

# CHAPTER VII

## COMPARISON STUDY WITH ACTIVATED CARBON

Adsorption is generally regarded as an effective technique for the treatment of dye-containing wastewater. One of the most widely used sorbents is activated carbon which has relatively high sorption capacity for a wide variety of dyes (Choy et al., 1999; Robinson et al., 2001). Due to economical reasons, several attempts have been made to find alternative sorbents particularly for the sorption of basic dyes. Examples of these biosorbents include orange peel (Namasivayam et al., 1996), palm fruit bunch (Nassar and Magdy, 1997), peat (Ho and McKay, 1998a), teak wood bark, cotton waste, rice husk (McKay et al., 1999), sugar cane dust (Khattari and Singh, 1999), bagasse fly ash (Gupta et al., 2000), and bagasse pith (McKay et al., 2003).

This work aimed to extend the basic knowledge on the application of macroalga *C. lentillifera* on the sorption of a wider range of basic dyes, including the two widely used, commercial basic dyes: Astrazon<sup>®</sup> Blue FGRL and Astrazon<sup>®</sup> Red GTLN. In addition, the effectiveness of this biosorbent on the removal of basic dyes was compared with that of activated carbon (Appendix C), the commonly used sorbent, using 'methylene blue' as a common dye for comparative evaluation.

### 7.1 Sorption kinetics

The sorption kinetics of dye removal by *C. lentillifera* and activated carbon were investigated. Six systems (Table 4.2) were set up for comparison purpose. Equilibriums were reached within one hour for all sorption systems, i.e. the equilibrium times were 10 min for the ALGA/AB system, 30 min for ALGA/AR, 30 min for ALGA/MB, 10 min for CARBON/AB, 60 min for CARBON/AR, and 30 min for CARBON/MB. AR was shown to be more easily sequestered by ALGA than by CARBON, as it only required 30 min to reach equilibrium for ALGA whereas the equilibrium time for CARBON was as long as 60 min. This finding suggested that the functional groups on algal surface could have more affinity for AR than for activated carbon. Both sorbents seemed to have similar affinities for AB and MB. The rates of

sorption for each system were also examined by applying the results with kinetic models.

Three kinetic models, first order, pseudo second order, and intra-particle diffusion models, were employed to determine the kinetic nature of each sorption system. The first order kinetic model (Lagergren, 1898) has been widely used to predict the dye sorption kinetics. This can be expressed in a mathematical form as shown in Eqs. (3.8)-(3.9).

The first order rate constant,  $k_1$ , can be calculated from the plot of  $\log(q_e - q)$  versus time  $t$  (Fig. 7.1). The resulting  $k_1$  value and  $R^2$  for each sorption system are shown in Table 7.1. Due to low correlation coefficient,  $q_{e,1}$  could not be interpreted from the plot. The results implied that the first order model was not appropriate in describing such relationships. The pseudo second order kinetic model derived by Ho and McKay (1999), on the other hand, has been proven to be suitable for several sorption systems (Ho and McKay, 1998b; Ho and McKay, 1998c; Fu and Viraraghavan, 2000; Banat et al., 2003). Mathematical form of the pseudo second order models are showed in Eqs. (3.10)-(3.11).

The linear plots of  $t/q$  versus  $t$  for the pseudo second order in Eq. (7.4) were obtained for all sorption systems as shown in Fig. 7.2.  $q_e$  and  $k_2$  can be directly determined from the slope and intercept of the plot. The model parameters are also shown in Table 7.1. The  $q_e$  values calculated from the pseudo second order were in good agreement with the experimental data,  $q_{e,exp}$ , and the extremely high  $R^2$  ( $>0.999$ ) for all sorption systems indicating that the sorption kinetics could be best described by this model. This finding supported the assumption of the pseudo second order model that the sorption process was due to chemisorption (Ho, 2003). In this case, chemical sorption could have occurred by the interaction between polar functional groups on the sorbent surface and dyes. Similar phenomena have been observed in the biosorption of Remazol Black B on biomass (Aksu and Tezer, 2000), the sorption of Congo Red on activated carbon (Namasivayam and Kavitha, 2002), and Methylene Blue on perlite (Doğan et al., 2004).

