on dead bacteria (Nacèra and Aicha, 2006), bismask brown on activated carbon (Kumar et al., 2005a). Increasing the dye

concentration could lead to a clearer difference between the usages of these two models, however, higher dye concentrations than 100 mg l^{-1} is highly unlikely to take place in conventional textile wastewater.

6.3 Sorption kinetics

The sorption kinetics was studied in the concentration range of 20-1280 mg l^{-1} (20, 40, 80, 160, 320, 640, and 1280 mg l^{-1}). The kinetic plots as shown in Fig. 6.5 indicated that the sorption capacity increased with time, and at a certain time period, reached a constant value indicating that no dye was further removed from the solution. At this point, the amount of dye being adsorbed onto the alga was in a state of dynamic equilibrium with the amount of dye desorbed from the alga. The time it took to reach an equilibrium varied with the initial concentration, i.e. the solution with a higher initial concentration required a slightly longer time than the solution with a lower initial concentration. However, for the range of dye concentrations employed in this work, equilibrium was reached within the first hour of sorption.

The sorption capacity at equilibrium was found to be proportional to the initial concentration (Fig. 6.5). This characteristic was also found even with the extremely high dye concentration solution. The highest concentration of the dye in this experiment was 1,280 mg l^{-1}, and at this point, the sorption capacity of the alga was still two times higher than that with the dye concentration of 640 mg l^{-1}. This indicated that the alga still could accommodate more dye sorption. However, a higher dye concentration than 1,280 mg l^{-1} could not be prepared and dealt with easily due to its extremely high viscosity and difficulty in handling. Nevertheless, a dye concentration above 1,280 mg l^{-1} is far beyond the level found in industrial effluent, which is only approximately 100 mg l^{-1} (U.S. EPA, 1996). Hence, the sorption characteristic of a dye solution above 1,280 mg l^{-1} was not investigated in this work.

In order to characterize the kinetic behavior of a reaction, it is desirable to determine how the rate of reaction varies as the reaction progresses. Lagergren's first order kinetics (Lagergren, 1898) and pseudo second order kinetics (Ho and McKay, 1999) have been most widely used to describe the solute sorption on various sorbents (Eqs. (3.10)-(3.11)). The first order and the pseudo second-order kinetics models were

applied to the experimental data. The plots of these two kinetic models at all initial concentrations were illustrated in Figs. 6.5 and 6.6. For the data to follow the first order kinetics in Eqs. (3.8)-(3.9), the linear plot between $\log(q_e-q)$ and t should be observed. However, the results illustrated that this linear dependency could not be obtained indicating that the first order Lagergren rate kinetics was not appropriate for the sorption of basic dye on the alga. For the pseudo second-order kinetics, the parameters, q_e and k_2, could be determined from the intercept and the slope of the plots in Fig. 6.7 and these are summarized in Table 6.2. Extremely good agreements between the results and the model were obtained as illustrated by the very high R^2 for the whole range of initial dye concentrations. Hence, it was concluded that the sorption here could be better represented by the pseudo second-order rate kinetics. The values of R^2 calculated from the pseudo second order model, in all cases, were higher than those from the first order model. A better fit of experimental data with the pseudo second order model indicated that the sorption took place quite rapidly. This could be because the concentration employed in this work was quite low which allowed a rapid sorption rate. The results also indicated that an increase in the initial dye concentration increased the equilibrium sorption capacity, q_e, whilst decreasing the rate constant, k_2. Azizian (2004) suggested that the pseudo second order kinetic model was best used to describe the sorption at low initial concentration which could be the case for this work. This finding was similar to other studies on the biosorption of several other dyes. For instance, the pseudo second-order kinetics was also observed in the biosorption of Remazol Black B on biomass (Aksu and Tezer, 2000), the adsorption of Congo Red on activated carbon (Namasivayam and Kavitha, 2002), and methylene blue on perlite (Doğan et al., 2004).

6.4 Sorption thermodynamics

The apparent heat or net enthalpy of sorption, ΔH, is related to the Langmuir constant, b, as present in Eq. (3.16) (Faust and Aly, 1987). The slope of the plot in Figure 6.8 represented $-\Delta H/R$, and therefore, ΔH could be calculated. Only four sets of experimental data, 18°C, 27°C, 40°C, and 50°C, were used in this section. The data at 70°C was not used because such high temperature could reduce the active sorption site on the alga surface. For this experiment, ΔH took the value of 14.87 kJ mol^{-1}. The positive enthalpy

indicated endothermic nature of the adsorption process and also the low number of enthalpy change implied physical sorption. Moreover, the value of enthalpy obtained from this work was relatively small. This implied that the sorption mechanism was mainly physical sorption.

The sorption process resulted in an increase in entropy of the system ($\Delta S = 12.08$ J mol^{-1} K^{-1}). Usually adsorption of gases on solids is accompanied by a decrease in entropy as the molecules from the disordered gaseous state find an ordered arrangement on the surface of the solids (Bhattacharyya and Sharma, 2005). In case of adsorption from solutions, it was likely that the dye molecules on the algal surface were more chaotically arranged. The large size of dye molecules might be responsible for this. The positive values of ΔS confirm a high preference of Astrazon® Blue molecules for the algal surface and suggest possibility of some structural changes or readjustments in the dye–alga adsorption complex (Ho, 2003).

Despite being endothermic in nature, the spontaneity of the sorption process was ensured by a negative Gibbs energy of the system. The ΔG values varied in a narrow range with the mean values showing a gradual decrease from -3.85 to -8.15 kJ mol^{-1} in the temperature range of 18–70°C. The parameters, ΔH, ΔS, and ΔG, for the dye–algal interactions changed in a way that made the sorption more thermodynamically feasible.

