CHAPTER IX

QUANTITATIVE MEASUREMENT TECHNIQUE
FOR BINARY DYE MIXTURE:
CASE STUDY IN SORPTION SYSTEM

Dyestuffs play an important role in many industries such as textile, food, and cosmetics. Textile industry, one of the major industries in Thailand, consumes large amount of dyes in dyeing process. Wastewaters generated from this industry are often treated with conventional secondary treatment systems, however, there are still some recalcitrant components left untreated in the effluent, and this includes substances like dyes and other chemicals such as heavy metals, bleaching agents, inorganic salts, etc., all of which are generally considered highly toxic to aquatic biota (Walsh et al., 1980). The treatment of this wastewater requires that the measurement for dyes is accurate and reliable.

Typically, the measurement for a single dye solution is performed using a simple spectrophotometric technique as most research work on the treatment of colored wastewater only focused on single-dye systems (Aksu and Tezer, 2000; Bhattacharyya and Sharma, 2005; Doğan et al., 2004; Fu and Viraraghavan, 2000; Namasivayan and Kavitha, 2002]. However, a mixed dye system is more likely to occur in actual applications and therefore a simple and accurate technique for the measurement of mixed dyes will be extremely useful. The standard methods used in the measure of color intensity for the mixed dye solution include SU (Space Unit) (Eckenfelder et al., 2000) and ADMI (American Dye Manufacturers Institute) (Allen et al., 1973). However, these methods only measure overall color intensity of the mixture, and cannot indicate the concentration of each individual dye.

This chapter proposed a simple, novel technique for the measurement of dye in the binary dye mixture. This technique was based on the light absorption nature of the dye mixture which could be classified into two main groups: non-interacting and interacting mixtures. The practice of such proposed technique was illustrated using the

adsorption application where the dye mixture was adsorbed onto dried biomass of green macroalga *Caulerpa lentillifera*.

9.1 Light absorbent spectra for single dyes and binary dye component mixtures

Fig. 9.1 illustrates that the spectra of each individual dye (AB, AR, and AY) exhibited similar single mount shape. The maximum light absorptions were observed at the wavelengths of 448, 495, and 572 nm for AY, AR and AB, respectively. These are hereafter called wavelength of maximum light absorption (λ_m). The individual dye spectra would subsequently be compared with the spectra of the dye mixtures.

Three sets of new colors were obtained when mixing two dyes together, i.e. violet from AB and AR, green from AB and AY, and orange from AR and AY. The spectra of the three dye mixtures (AB + AR, AR + AY, AB + AY) are shown in Fig. 9.2. For binary dye mixtures, the shape of the spectra could be classified into two patterns: single mount, and double peak, and these were discussed below.

9.2 Binary component that acts like a single component

For AB + AR and AR + AY, the mixture spectra were found to be single mount shape (Fig. 9.2). In order to investigate the relationship between mass ratio of dye components and the dye spectrum, both AB + AR and AR + AY mixtures were prepared in different mass ratios. The resulting absorbance in Table 9.1 demonstrates that λ_m shifted from 495 to 572 nm when AB mass in AB + AR increased from 0-0.2 mg. Similar trend was found in the spectra of AR + AY. The shift of spectra peaks in AB + AR and AR + AY was found to be related to the mass fraction of the each dye in the mixture. The relationships between dye component ratio and λ_m for AB + AR and AR + AY were shown in Fig. 9.3(a) and 9.3(b), respectively. This was also plotted together with the predicted λ_m estimated from the weighted mean method. It was clear that experimental results did not agree well with the predictions from the weighted mean method. This indicated that the shift in λ_m was not linearly dependent on the mass fraction of the dyes. For this experiment, the data could be better fitted with the polynomial model where the polynomial equations of the prediction of λ_m as a function of AB in AB + AR and of AR in AR + AY could be written in Eqs. (9.1) and (9.2), respectively.

$$\lambda_m = -274x_{AB}^3 + 449x_{AB}^2 - 102x_{AB} + 500, \ R^2 = 0.9905 \qquad (9.1)$$

$$\lambda_m = -37x_{AR}^3 + 90x_{AR}^2 - 4x_{AR} + 448, \ R^2 = 0.9955 \tag{9.2}$$

where x_{AB} is the mass fraction of AB component in AB + AR, x_{AR} the mass fraction of AR in AR + AY. The mass fraction (x) of each dye component is calculated from:

$$x = \frac{w_1}{w_1 + w_2} \tag{9.3}$$

where w_1 is the mass of the dye component 1 (mg), w_2 mass of another dye component 2 (mg). A high R^2 for both mixtures indicated the suitability of the polynomial model to the experimental data. With this technique, the dye component ratio in the mixture could be indicated from the shift of spectrum (λ_m).

In fact, the binary dye mixture with single-mount shape spectrum is also the case of dyes with two subcomponents, e.g. AB and AR, in that AB consisted of C.I.Basic Blue 159 and C.I.Basic Blue 3 whilst AR consisted of C.I. Basic Red 18:1 and C.I. Basic Yellow 28. Therefore the analysis for the quantity of the mixture at each particular composition could be performed using a conventional method where the concentration was related to the area underneath the light absorbance curve.

9.3 Binary component with two non-interacting dyes

Fig. 9.4 illustrates that the spectra of AB + AY mixtures exhibited double peak, or in other words, two-mount shape. The left peak occurred at the wavelength of 448 nm which was the same as λ_m for AY, and the right peak occurred at the same wavelength as λ_m of AB (572 nm). Hence, it was speculated that the left peak represented the AY component whereas the right one represented the AB component. This was proven to be correct in the experiment where the mass ratio of AB + AY was varied (and the different shades of color were observed), and the two peaks still occurred at the same wavelengths of AB and AY (see also Fig. 9.4). The area under each peak was linearly related to the quantity of each dye component as discussed later.