In order to understand the sorption mechanism, the functional groups on the algal surface were specified using FTIR technique. Table 5.1 displays possible functional groups on the algal surface, including hydroxyl, carbonyl, amine, sulfonyl, carbonyl, and alkyl groups. These functional groups can act as chemical binding agents. Carboxyl, hydroxyl, and sulfonyl groups can dissociate and become negative

charge. That means these functional groups could attract the positive charge functional groups on dye structures such as quaternary ammonium ion ( $\text{NR}_4^+$ ) and nitronium ion ( $\text{NO}_2^+$ ) (see Fig. 2.1), and this is called “Negative sorption” which is the sorption of the positive species by negative sorption sites (Volesky, 1990). The second order rate constants for the sorption of methylene blue onto *C. lentillifera* took the value of  $0.21 \text{ g mg}^{-1} \text{ min}^{-1}$ . This was relatively high with respect to the rate constants for other biosorbents, e.g.  $k_2 = 0.087 \text{ g mg}^{-1} \text{ min}^{-1}$  for the sorption of methylene blue on perlite (Acemioğlu, 2005), or  $= 0.0137 \text{ g mg}^{-1} \text{ min}^{-1}$  for the sorption of methylene blue on rice husk (Vadivelan and Kumar, 2005). High  $k_2$  suggested that the basic dyes could be rapidly uptaken by the algal functional groups, resulting in the system quickly reaching equilibrium as reported earlier.

It is interesting to note that the second order rate constants for the sorption of methylene blue for the two sorbents were in the same range. Conventionally, this implies that the two sorbents could be regarded as equally effective in the sorption of dyes. However, activated carbon gave a higher second order rate constant for the sorption of AB than *C. lentillifera*, whilst *C. lentillifera* exhibited a higher second order rate constant for AR. Generally,  $k_2$  acquired from the pseudo second order model indicates the rate at which color removal takes place. Hence, the  $k_2$  results indicated that *C. lentillifera* could more rapidly sequester AR when compared with activated carbon, but was more slowly in the sorption of AB. With respect to the sorption of MB, both ALGA and CARBON seemed to have the same sorption characteristics, i.e. the same sorption capacity and the same equilibrium time. The finding illustrated that methylene blue might not be a good representative of sorption efficiency as it does not reflect the actual sorption capacity of the sorbent for other types of dyes.

## 7.2 The rate limiting step

The analysis for the rate limiting step is an important step in the investigation of sorption processes (Sarkar et al., 2003). Generally, the sorption process can be described by three consecutive steps, starting with the liquid film diffusion, internal diffusion, and sorption of solute on the interior surfaces of the pores and capillaries space of the sorbent (Vadivelan and Kumar, 2005). Among these three steps, the last step is often relatively fast and thus is not considered as a rate determining step (Crank, 1956). The sorption of basic dyes onto both activated carbon and *C.*

*lentillifera* should therefore be governed by film diffusion process and/or intra-particle diffusion.

Intra-particle diffusion model developed by Weber and Morris (1963) described the process in which the rate limiting step was not external mass transfer. The rate of intra-particle diffusion is a function of  $t^{0.5}$  (Eq. (3.7)). The plots of  $t^{0.5}$  versus  $q_t$  are shown in Fig. 7.3. It was noticed that all plots showed multi-linearity where a steeper curve at the beginning of experiment implied a faster sorption than the sorption at the later stage. In other words, during the initial period, the sorption could take place more easily as the sorbate could move at a faster speed and not restricted by the difference in the concentration levels. In this case, both film and pore (intra-particle) diffusions were rate limiting steps. The later portion of the curve increased at a much slower rate and this suggested the situation where the concentration of sorbate inside the particle was already quite high, exhibiting a smaller concentration gradient which restricted the movement of the sorbate. Hence, at later stage, intra-particle diffusion was considered to be the main rate limiting step.

### 7.3 Sorption isotherms

For the equilibrium studies, experimental results were analyzed with Langmuir (1918) (Eq. (3.3)) and Freundlich (1906) (Eq. (3.4)) models. Straight lines could be well observed between  $1/q_e$  and  $1/C_e$  indicating that experimental data followed Langmuir model (Fig. 7.4). This finding suggested that the sorption of dyes on *C. lentillifera* and activated carbon was monolayer coverage. On the other hand, parameter fitting revealed that experimental data could not be arranged in linear form. Hence, Freundlich isotherm (Fig. 7.5) was considered not appropriate for describing the sorption nature of all six systems.