6.5 Desorption

Desorption of basic dye from algal sorbent in batch experiments was investigated. The main purpose was not to regenerate the adsorbent since this alga was known to be the natural abundant material. However, the desorption using various solutions and conditions were tested in order to obtain the knowledge of sorption mechanism. The used alga was shaken for 1 h using 7 desorption methods (Table 4.1). Different solutions and conditions gave different desorption percentage. The results are shown in Fig.6.9. Comparatively higher desorption of dye was observed in acidic solution (1N HCl (87%); 0.1 N HCl (32%), and 0.1 N acetic acid (25%)) followed by deionized water (in shaker water bath controlled at 70°C (15%), preheated to 70°C and shook at room temperature (11%), and submerged in water (11%)) and basic solution (0.1 N NaOH (6%)).

The resultant desorption phenomenon observed in acidic solution might be attributed to ion-exchange type (Mohan et al., 2008). This happened when H+ ion competed with the dye molecules for target functional groups on the algal surface. An increase in the concentration of HCl from 0.1 N to 1 N increased the desorption percentage from 32% to 87%. The pH of PZC could also be used to explain this. At low pH region, the surface charge of the alga became less negative and the sorption was worse than at the higher pH. However, the use of water and high temperature could desorb small amont of dye. Hence, the combined ion-exchange and physical sorption phenomena could possibly control the dye-algal sorption.

6.6 Concluding remarks

The experimental results showed that *Caulerpa lentillifera* could potentially be employed as a biosorbent in the removal of a basic dye, Astrazon® Blue FGRL. The adsorption equilibrium and kinetic parameters such as the Langmuir and Freundlich constants, maximum capacity of adsorption, enthalpy of adsorption, and kinetic rate constants were also obtained from these experiments. These parameters could be used in the design of continuous flow experiments or scale-up batch experiments. The comparison of the sorption capacity between this algal sorbent and commercial activated carbon was discussed in the next chapter.

Table 6.1 Constants of Langmuir and Freundlich isotherms for sorption of Astrazon blue FGRL by *C. lentillifera*

Temperature (°C)	Langmuir constants			Freundlich constants		
	q_m (mg g^{-1})	b (l mg^{-1})	R^2	K_F (mg$^{1-1/n}$ l$^{1/n}$ g^{-1})	n	R^2
18	30.67	0.015	0.94	0.43	1.04	0.97
27	37.17	0.020	0.96	0.77	1.10	0.96
40	48.65	0.021	0.99	0.93	1.11	0.99
50	49.26	0.031	0.99	1.4	1.10	0.97
70	46.73	0.053	0.99	2.4	1.20	0.99

Table 6.2 First- and pseudo second-order rate constants obtained at different initial dye concentrations

C_i	$q_{e,exp}$	First-order rate constants			Second-order rate constants		
(mg l^{-1})	(mg g^{-1})	$k_1 \times 1000$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	$k_2 \times 1000$ (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2
20	0.98	22.3	0.51	0.9793	555.8	0.98	0.9999
40	2.19	32.0	0.55	0.8483	511.2	2.20	1.0000
80	4.56	39.8	0.82	0.8723	491.4	4.57	1.0000
160	9.05	40.8	1.23	0.9656	117.5	9.10	1.0000
320	18.56	43.5	1.21	0.9545	88.2	18.62	1.0000
640	37.75	47.9	3.06	0.9552	8.0	38.61	0.9997
1280	72.95	59.9	4.68	0.9676	2.2	75.76	0.9993

Table 6.3 Thermodynamic parameters for sorption of Astrazon® FGRL on *C. lentillifera*