9.4 Case study: sorption experiments

The sorption experiments were conducted as a case study that represented actual applications of the use of the proposed measuring technique. Two binary dye mixtures, AB + AR and AR + AY, were used as modeled binary dye mixtures. Both mixtures were prepared from the two dyes at equal quantity (1:1 by mass). The AB + AR mixture

was the representative of the mixture that gives a single mount shape spectrum. Fig 9.5(a) shows the light absorbance spectra of the sample of dye mixture along with the spectra of the sample from the dye mixture after being adsorbed with *Caulerpa lentillifera*. The results in this figure demonstrated that there was a decrease of the area under the peaks after AB + AR was adsorbed to the algal adsorbent which corresponded to the decreasing quantity of the dyes. Conventionally, the removal of overall amount of dye could be calculated from the decrease of the area under peaks. The relationship between algal mass and the removal percentage (as the total color intensity) was illustrated in Fig. 9.5(b) where up to 80 percent removal could be achieved. However, with this conventional technique, only the total color intensity could be calculated. To separately find the removal percentage of each dye component, the following quantitative method based on the new proposed measuring method was suggested.

Figure 9.5(a) demonstrates that there was a shift in λ_m after the adsorption process. Without the adsorption (no alga), λ_m was found at 524 nm whereas the peak shifted to 512 and 496 nm after the adsorption with 0.1 and 0.5 g of alga biomass, respectively. This new λ_m could then be correlated to the mass fraction of the dye component using the information in Eq. (9.1) or in Table 9.1. For this case, λ_m at 512 nm corresponded to the mixture with the AB mass fraction of 0.39 and AR of 0.61, and λ_m at 496 was for the mixture with the AB mass fraction of 0.22 and AR of 0.78. To find the quantity of each dye at these new λ_m, two calibration curves at these two wavelengths must be constructed as shown in Fig. 9.6 and the equations for the absorbance with the total dye concentration are:

$$A = 0.0356C_T + 0.0024, R^2 = 0.9982 \tag{9.4}$$

$$A = 0.0389C_T + 0.0017, R^2 = 0.9997 \tag{9.5}$$

where A is the light absorbance and C_T the total dye concentration. The maximum light absorbance (A_{max}) or the absorbance at its λ_m of each data set was then substituted as A in the calibration curve equations (Eqs. (9.4) – (9.5)) to get the total concentration (C_t). Since the mass fractions of AB (x_{AB}) and AR (x_{AR}) were already known, they were used to calculate the concentrations of AB (C_{AB}) and AR (C_{AR}) using the following equations:

$$C_{AB} = x_{AB}.C_T \tag{9.6}$$

$$C_{AR} = x_{AR}.C_T \tag{9.7}$$

At this point, individual concentrations of AB and AR in the mixture were known, and therefore the sorption capacity, q (mg g^{-1}) for each dye component could be calculated from:

$$q = \frac{C_0 - C}{W} \times V \qquad (9.8)$$

where C_0 is the initial concentration of each dye component (mg l^{-1}), C the concentration of each dye component after being sorbed (mg l^{-1}), W mass of algal sorbent (g), V volume of the dye mixture (l).

A summary of the results from this experiment with the adsorbent dose of 0.1 and 0.5 g is given in Table 9.2 including adsorption capacities and percent removals of both dye components. The adsorption with 0.9 g of algal biomass, however, resulted in a flat peak where the point of maximum light absorption (λ_m) could not be observed. In this particular case, the estimation of each dye component in the dye residue could not be accomplished.

While AB + AR was the representative of the mixture that gave a single mount shape spectrum, AB + AY represented the mixture with double peaks. Fig. 9.7(a) shows a decrease of area under the peaks after the dye mixtures were adsorbed to the algal adsorbent at various dosages. It was obvious from Fig. 9.7(a) that, after adsorption process, the peaks still exhibited a two-separated mount shape. Hence, the removal of each dye in the dye mixture could be interpreted from the area under both peaks ($\lambda_m = 572$ for AB and $\lambda_m = 448$ for AY). The calculated results on the removal percentages for each dye are presented in Fig. 9.7(b) whereas Table 9.3 summarizes the results of the removal characteristics for each dye in the AB + AY mixture with the dried biomass.

It was interesting to note that, from the results in Fig. 9.7, the algal adsorbent had more affinity to AB than AY particularly at low adsorbent dose. This could be due to differences in dye structures. In Fig. 2.1, C.I. Basic Blue 159 which is composed in AB has 6 nitrogen atoms and electron could be localized among these atoms and yielded positive charges. On the other hand, C.I. Basic Yellow 28, the composition of AY, has only 3 nitrogen atoms which is lower that that of C.I. Basic Blue 159. Hence, there are more positions of positive charges on AB and, as a result, increases the possibility of the dye to adsorb on the alga surface. However, at high adsorbent doses, the removal percentage of AB and AY were not significantly different.

9.5 Concluding remark

Certain general points may be deduced from the experiments on the synthetic dye mixtures and the adsorption of the mixtures by *C. lentillifera*. Firstly, the spectrum shapes of the mixture could be one mount or double mount shapes. The shapes of the spectrum revealed whether the dye component could react with each others where the shift of spectra peaks indicated the dye components ratio. In terms of actual applications, this proposed measuring technique could well be used effectively, and in this work, the adsorption of dye with dried biomass of *C. lentillifera* was employed to illustrate an estimate of removal efficiency for each individual dye in the dye mixture. The shift of spectra was found in the adsorption experiments, and therefore, an unequal affinity of the alga to each dye component could be evaluated. Overall, this analytical method was proposed as a simpler approach for the measurement of individual dye component in the mixture of two dyes. Since this required no extra-expense on chemicals or instruments, this technique could be an add-on step to any existing dye researches in order to quantify the dye components in the mixtures.

