RESEARCH ARTICLE

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Quantitative measurement techniques for binary dye mixtures: a case study in an adsorption system

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ABSTRACT: Three binary dye mixtures prepared from the basic textile dyes Astrazon Blue FGRL (AB), Astrazon Red GTLN (AR), and Astrazon Golden Yellow GL-E (AY), were employed to demonstrate two different mixture characteristics. The first type of mixture (AB + AY) was the case where the optical absorbance spectra of the dye mixtures exhibited double peaks. Each peak occurred at the same wavelength as the single dye and the area under each light absorbance curve varied with the concentration of the dye in the solution. The second type was the case of the other two mixture combinations (AR + AY and AB + AR) whose spectra exhibited a single peak. In this case, shifts of the spectral peaks were observed as the composition of the mixture changed, and the area beneath the light absorbance curve corresponded to the quantity of the dyes in the mixture. With these techniques, it was possible to determine the quantity of each individual dye component in the binary dye mixture. The application of these techniques was demonstrated through estimation of the amount of dye adsorbed from simulated dye wastewater by dried biomass of *Caulerpa lentillifera*.

KEYWORDS: mixed dyes, wastewater, spectrum, biosorbent algae, polynomial fit, spectrophotometry

INTRODUCTION

Dyestuffs play an important role in the textile, food, and cosmetic industries. The textile industry, one of the major industries in Thailand, consumes large amounts of dyes and the resulting wastewater is often treated with conventional secondary treatment systems. However, there are still some components such as dyes, heavy metals, bleaching agents, and inorganic salts, that remain in the effluent and are highly toxic to aquatic biota[1]. The treatment of this wastewater requires that the measurement of dyes is accurate and reliable.

Typically, the measurement for a single dye solution is performed using a simple spectrophotometric technique as most studies on the treatment of coloured wastewater have only focused on single-dye systems[2–6]. However, a mixed dye system is more likely to occur in actual applications, and therefore a simple and accurate technique to measure mixed dyes would be extremely useful. Standard methods to measure the colour intensity of a mixed dye solution only measure the overall colour intensity of the mixture, and cannot indicate the concentration of each individual dye[7,8].

This work proposes a simple technique to measure dyes in binary mixtures using their light absorption. The application of this technique is demonstrated using a dye mixture adsorbed onto a dried biomass of the green macroalga *Caulerpa lentillifera* which has been proposed as an effective biosorbent for basic dyes[9].

MATERIALS AND METHODS

The basic dyes examined were Astrazon Blue FGRL (AB), Astrazon Red GTLN (AR), and Astrazon Golden Yellow GL-E (AY), all supplied by Dystar Thai Co., Ltd. AB consists of C.I. Basic Blue 159 and C.I. Basic Blue 3 (weight ratio $\sim$ 5:1). AR consists of C.I. Basic Red 18:1 and C.I. Basic Yellow 28 (weight ratio $\sim$ 40:1). AY has only one component, C.I. Basic Yellow 28.

The dyes were dried at 60 °C in an oven to ensure certain weight. Stock solutions of the dyes (1 g/l) were then prepared using deionized water. These were later diluted to 50 mg/l and their light absorbance was measured at wavelengths of 400–700 nm. UV-VIS spectra were determined on a Spectronic Helios alpha spectrophotometer operated with VISION32, and 1 cm $\times$ 1 cm quartz cuvettes (Starna) were used as sample cells. All measurements were performed at

25 °C.

Binary dye mixtures of AB + AR, AB + AY, and AR + AY were prepared in various mass ratios. The light absorbance of the mixtures was measured using the procedure described above.

To study the adsorption of dyes by algae, two dye mixtures (AB + AR and AB + AY) were prepared with a mass ratio of 1:1 (using 50 mg/l of AB, AR, and AY). Flasks containing 0.1, 0.5, and 0.9 g of dried *C. lentillifera* in 30 ml of the dye mixture (resulting in algae concentrations of 3.3, 16.7, and 30 g/l, respectively) were placed in a shaker operating at 130 rpm for 1 h. The residue dye mixtures were then collected and their absorption spectra (400–700 nm) were determined as previously described[9].

RESULTS AND DISCUSSION

Absorbtion spectra for single dyes and binary dye mixtures

The spectra of each individual dye (AB, AR, and AY) exhibited a single peak (Fig. 1a). The wavelengths of maximum light absorption (λ_m) for AY, AR, and AB, were 448, 495, and 572 nm, respectively.