Temperature (°C)	Thermodynamic parameters		
	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
18	-3.85	14.87	12.08
27	-4.69		
40	-5.02		
50	-6.23		
70	-8.15		
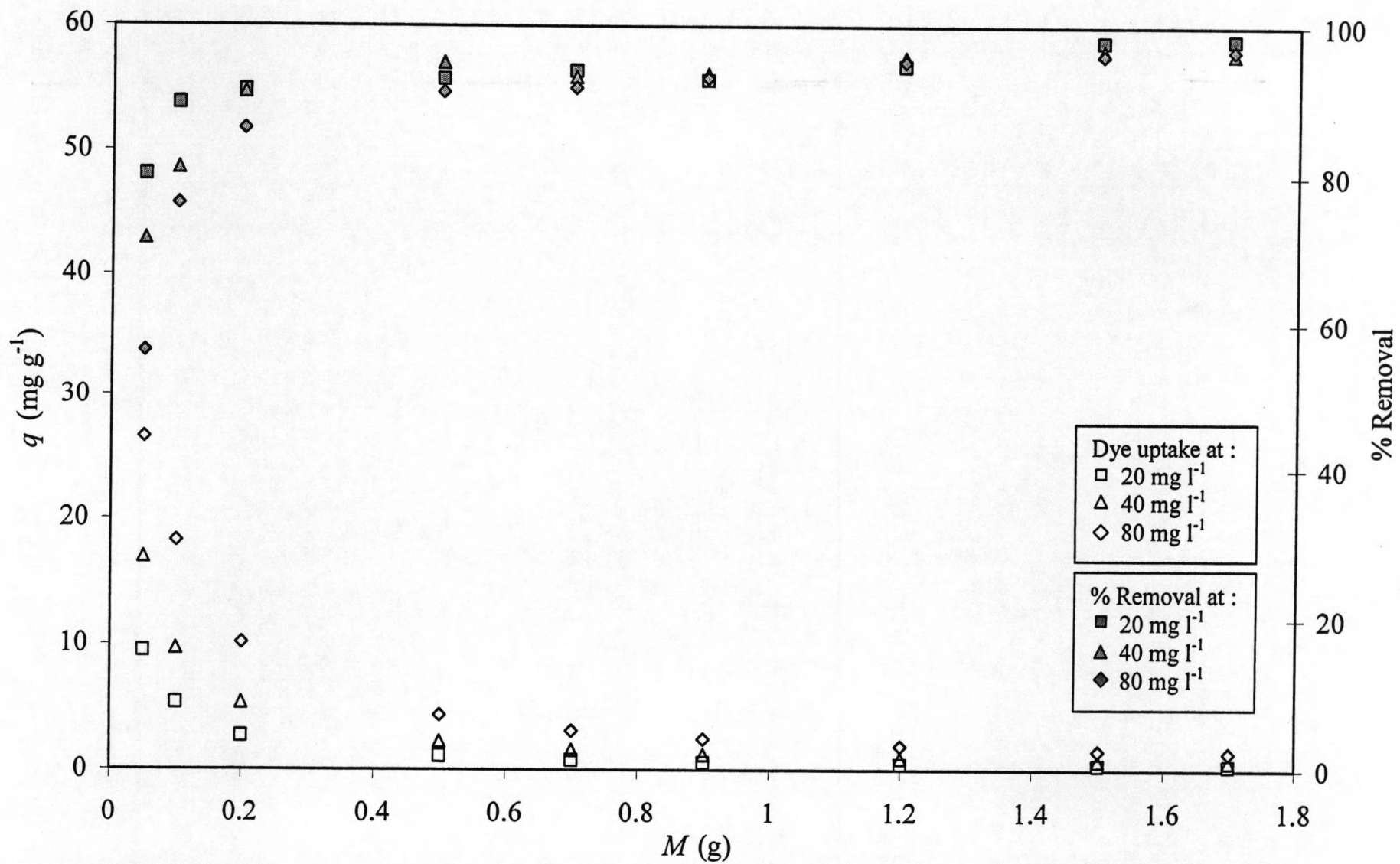
Fig. 6.1 Isotherm plots of the sorption of Astrazon® Blue FGRL on *C. lentillifera* (initial concentration=100 mg l^{-1}, pH=7±0.5)