Table 9.1 Shift of λ_m due to changes in the mass ratio

Dye mixture	Mass of each dye component (mg)			λ_m (nm)
	AB	AR	AY	
AB + AR	0	0.200	0	495
	0.025	0.175	0.025	498
	0.050	0.150	0.050	500
	0.075	0.125	0.075	505
	0.100	0.100	0.100	524
	0.125	0.075	0.125	546
	0.150	0.050	0.150	563
	0.175	0.025	0.175	569
	0.200	0	0.200	572
AR + AY	0	0	0.200	448
	0	0.025	0.175	449
	0	0.050	0.150	454
	0	0.075	0.125	457
	0	0.100	0.100	462
	0	0.125	0.075	472
	0	0.150	0.050	482
	0	0.175	0.025	488
	0	0.200	0	495

Table 9.2 Concentration and sorption capacity of each dye component (AB and AR) in binary dye mixture (AB + AR)

Algal mass (g)	λ_m (nm)	X_{AB} (-)	X_{AR} (-)	A_{max} (-)	C_t (mg l^{-1})	C_{AB} (mg l^{-1})	C_{AR} (mg l^{-1})	q_{AB} (mg g^{-1})	q_{AR} (mg g^{-1})	%Removal of AB	%Removal of AR
0.1	512	0.39	0.61	1.009	28.3	11.0	17.2	4.19	2.33	78	65
0.5	496	0.22	0.78	0.407	10.4	2.29	8.13	1.36	1.01	95	84

Table 9.3 Concentration and sorption capacity of each dye component (AB and AY) in binary dye mixture (AB + AY)