Three sets of new colours 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. For AB + AR and AR + AY, the spectra were found to have a single peak, whereas AB + AY showed a double peak (Fig. 1b).

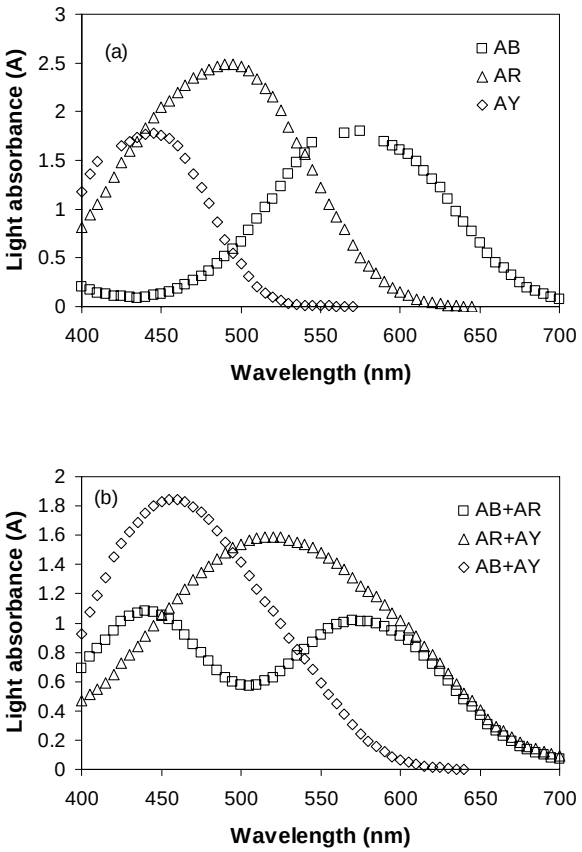

Fig. 1 Spectra of (a) single dyes (b) binary dye mixtures.

Mixture with a single-peaked spectrum

The value of λ_m for AB + AR and AR + AY was found to be related to the mass fraction of each dye in the mixture (Table 1). However, the relation was not linear and hence the experimental results did not agree well with the predictions from the weighted mean method (Fig. 2). The data could be fitted better to the cubic polynomials,

$$\lambda_m = -274\,x_{AB}^3 + 449\,x_{AB}^2 - 102\,x_{AB} + 500, \quad (1)$$
$$(R^2 = 0.9905)$$

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

Table 1 Dependence of λ_m on mass ratios of dye components.

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

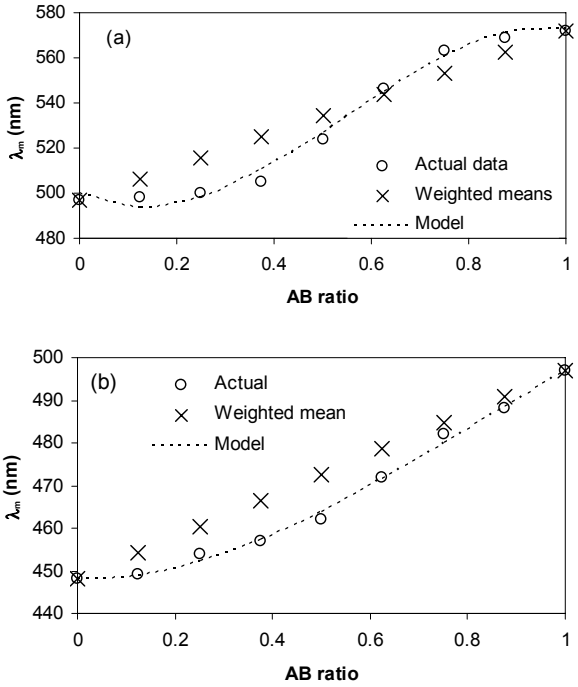

Fig. 2 Wavelength of maximum light absorption (λ_m) as a function of the mass fraction of (a) AB in AB + AR mixture and (b) AR in AR + AY mixture.

where x_{AB} and x_{AR} are the mass fractions of AB in AB + AR, and AR in AR + AY, respectively. The high R^2 indicates the suitability of the polynomial model to the experimental data. With this technique, the dye component ratio in the mixture could be determined from λ_m.