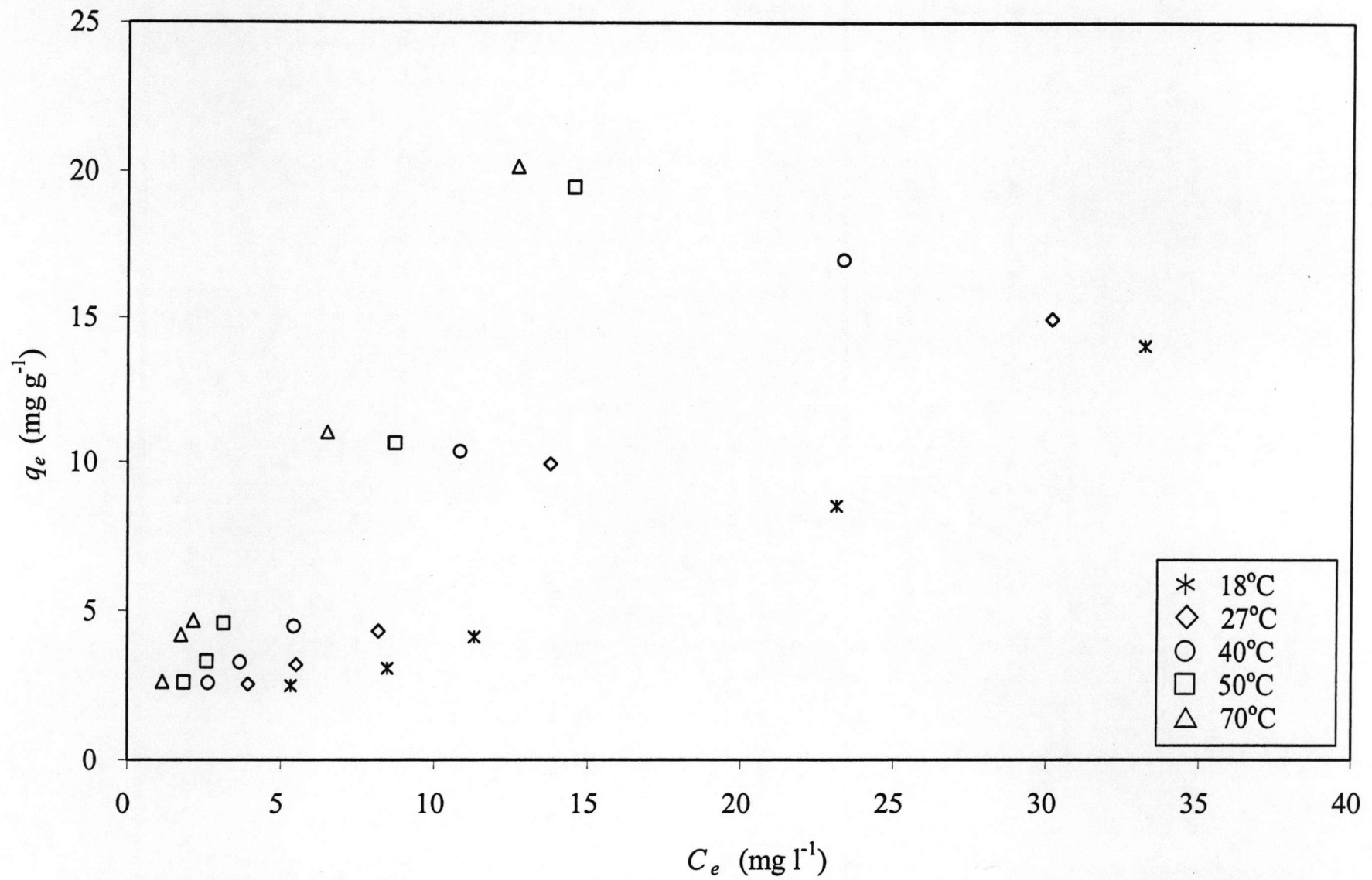
Fig. 6.2 Isotherm plots of the sorption of Astrazon® Blue FGRL on *C. lentillifera* (initial concentration=100 mg l⁻¹, pH=7±0.5)
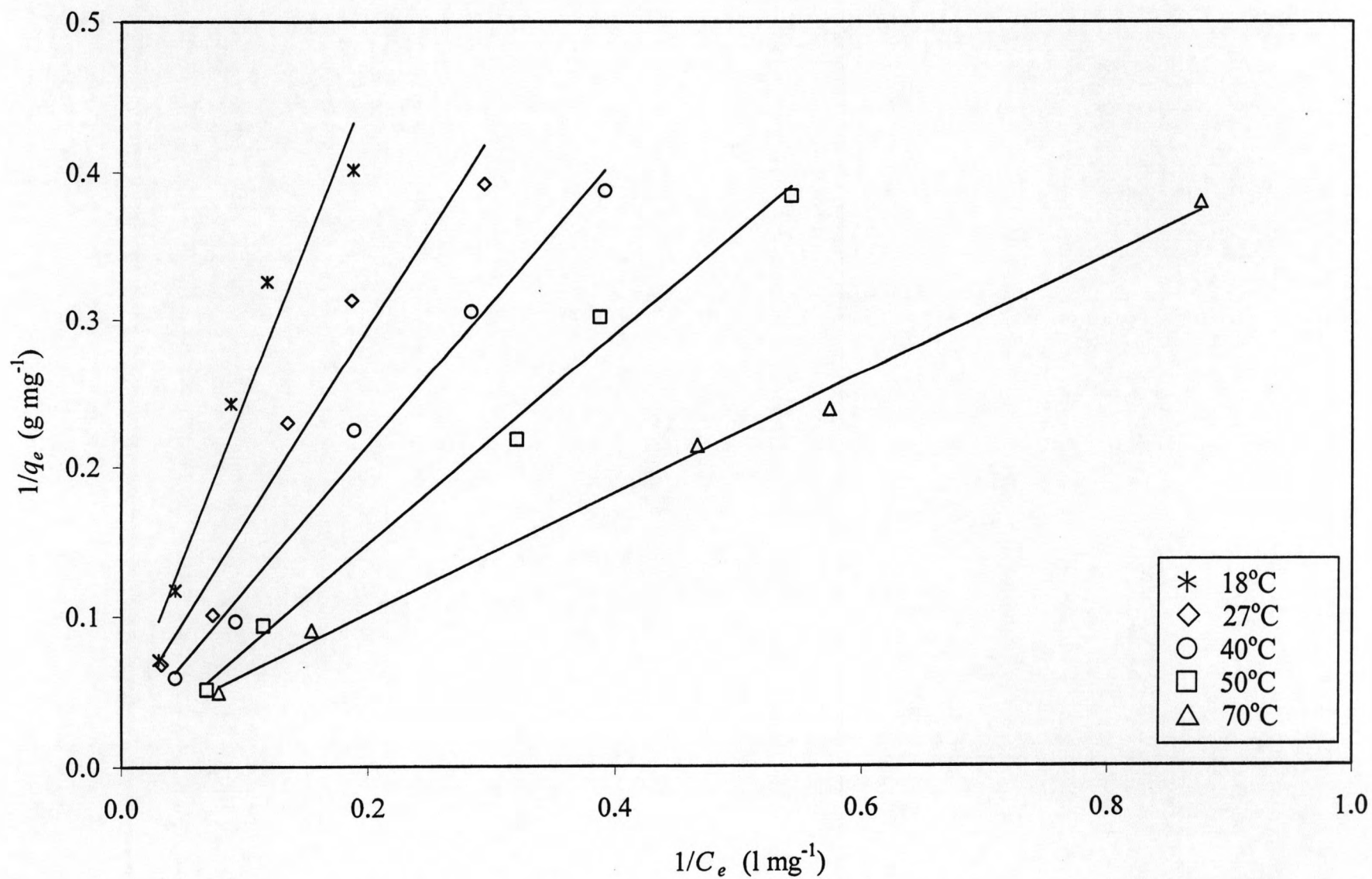
Fig. 6.3 Langmuir plots of the sorption of