Algal mass (g)	A_{AB} (-)	A_{AY} (-)	C_{AB} (mg l^{-1})	C_{AY} (mg l^{-1})	q_{AB} (mg g^{-1})	q_{AY} (mg g^{-1})	%Removal of AB	%Removal of AY
0.1	0.093	0.363	2.4	8.0	0.64	0.95	83	68
0.5	0.045	0.120	1.3	3.0	0.70	1.25	92	89
0.9	0.028	0.086	0.9	2.0	0.63	1.31	95	94
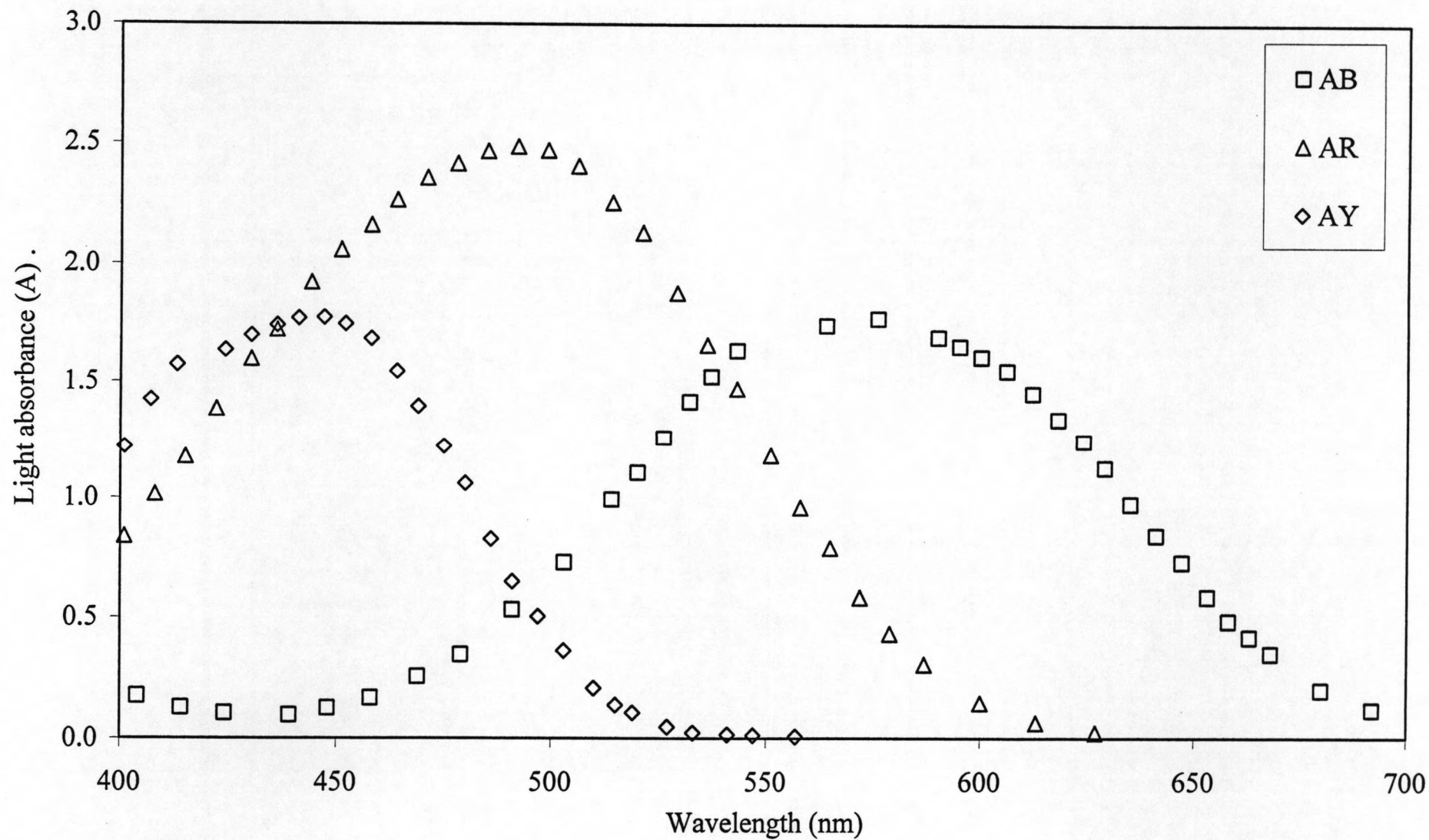
Fig. 9.1 Spectra of three single dyes, Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR), and Astrazon® Golden Yellow GL-E (AY)
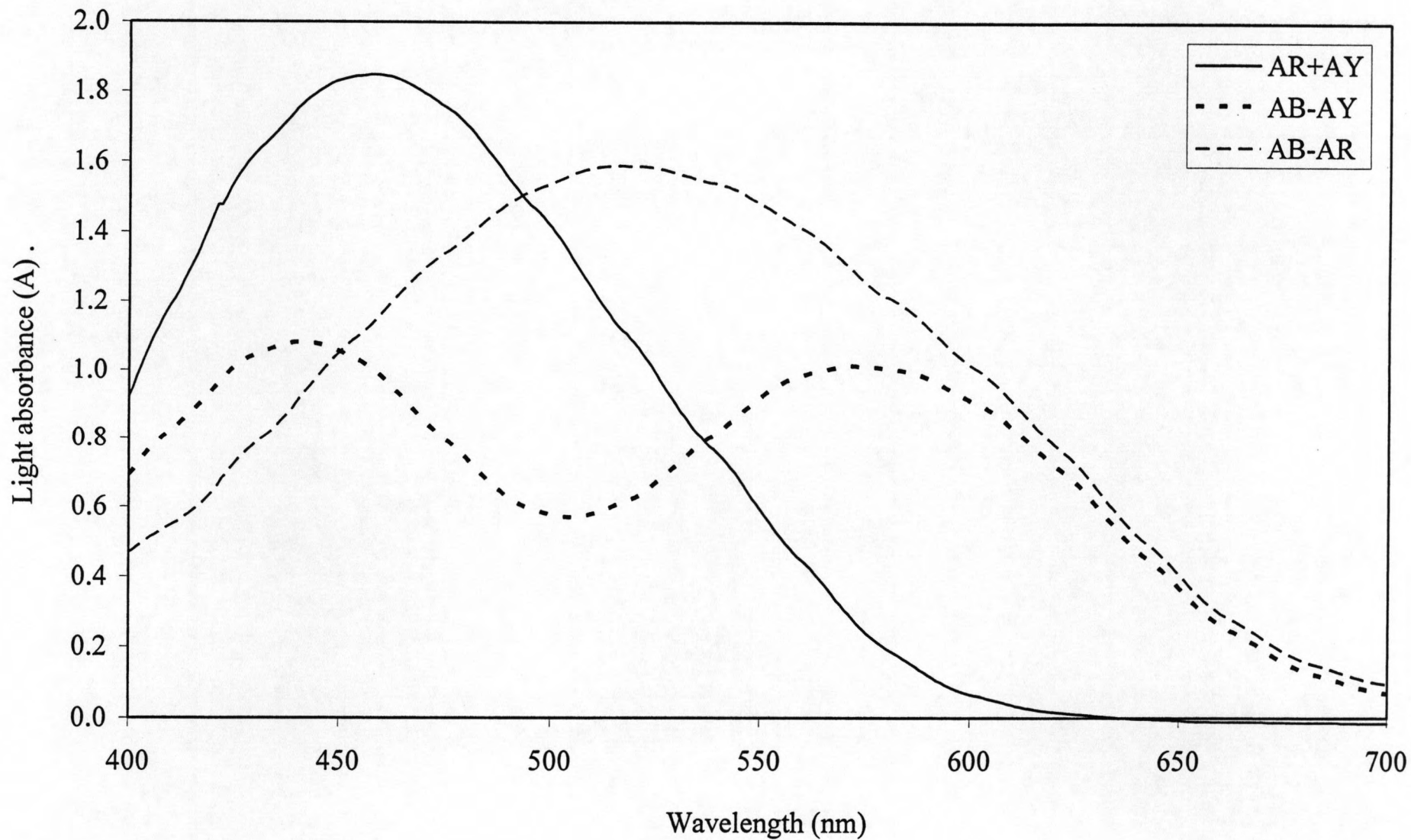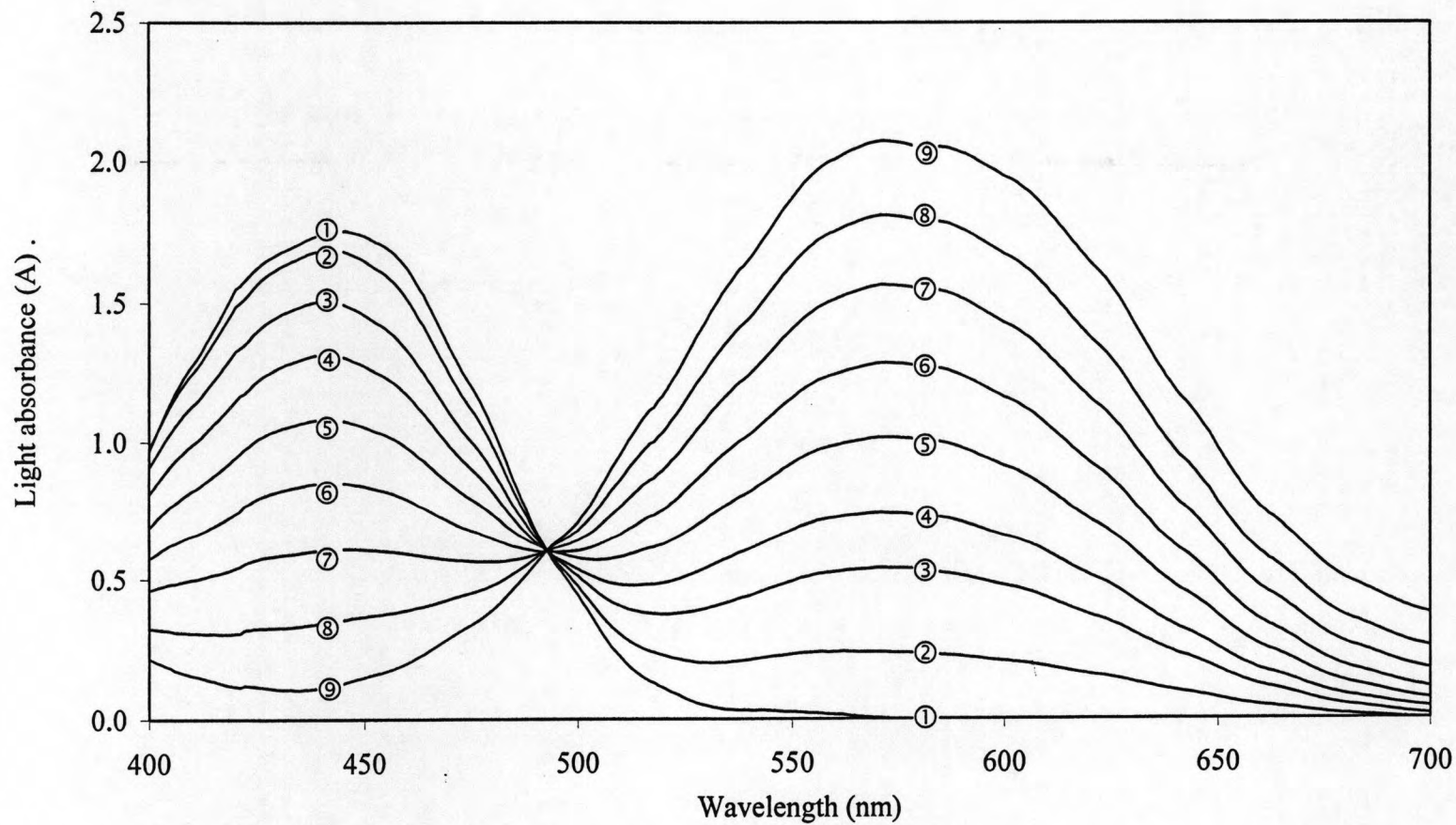