Isotherm parameters are tabulated in Table 7.2. For AB and AR, the sorption onto activated carbon gave higher Langmuir constant,  $b$ , which meant higher affinity than those of *C. lentillifera*. The parameter  $b$  of ALGA/MB was higher than that of CARBON/MB, indicating that methylene blue had more affinity with *C. lentillifera*. Although the highest  $b$  of  $0.107 \text{ l mg}^{-1}$  was obtained from the sorption of AB onto activated carbon (CARBON/AB), a higher  $q_m$  for *C. lentillifera* suggested that the alga had higher sorption capacity than activated carbon. For all three dyes, *C. lentillifera* gave higher  $q_m$  than activated carbon where the highest  $q_m$  of  $417 \text{ mg g}^{-1}$  was achieved for the sorption of methylene blue on *C. lentillifera* (ALGA/MB).

#### 7.4 Concluding remarks

Maximum sorption capacity ( $q_m$ ) obtained from the sorption of MB onto *C. lentillifera* was  $417 \text{ mg g}^{-1}$  which was relatively high in comparison with the previous records as summarized in Table 7.3. Sorption behaviors of the six systems were compared in order to give comparative evaluation where the sorption capacity of the alga was proven to be superior to that of activated carbon. Moreover, the equilibrium times of the algal systems were found to be shorter and this rendered the alga a potential biosorbent for color removal.

Table 7.1 Comparison of kinetic parameters for the sorption of basic dyes onto *C. lentillifera* and activated carbon

Sorption system	$q_{e,exp}$ (mg g <sup>-1</sup> )	First order		Pseudo second order		
		$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{e,2}$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
ALGA/AB	4.55	$(18.3 \pm 1.8) \times 10^{-2}$	0.8266	4.57 ± 0.34	$(25.3 \pm 1.8) \times 10^{-2}$	1
CARBON/AB	3.67	$(36.4 \pm 3.8) \times 10^{-2}$	0.7121	3.68 ± 0.42	$(74.7 \pm 8.3) \times 10^{-2}$	1
ALGA/AR	4.55	$(33.8 \pm 3.4) \times 10^{-2}$	0.8428	4.55 ± 0.33	$(36.1 \pm 3.5) \times 10^{-2}$	1
CARBON/AR	4.61	$(16.4 \pm 1.8) \times 10^{-2}$	0.7671	4.65 ± 0.40	$(18.8 \pm 2.3) \times 10^{-2}$	0.9999
ALGA/MB	4.70	$(10.2 \pm 1.2) \times 10^{-2}$	0.7618	4.73 ± 0.39	$(21.3 \pm 1.9) \times 10^{-2}$	1
CARBON/MB	4.80	$(4.39 \pm 4.8) \times 10^{-2}$	0.8850	4.88 ± 0.47	$(21.4 \pm 2.2) \times 10^{-2}$	0.9998

Confidential interval of the data by t-test of 95% ( $\alpha = 0.05$ )

Table 7.2 Langmuir parameters of the sorption of basic dyes onto *C. lentillifera* and activated carbon