Astrazon® Blue FGRL on *C. lentillifera* (initial concentration=100 mg l⁻¹, pH=7±0.5)
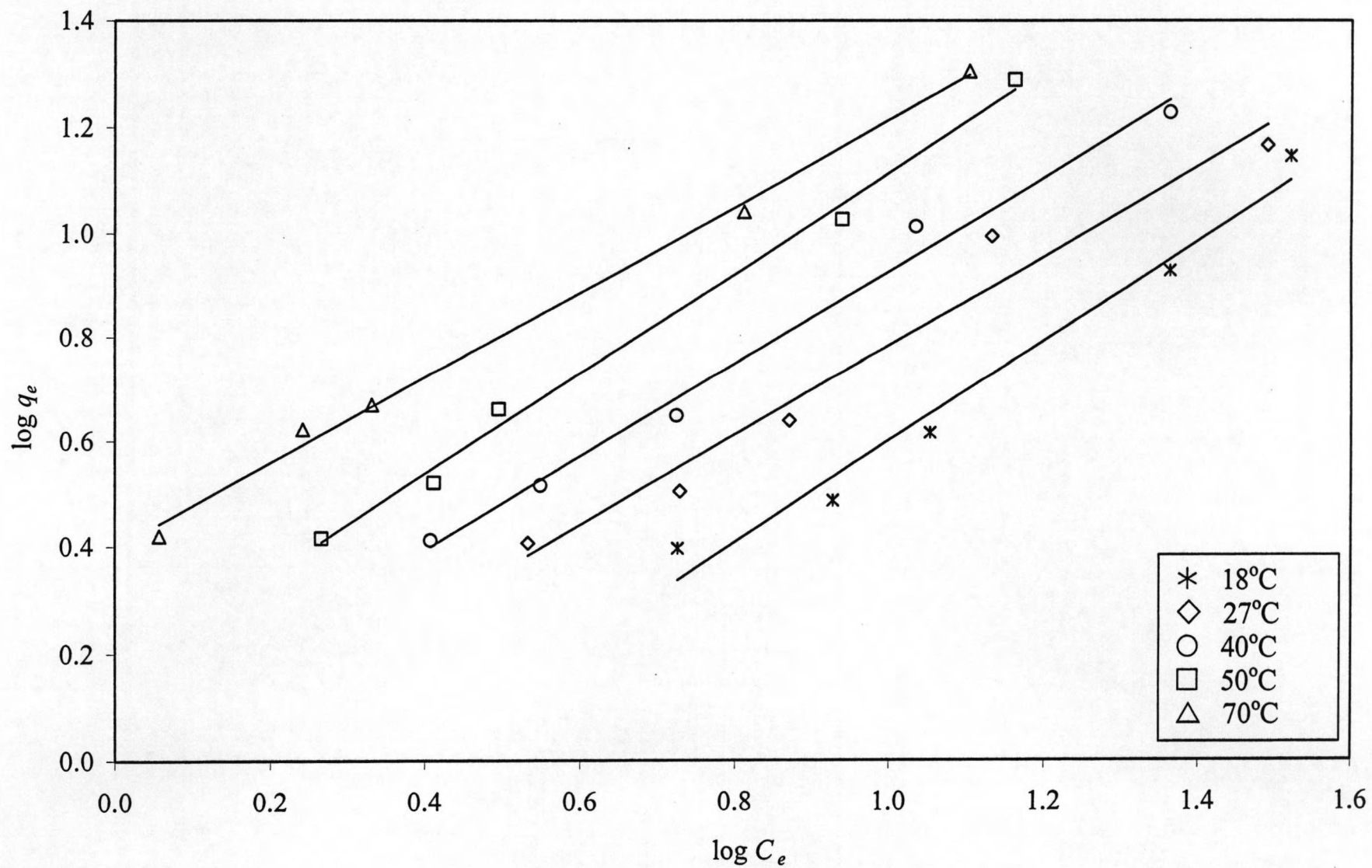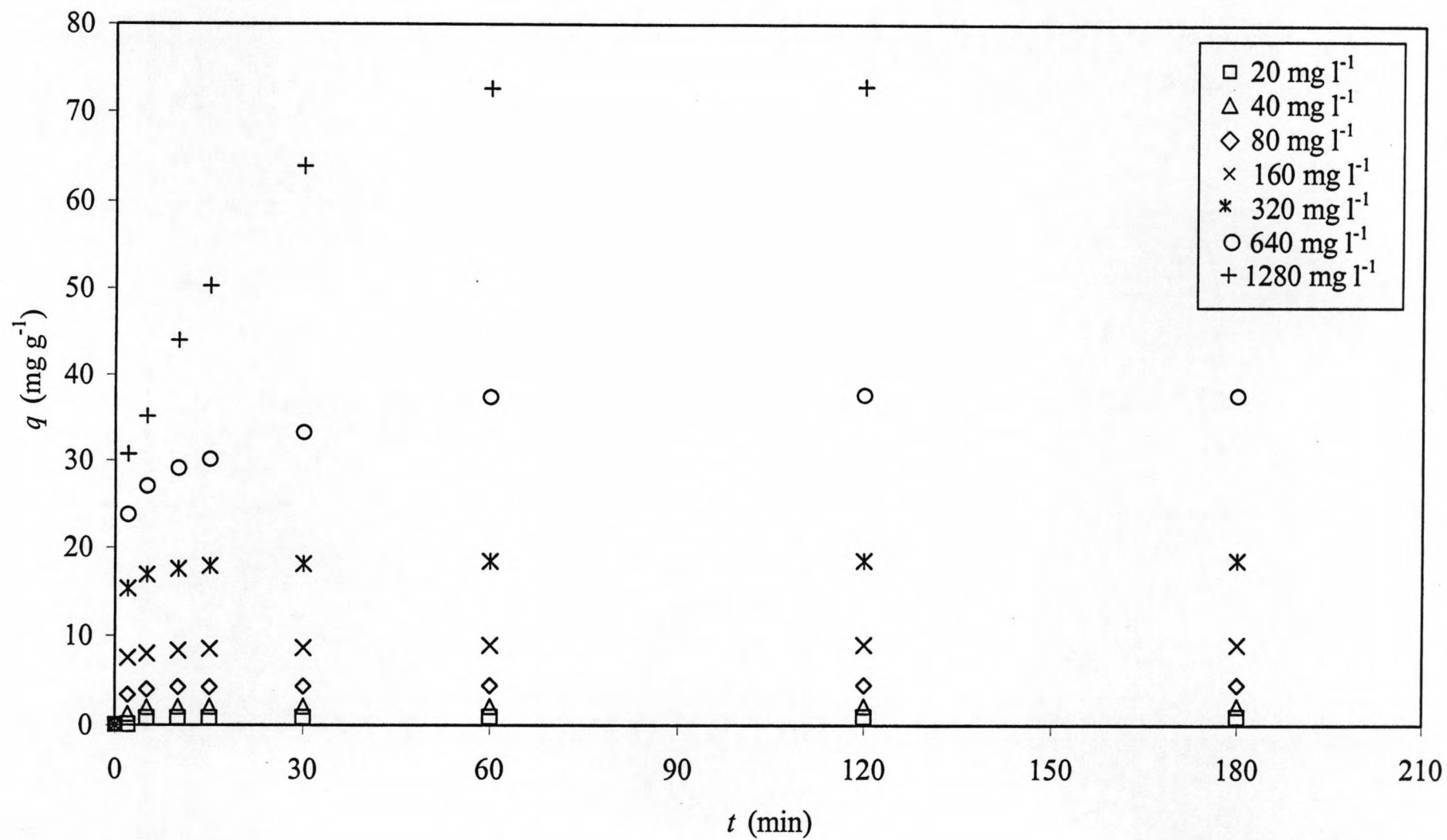
Fig. 6.4 Freundlich plots of the sorption of Astrazon® Blue FGRL on *C. lentillifera* (initial concentration=100 mg l^{-1}, pH=7±0.5)