Fig. 9.2 Spectra of three binary dye mixtures
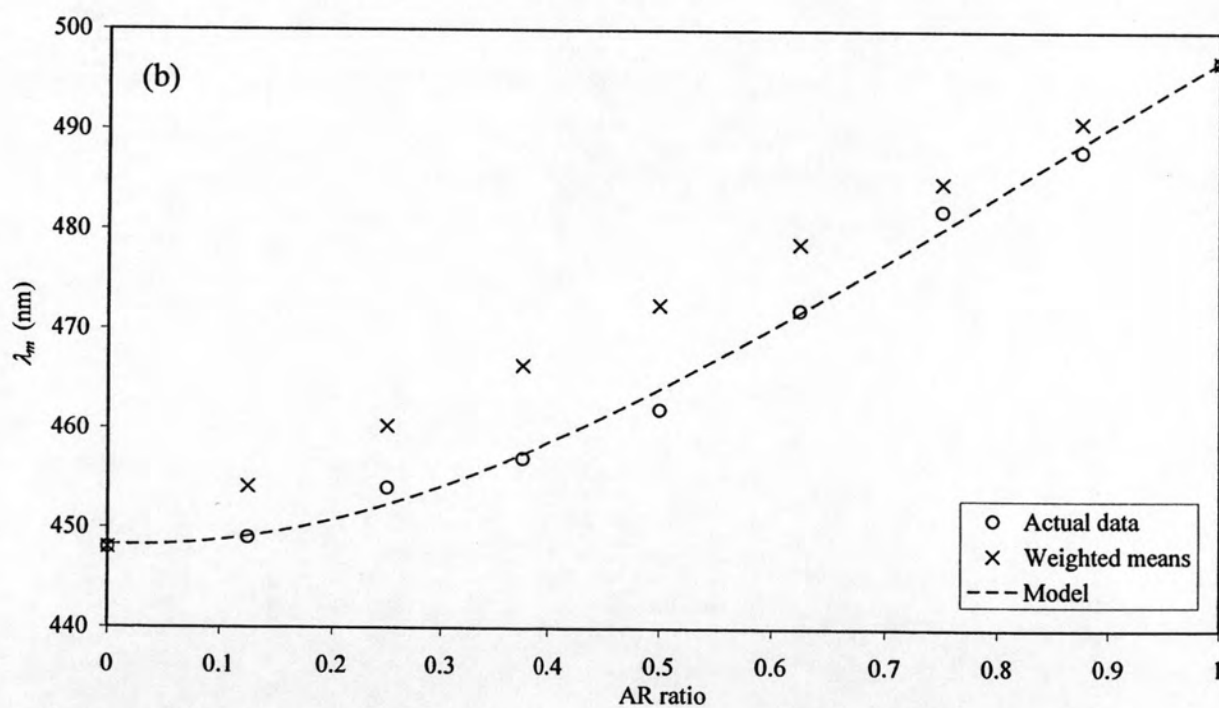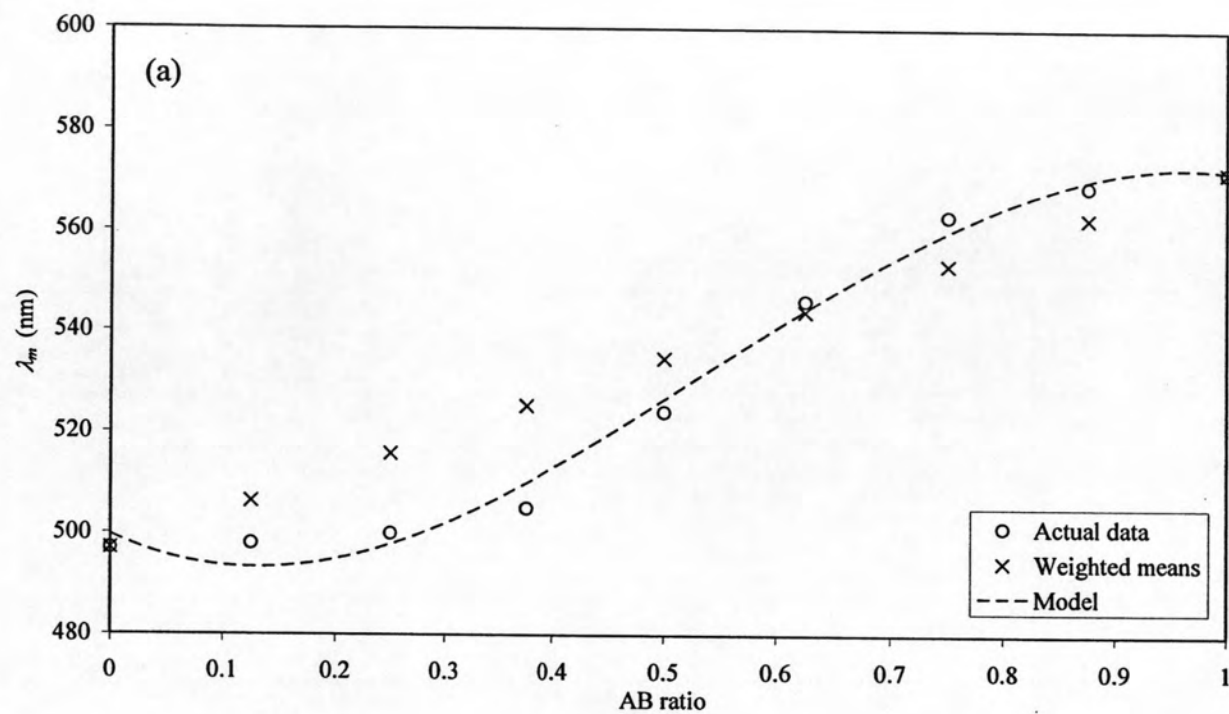
Fig. 9.3 Shift of wavelength of maximum light absorption (λ_m) with the mass fraction of (a) AB in AB + AR mixture and (b) AR in AR + AY mixture