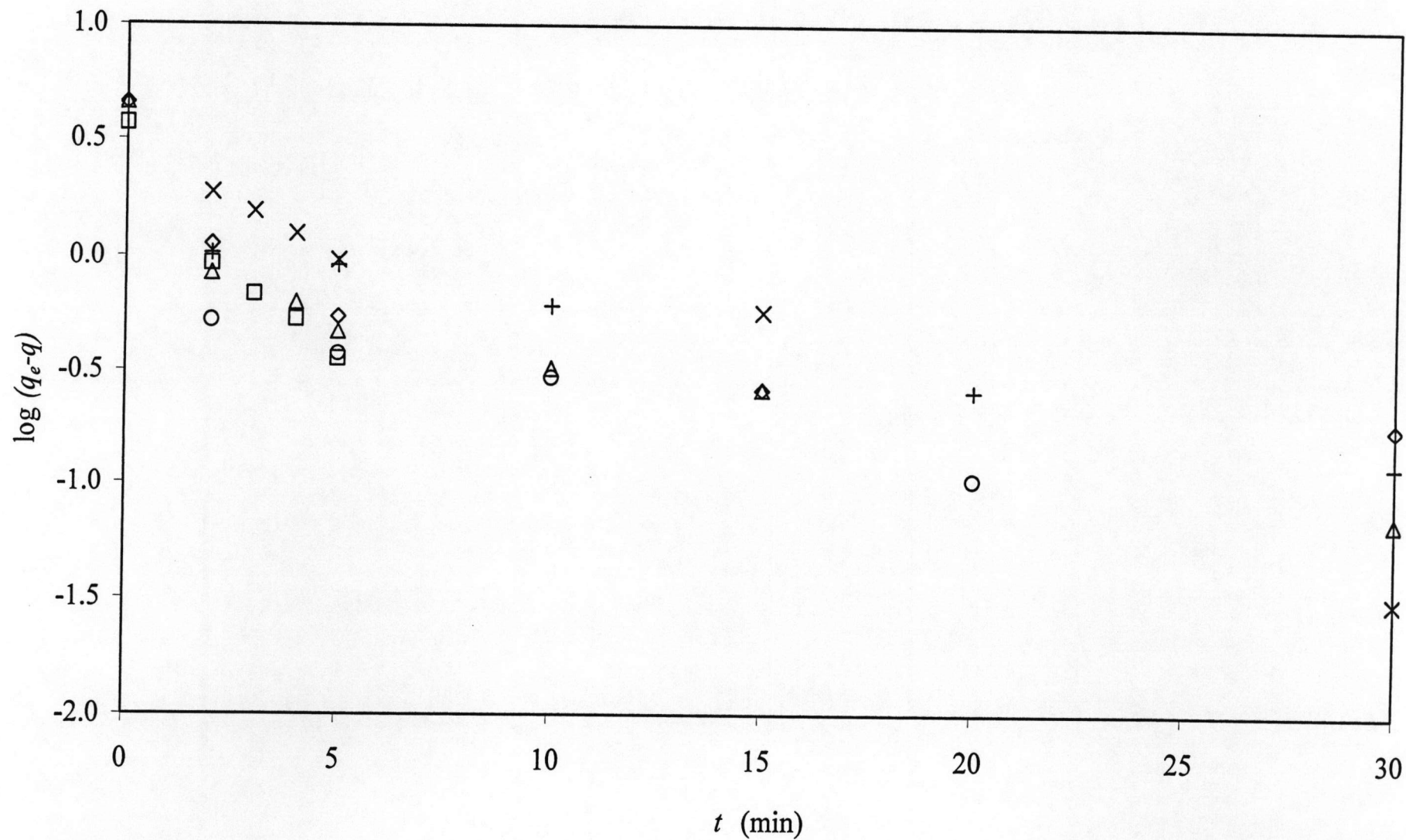
Sorption System	Langmuir isotherm parameters			Freundlich isotherm parameters		
	$q_m$ (mg g <sup>-1</sup> )	$b$ (l mg <sup>-1</sup> )	$R^2$	$K_F$	$n$	$R^2$
ALGA/AB	38.9±3.4	(1.44±0.23)×10 <sup>-2</sup>	0.9873	1.68±0.35	1.01±0.15	0.9413
CARBON/AB	21.6±2.4	(1.07±0.12)×10 <sup>-1</sup>	0.9797	0.68±0.12	1.18±0.14	0.9332
ALGA/AR	47.6±4.2	(2.02±0.18)×10 <sup>-2</sup>	0.9477	0.74±0.28	0.93±0.10	0.9071
CARBON/AR	6.20±0.92	(7.86±1.2)×10 <sup>-2</sup>	0.9930	1.12±0.12	0.93±0.08	0.9669
ALGA/MB	417±19	(6.29±0.29)×10 <sup>-3</sup>	0.9581	1.25±0.53	1.10±0.15	0.9087
CARBON/MB	238±12	(8.82±0.44)×10 <sup>-4</sup>	0.9703	2.01±0.71	1.14±0.11	0.9084

Confidential interval of the data by t-test of 95% ( $\alpha = 0.05$ )

Table 7.3 Comparison of sorption capacity of methylene blue onto various sorbents