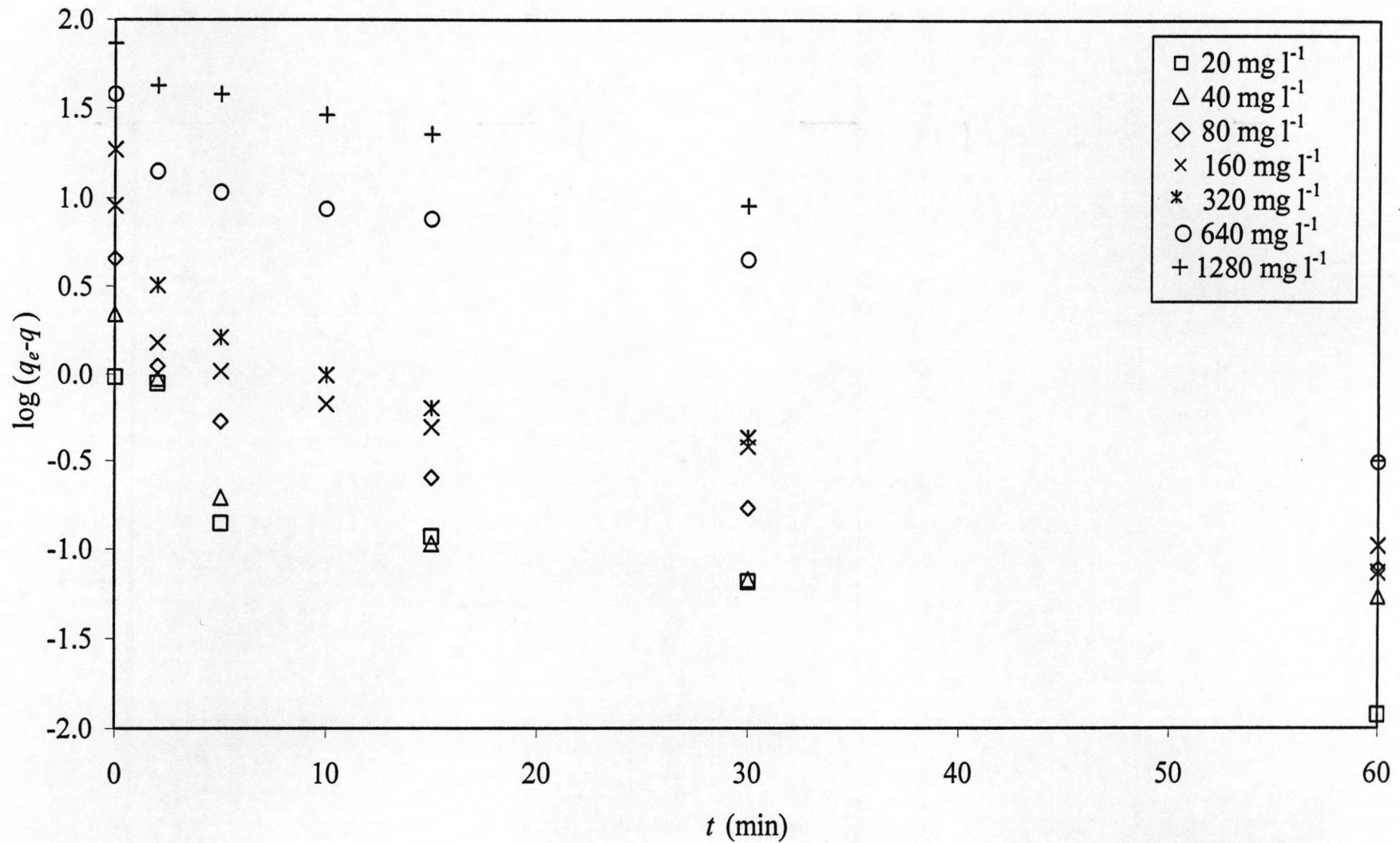Fig. 6.5 Kinetics of Astrazon Blue FGRL uptake by *C. lentillifera* (adsorbent dose = 0.5 g, temperature = 27°C)