The numbers in the figure indicate the mass ratio of AY (mg) : AB (mg) in the binary mixture where:

① 0.200:0.000 ② 0.175:0.025 ③ 0.150:0.050 ④ 0.125:0.075 ⑤ 0.100:0.100

⑥ 0.075:0.125 ⑦ 0.050:0.150 ⑧ 0.025:0.175 ⑨ 0.000:0.200

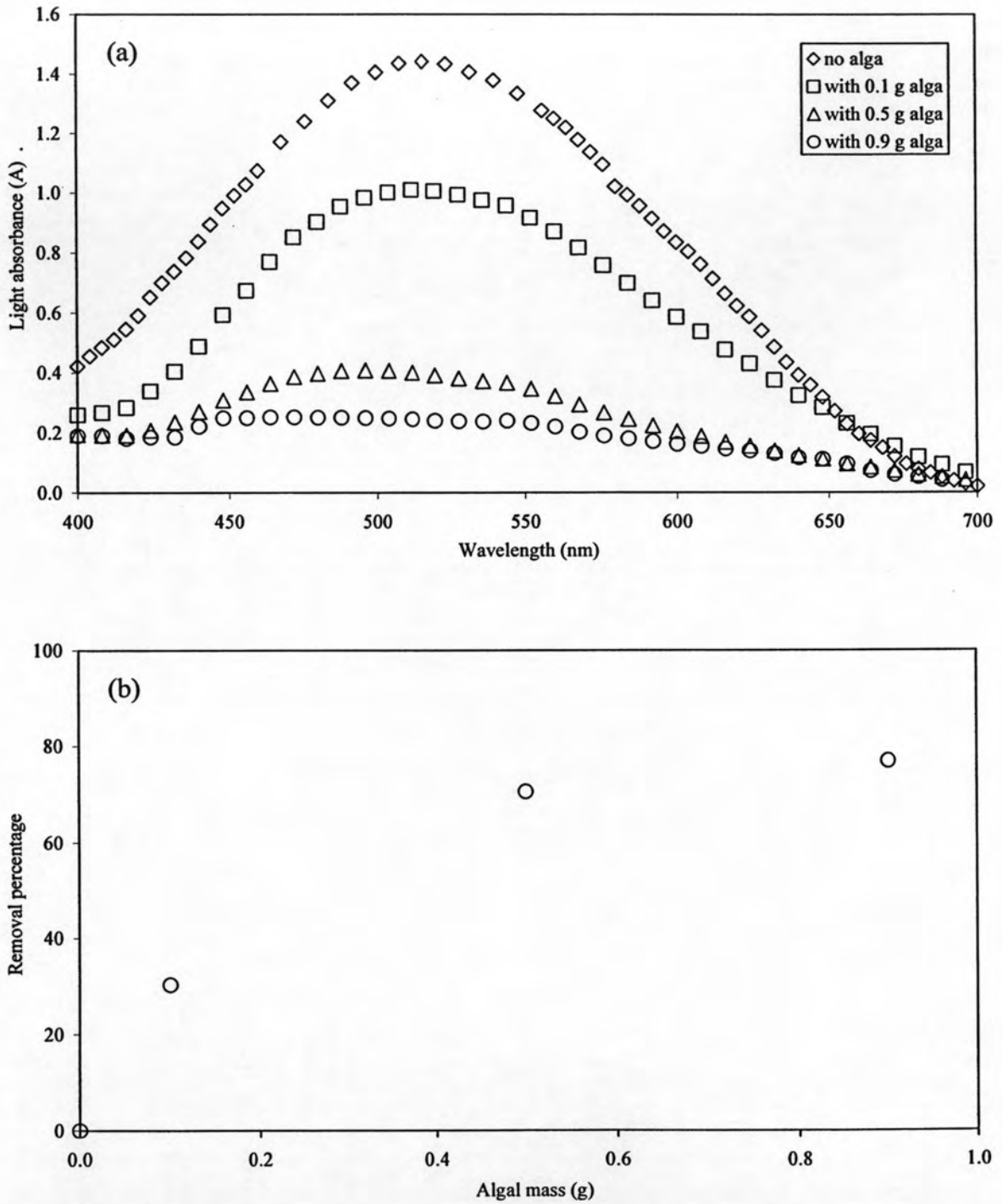Fig. 9.4 Spectra shift resulted from varying component mass ratio in AB + AY 4