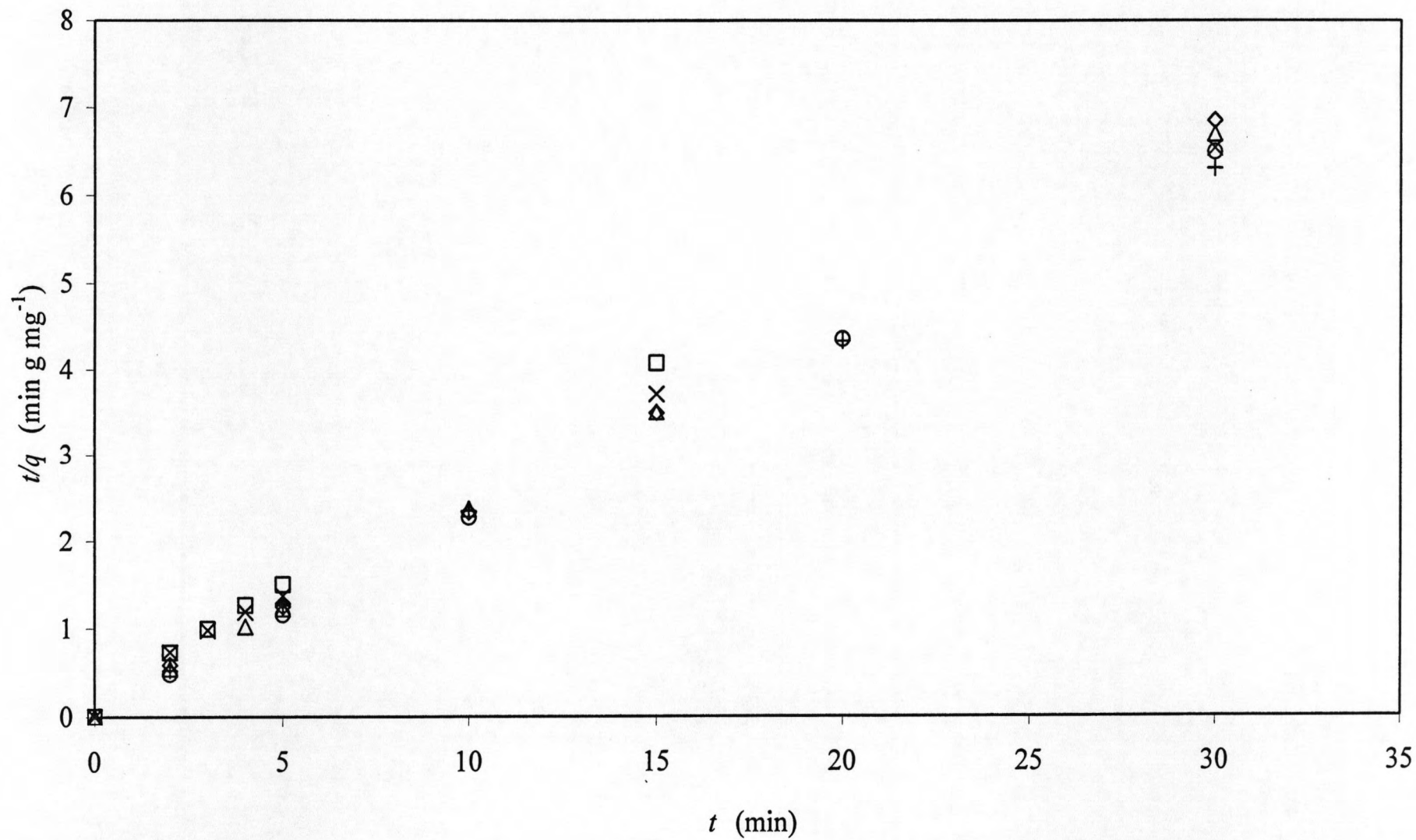
Sorbent	Temperature (°C)	$q_m$ (mg g <sup>-1</sup> )	References
Teak wood bark	20	915	McKay et al., 1999
<i>C. lentillifera</i>	25	417	<i>This study</i>
Rice husk	20	312	McKay et al., 1999
Cotton waste	20	278	McKay et al., 1999
<b>Activated carbon</b>	<b>25</b>	<b>238</b>	<i>This study</i>
Giant duckweed	25	145	Waranusantigul et al., 2003
Activated tires	-	130	Saniz-Diaz and Griffith, 2000
Activated sewage char	-	120	Saniz-Diaz and Griffith, 2000
Rice husk	32	40.6	Vadivelan and Vasanth Kumar, 2005
Raw date pits	20	80.3	Robinson et al., 2001
Amorphous silica	-	26.5	Woolard et al., 2002
Zeolite	-	12.7	Woolard et al., 2002