Fig. 6.6 First-order sorption kinetics of Astrazon Blue FGRL by *C. lentillifera* at various initial dye concentrations (adsorbent dose = 0.5 g, temperature = 27°C)
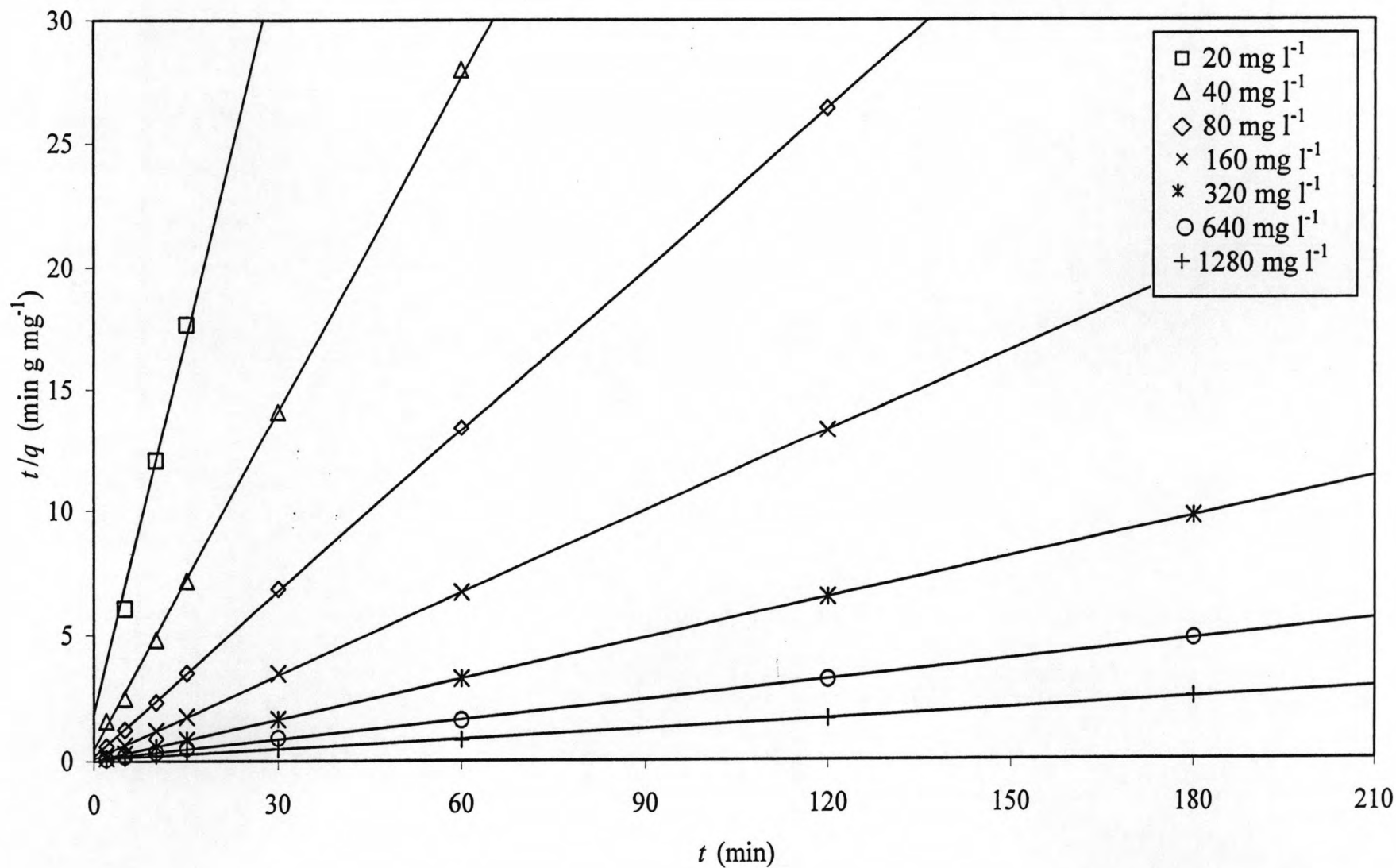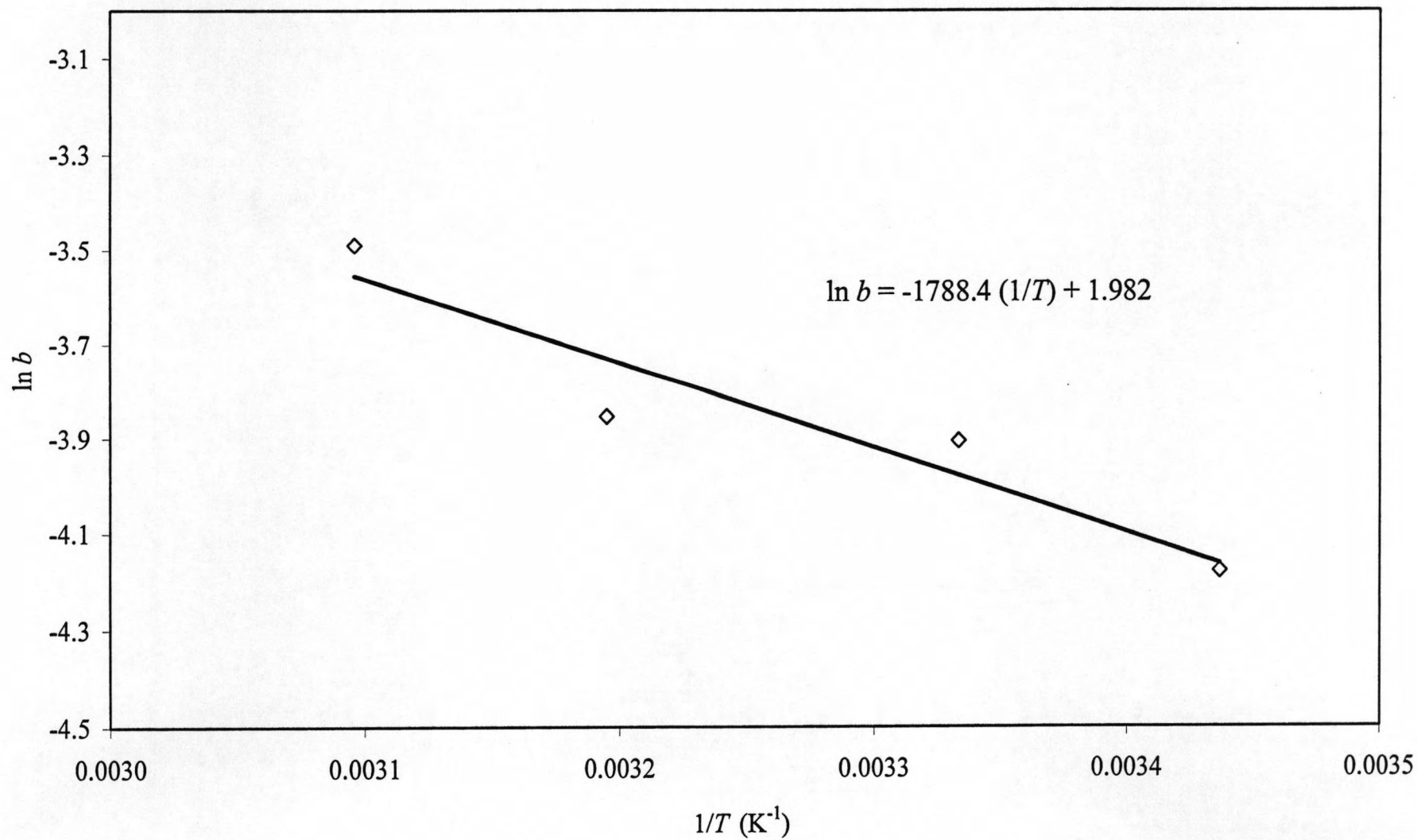
Fig. 6.7 Pseudo second-order sorption kinetics of Astrazon Blue FGRL by *C. lentillifera* at various initial dye concentrations (adsorbent dose = 0.5 g, temperature = 27°C)