Fig. 9.5 (a) Light absorbance of effluents and (b) relationship between algal mass and removal percentage from the sorption of binary dye mixture (AB + AR) by *C. lentillifera*
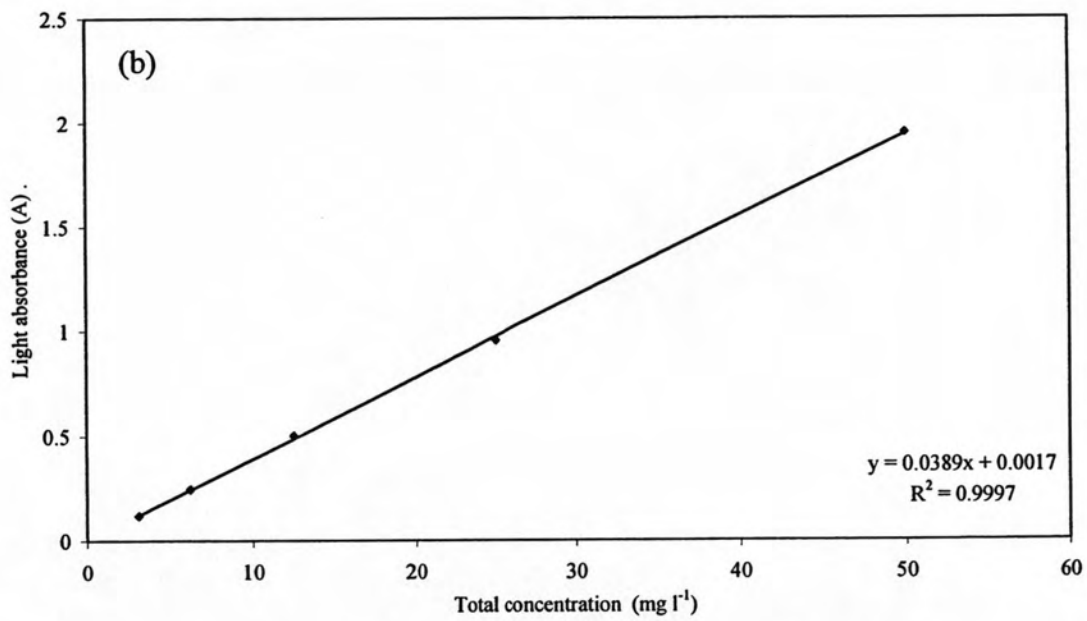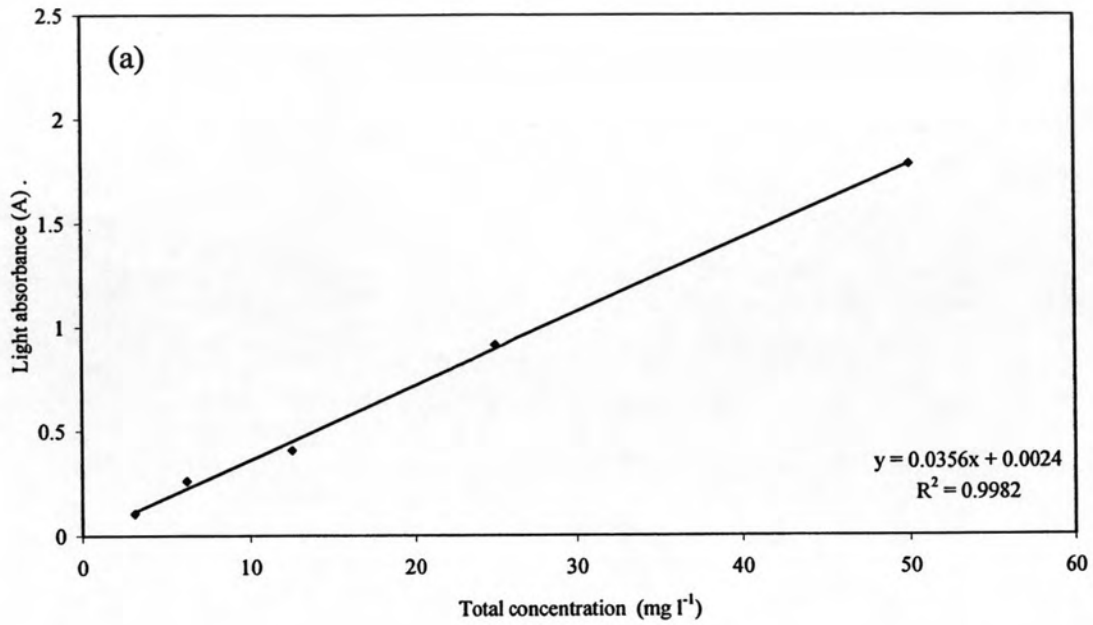
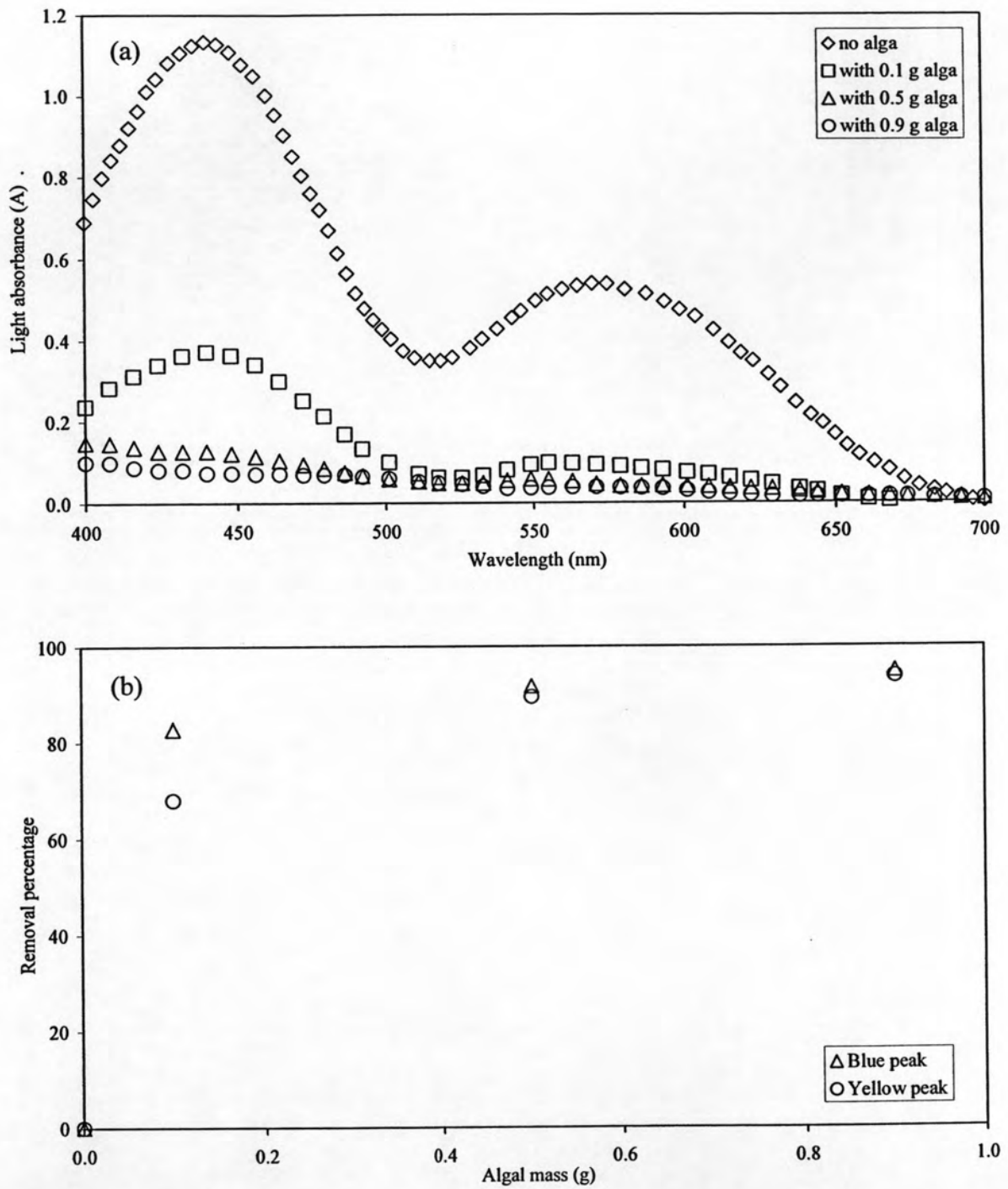Fig. 9.6 Calibration curves of AB + AR with the mass ratio (AR:AB) of (a) 0.39:0.61, and (b) 0.22:0.78

Fig. 9.7 (a) Light absorbance of effluents and (b) relationship between algal mass and removal percentage from the sorption of binary dye mixture (AB + AY) by *C. lentillifera*