The binary dye mixture with a single-peak spectrum is similar to the case of dyes such as AB which have two components. Therefore the analysis for the quantity of the mixture at each particular composition could be performed using conventional methods where the concentration was related to the area underneath the light absorbance curve.

Binary mixtures with two spectral peaks

The spectra of AB + AY mixtures exhibited two peaks (Fig. 3). The peaks occurred at the values of λ_m for AY and AB. 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 different shades of colour were observed), and the two peaks still occurred at the same wavelengths of AB and AY (Fig. 3). The area under each peak was linearly related to the quantity of each dye component as is discussed later.

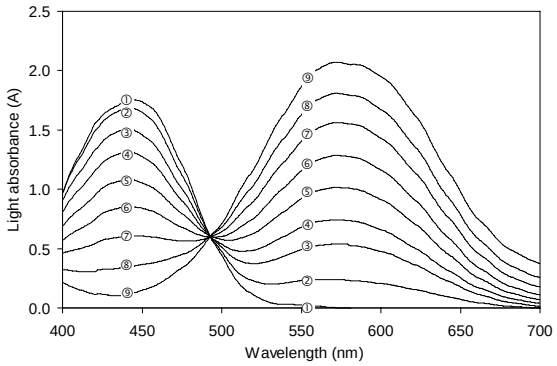

Fig. 3 Spectra resulted from varying component mass ratio in AB + AY. The numbers in the figure indicate the mass ratio of AY (mg):AB (mg) in the binary mixture: (1) 0.200:0.000; (2) 0.175:0.025; (3) 0.150:0.050; (4) 0.125:0.075; (5) 0.100:0.100; (6) 0.075:0.125; (7) 0.050:0.150; (8) 0.025:0.175; (9) 0.000:0.200.

Case study: adsorption experiments

The adsorption experiments were conducted as a case study for the application of the proposed measuring technique. The total amount of dye removed can be calculated from the decrease in the area under the peaks (Figs. 4a and 4b). In the case of AB + AR, up to 80% removal could be achieved (Fig. 4c).

Using the above technique, only the total amount of dye removed could be calculated. To determine the removal percentage of each individual dye component, we examined the shift in λ_m after the adsorption process (Fig. 4a). Without adsorption (no algae), λ_m occurred at 524 nm, and it shifted to 512 and 496 nm after adsorption to algae at concentrations of 3.3 and 16.7 g/l, respectively. This new λ_m could then be used to determine the mass fraction of the dye components by using (1) or Table 1. We found that λ_m of 512 nm and 496 nm corresponded to x_{AB} of 0.39 and 0.22, respectively. To calculate the quantity of each dye at these new λ_m, two calibration curves at these two wavelengths were constructed (Fig. 5) and the equations for the absorbance as a function of the total dye concentration are

$$A = 0.0356\,C_t + 0.0024, \qquad (R^2 = 0.9982) \quad (3)$$

$$A = 0.0389\,C_t + 0.0017, \qquad (R^2 = 0.9997) \quad (4)$$

where A is the light absorbance and C_t is the total dye concentration (Fig. 5).

After the calibration curve equation was developed, the maximum light absorbance (A_{max}) or the