$$\ln b = -1788.4\,(1/T) + 1.982$$

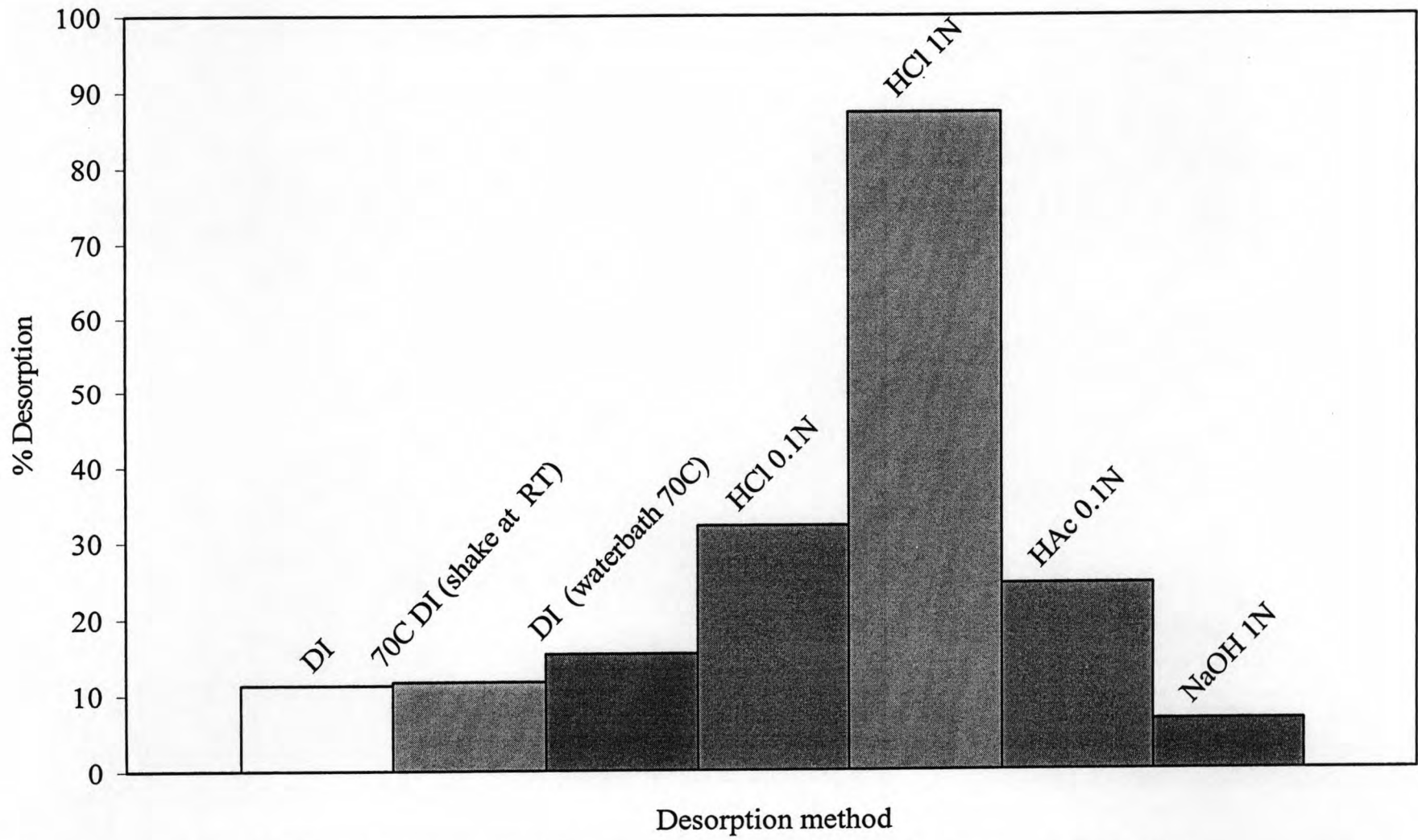Fig. 6.8 Plot of ln *b* versus 1/*T* for Astrazon blue FGRL

Fig. 6.9 Desorption percentage of Astrazon Blue FGRL from algal sorbent using various methods