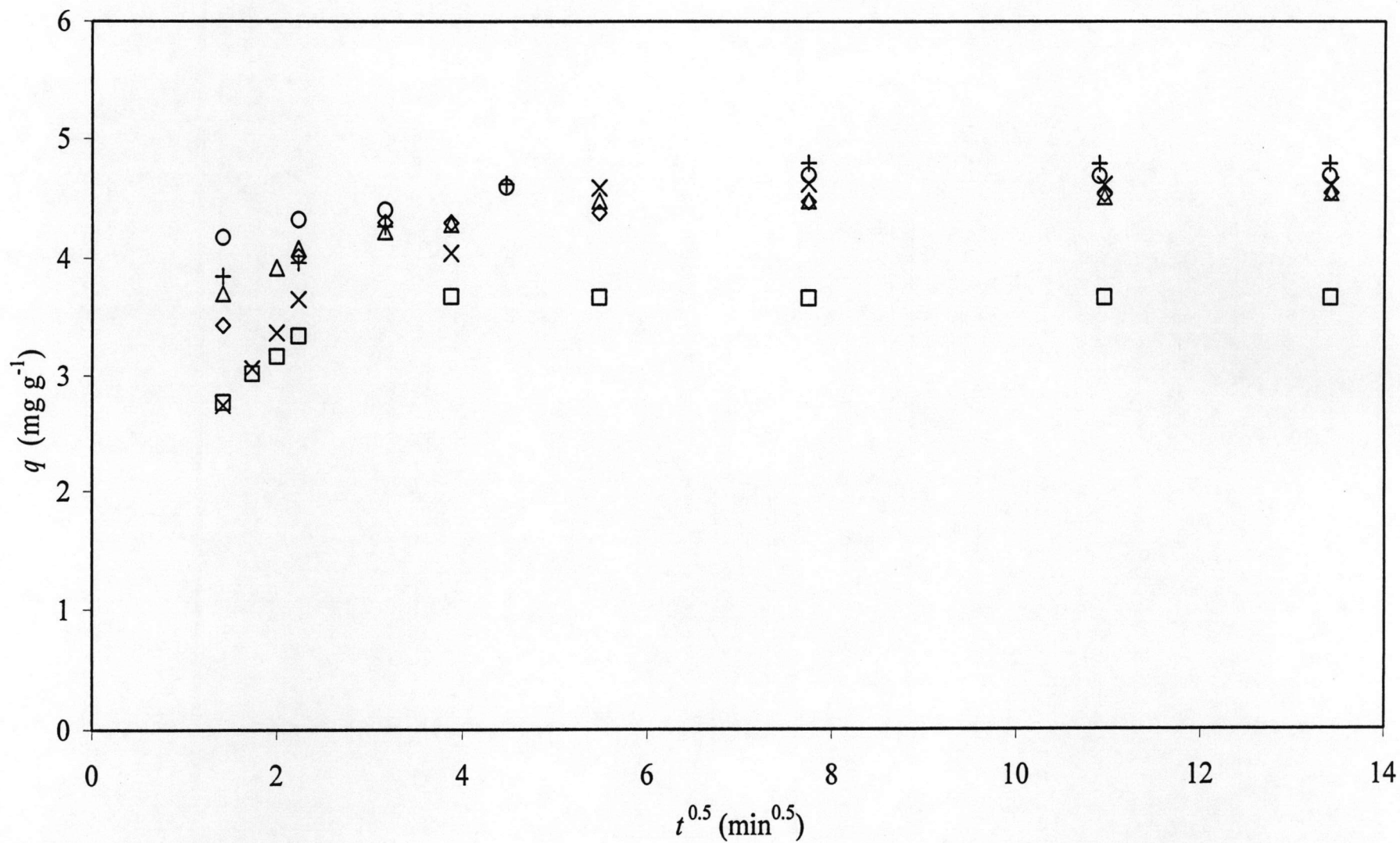
◇ ALGA/AB, △ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB

Fig. 7.1 First order kinetics for the sorption of basic dyes on dried *C. lentillifera* and activated carbon (adsorbent dose = 0.5 g, temperature = 27°C)