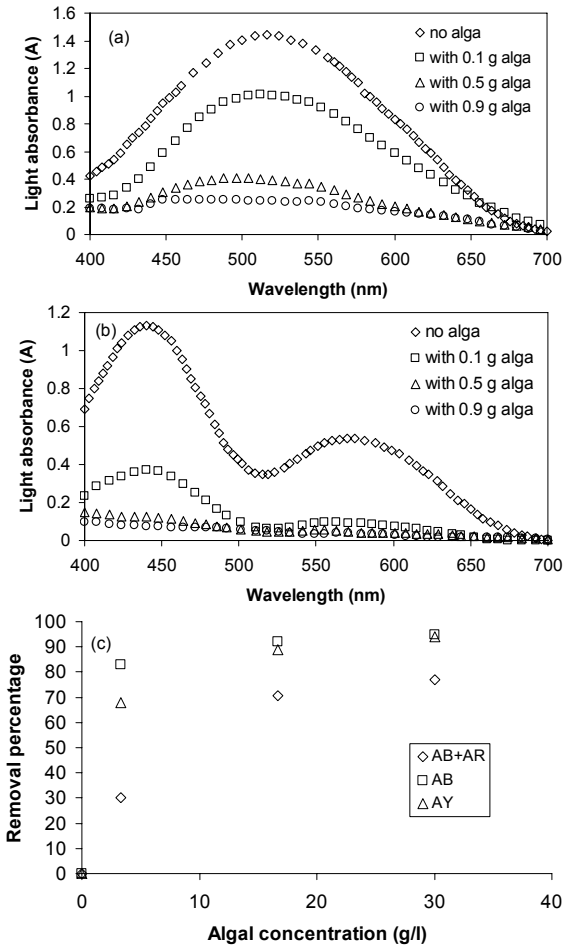

Fig. 4 (a) Light absorbance of effluents from the adsorption of binary dye mixture (AB + AR), (b) light absorbance of effluents from the sorption of binary dye mixture (AB + AY), and (c) relationship between algae concentration and removal percentage from the adsorption of binary dye mixtures (AB + AR, and AB + AY).

absorbance at its λ_{m} of each data set was then substituted as A into the (3) and (4) to obtain C_{t}. Since the mass fractions of AB and AR were already known, they were used to calculate the concentrations of AB (C_{AB}) and AR (C_{AR}) using

$$C_{\mathrm{AB}} = x_{\mathrm{AB}}\, C_{\mathrm{t}}, \tag{5}$$

$$C_{\mathrm{AR}} = x_{\mathrm{AR}}\, C_{\mathrm{t}}. \tag{6}$$

At this point, individual concentrations of AB and AR in the mixture were known, and therefore the adsorption capacity, q for each dye component could be calculated from

$$q = \frac{C_{\mathrm{i}} - C}{W} V \tag{7}$$

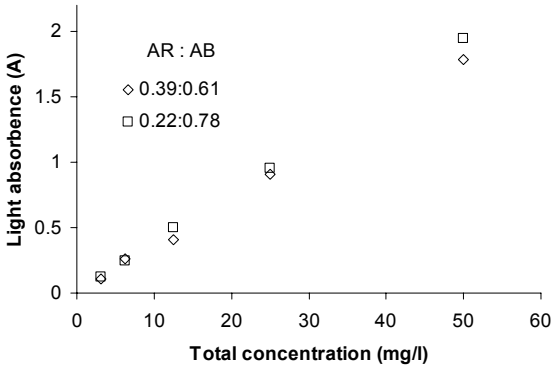

Fig. 5 Calibration curves of AB + AR with mass ratios (AR:AB) of 0.39:0.61 and 0.22:0.78.

where C_{i} is the initial concentration of each dye component, C is the concentration of each dye component after being adsorbed, W is the mass of adsorbent, and V is the volume of the dye mixture.

A summary of the results from this experiment with the adsorbent dose of 3.3 and 16.7 g/l is given in Table 2. The adsorption with 30 g/l of algae concentration resulted in a flat peak and so λ_{m} could not be observed. Hence in this particular case, the estimation of each dye component in the dye residue could not be accomplished.

In the case of the AB + AY mixture, after the adsorption process, the spectrum still exhibited two peaks (Fig. 4b). Hence, the removal of each dye in the dye mixture could be interpreted from the area under both peaks ($\lambda_{\mathrm{m}} = 572$ for AB and $\lambda_{\mathrm{m}} = 448$ for AY). The calculated results on the removal percentages for each dye are presented in Fig. 4c. Table 3 summarizes the results of the removal characteristics for each dye in the AB + AY mixture with the dried biomass.

It is interesting to note that, from the results in Fig. 4, the algae adsorbent had more affinity for AB than for AY particularly at low adsorbent dose. However, at high adsorbent doses, the percentage removal of AB and AY were not significantly different.

Although the experiments started with a mixture in a mass ratio of 1:1, the results indicated that the ratio between the two dyes changed during the course of adsorption, suggesting that the proposed method could also be employed for the two component mixtures at other weight ratios.

CONCLUSIONS

New quantitative measurement techniques for identifying each individual dye concentration in a binary

Table 2 Concentration and adsorption 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)	C_{AB} (mg/l)	C_{AR} (mg/l)	q_{AB} (mg/g)	q_{AR} (mg/g)	%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 3 Concentration and adsorption 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)	C_{AY} (mg/l)	q_{AB} (mg/g)	q_{AY} (mg/g)	%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

mixture were proposed. The shift of the spectral peaks indicated the changes in dye mass ratio. Two different types of dye mixture were given as an example to illustrate the estimation of removal efficiency for each individual dye. The shift of spectra suggested an unequal affinity of the algae to each dye component.

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