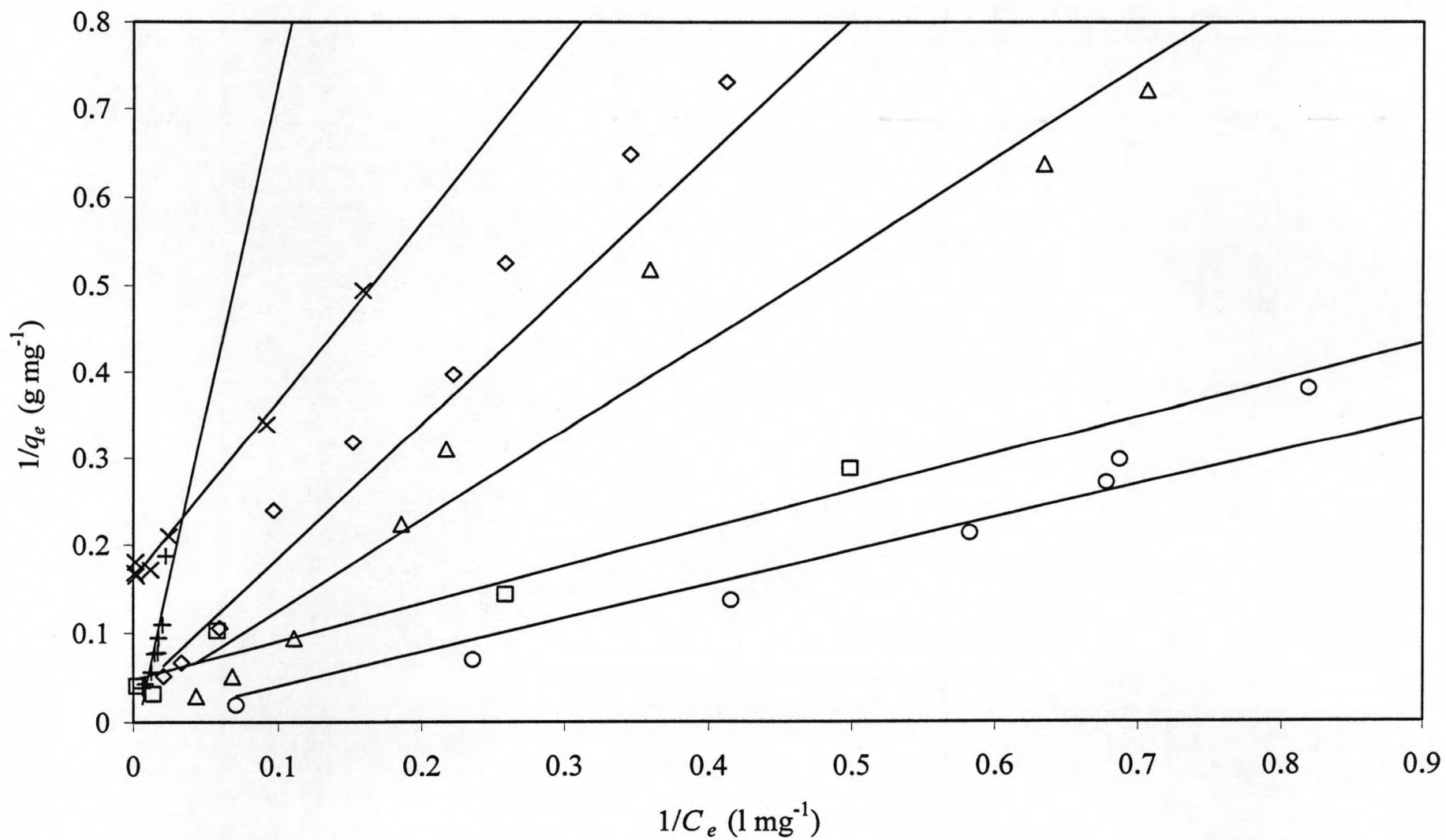
◇ ALGA/AB, △ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB

Fig. 7.2 Pseudo second order kinetics for the sorption of basic dyes on dried *C. lentillifera* and activated carbon (adsorbent dose = 0.5 g, temperature = 27°C)



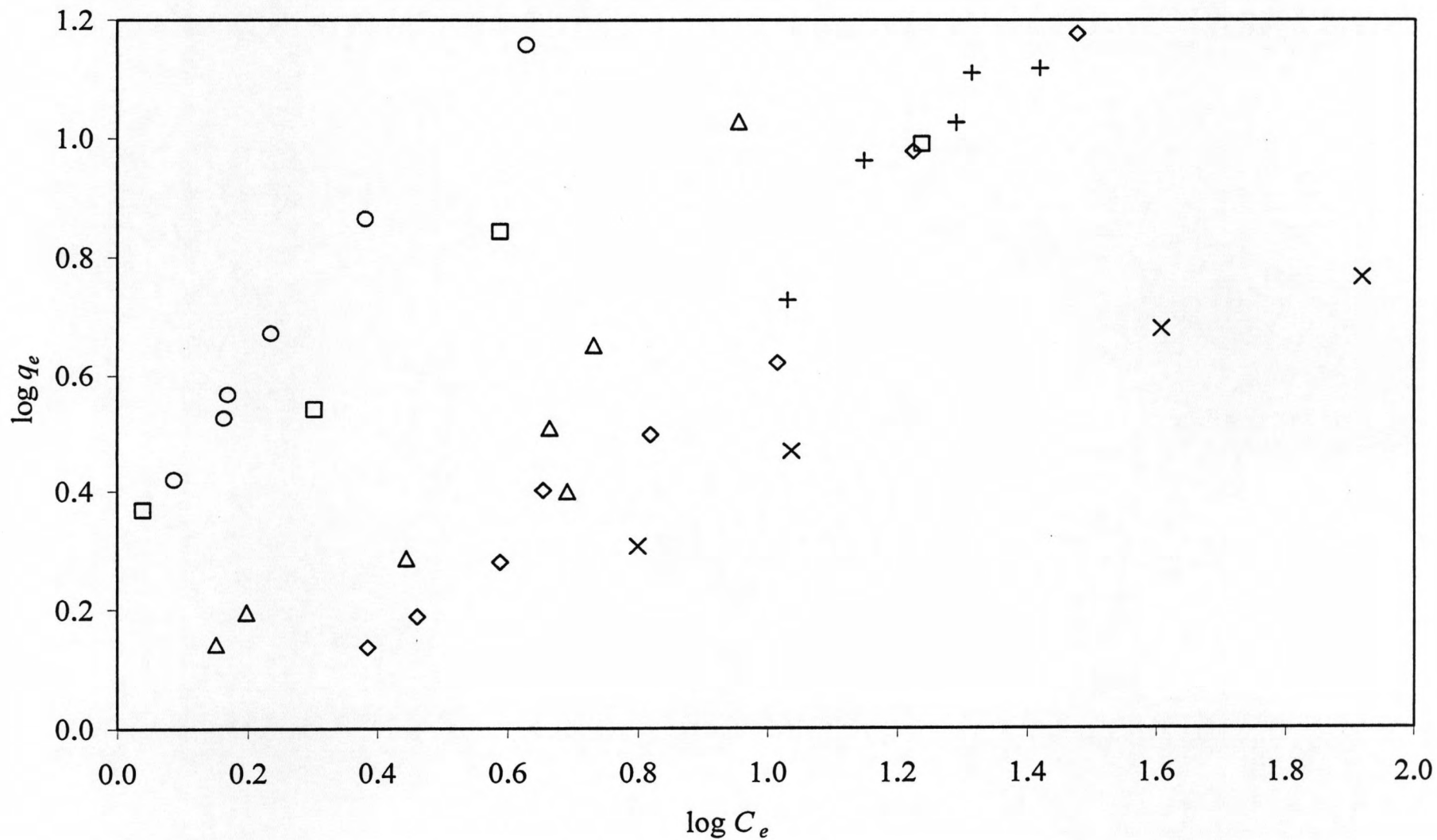
◇ ALGA/AB, Δ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB

Fig. 7.3 Intra-particle diffusion plots for the sorption of basic dyes on dried *C. lentillifera* and activated carbon (adsorbent dose = 0.5 g, temperature = 27°C)



◇ ALGA/AB, △ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB

Fig. 7.4 Langmuir plots for the six sorption systems (adsorbent dose = 0.5 g, temperature = 27°C)



◇ ALGA/AB, △ ALGA/AR, ○ ALGA/MB, □ CARBON/AB, × CARBON/AR, + CARBON/MB

Fig. 7.5 Freundlich plots for the six sorption systems (adsorbent dose = 0.5 g, temperature = 27°C)