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Influence of particle size and salinity on adsorption of basic dyes by agricultural waste: dried Seagrape (*Caulerpa lentillifera*)

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Abstract

Green macroalga *Caulerpa lentillifera* was found to have reasonable adsorption capacity for basic dyes, Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR), and Astrazon® Golden Yellow GL-E (AY). The initial dye concentration was in the range of 100–1,800 mg/L. The dried algal sorbent was ground and sieved into 3 sizes: S (0.1–0.84 mm), M (0.84–2.0 mm), and L sizes (larger than 2.0 mm). For all conditions examined in this work (at 25°C in batch systems), the adsorption reached equilibrium within the first hour. The kinetic data corresponded well with the pseudo second order kinetic model where the rate constant, k_2, decreased as the sorbent size increased for all dyes. The adsorption isotherms followed both Langmuir and Freundlich models. Among three sorbent sizes, S size gave the highest adsorption capacity followed by M and L sizes. A reduction of sorbent size increased the specific surface area for mass transfer, and also increased the total pore volume, thus providing more active sites for adsorption. The adsorption of AB was adversely influenced by the protonation of algal surface at low pH. On the other hand, the adsorption of AR and AY could be due to weak electrostatic interaction, which was not significantly affected by pH. Increasing salinity of the system caused a decrease in adsorption capacity possibly due to the competition between Na^+ and the dye cations for the binding sites on algal surface. Moreover, an increase in salinity generated a compressed electrical double layer on the algal surface which exerted repulsive force, retarding the adsorption of positive charged molecules such as the basic dyes.

Key words: textile dye; adsorption; decolorization; *Caulerpa lentillifera*; kinetics; isotherms; salt concentration

Introduction

Cationic dyes are synthetic pigments, commonly known as basic dyes and are widely used in textile industry. Basic dyes are used in several processes such as acrylic, nylon, silk, and wool dyeing. The efficiency of dyeing process is often poor, resulting in an escape of a large quantity of dyes through wastewater. This un-reacted color could reduce the light penetration through the water surface and decrease photosynthetic activity of aquatic organisms (Bhatnagar and Jain, 2005). The heavy metals in the basic dyes could accumulate in the environment and may cause serious long term effects to ecosystem. In addition, this group of dyes includes a broad spectrum of different chemical structures, primarily based on the substituted aromatic groups which are resistant to both chemical and biological breakdowns, which may otherwise produce small amount of toxic and carcinogenic products (Eren and Afsin, 2008).

To date, several technologies of physical and chemical methods for the removal of dyes are available such as the use of Fenton's reagent (Nerud *et al*., 2001; Ramirez *et al*., 2005), electrochemical (Vlyssides *et al*., 2000), adsorption (Garg *et al*., 2003; Namasivayam and Kavita, 2002), membrane filtration (Saffaj *et al*., 2004; Capar *et al*., 2006), etc. The adsorption by activated carbon is also well known and widely used. Activated carbon is often highly efficient particularly for low strength wastewater but it is relatively expensive. Recently, the use of biosorbent for dye removal has been intensively investigated as an alternative, economical, and feasible method (Allen *et al*., 2003; Sulak *et al*., 2007; El Qada *et al*., 2006). Examples of these biosorbent are bagasse pith for the adsorption of Basic Blue 69, Basic Red 22, Acid Red 114, and Acid Blue 25 (McKay *et al*., 1987); banana pith for the adsorption of wastewater containing basic violet (Namasivayam and Kanchana, 1992); palm-fruit bunch for the adsorption of Basic Yellow, Basic Red, and Basic Blue (Nassar and Magdy, 1997); wheat straw, corncobs and barley husks for the adsorption of Cibacron Yellow C-2R, Cibacron Red C-2G, Cibacron Blue C-R, Remazol Black B, and Remazol Red RB (Robinson *et al*., 2002); duckweed for the adsorption of Methylene Blue (Waranusantigul *et al*., 2003); and date pits for the adsorption of Methylene Blue (Banat *et al*., 2003).

Table 1 provides some examples on the adsorption capacity (q_m) for color molecules. Alga is a viable alternative

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Table 1 Maximum adsorption capacity of various types of basic dyes by natural adsorbents

Adsorbent	Adsorbate	q_m (mg/g)	Reference
Macroalga *C. lentillifera*	Astrazon® Blue FGRL	94.34	This study
	Astrazon® Red GTLN	113.64	
	Astrazon® Golden Yellow GL-E	35.46	
Wheat bran	Astrazon® Yellow 7GL	69.06	Sulak *et al*., 2007
Neam (*Azadirachta indica*) leaf powder	Methylene Blue	8.76	Bhattacharyya and Sharma, 2005
Fresh water algae *Pithophora* sp.	Malachite Green	117.65	Kumar *et al*., 2005
Cationic surfactant-modified bentonite clay	Tannin	69.80	Anirudhan and Ramachandran, 2006
Phosphoric acid modified rice straw	Basic Blue 9	208.33	Gong *et al*., 2007
	Basic Red 5	188.68	
Cyclodextrin-based	C.I. Basic Green 4 (Malachite Green)	91.90	Crini *et al*., 2007
Giant duck-weed (*Spirodela polyrrhiza*)	Methylene Blue	129.87	Waranusantigul *et al*., 2003
Raw date pits	Methylene Blue	80.29	Banat *et al*., 2003

biosorbent as its cell walls consist of many biomolecules with various functional groups which could form bonds with cations such as metals and basic dyes (Crist *et al*., 1981). A macroalga *Caulerpa lentillifera* grows rapidly in rainfed agricultural areas. This particular algal species is often cultivated in a polishing pond of a closed-loop shrimp farm system, as it helps in the balance of nitrogen compounds in the medium. Although some part of fresh *C. lentillifera* could be employed as a nutritional supplement, the rest of the alga could not, and it is often required that farmers remove and dispose of this over-grown alga as an unwanted material. Turning this alga into an adsorbent for basic dyes is therefore presented as low-cost alternative for the management of this unwanted agricultural material. Recent research demonstrated that the macroalga *C. lentillifera* could also be used effectively for the removal of basic dyes (Marungrueng and Pavasant, 2006, 2007) and some heavy metals (Apiratikul and Pavasant, 2006). There are several controlling factors for the removal of basic dyes, such as pH, initial dye concentration, adsorbent dosage, particle size, temperature, etc. This work intended to examine the fundamentals of the biosorption of basic dyes using the dried *C. lentillifera* from the work of Marungrueng and Pavasant (2006) and therefore was set out to investigate the effect of sorbent size and adsorbent dosage on the adsorption. In certain cases, the wastewater containing dye could have high salt concentration and this may interfere with the biosorption characteristics. Hence, it was also the intention of this work to examine the effect of salt on the adsorption.

1 Materials and methods

1.1 Basic dyes

The basic dyes examined in this work included Astrazon® Blue FGRL (AB), Astrazon® Red GTLN (AR), and Astrazon® Golden Yellow GL-E (AY) all supplied by Dystar Thai Co. Ltd. Astrazon®. Blue FGRL consists of two main components, which are C.I. Basic Blue 159 and C.I. Basic Blue 3. The ratio of the two components is approximately 5:1 by weight. Astrazon® Red GTLN also consists of two main components, which are C.I. Basic Red 18:1 and C.I. Basic Yellow 28. The ratio of the two components is approximately 40:1 by weight. Astrazon® Golden Yellow GL-E has only one main component, which is C.I. Basic Yellow 28. All chemical structures are shown in Fig.1. The wavelength for maximum light absorption (λ_{max}) was initially examined for each dye to allow effective measurement of dye concentration. This was per-

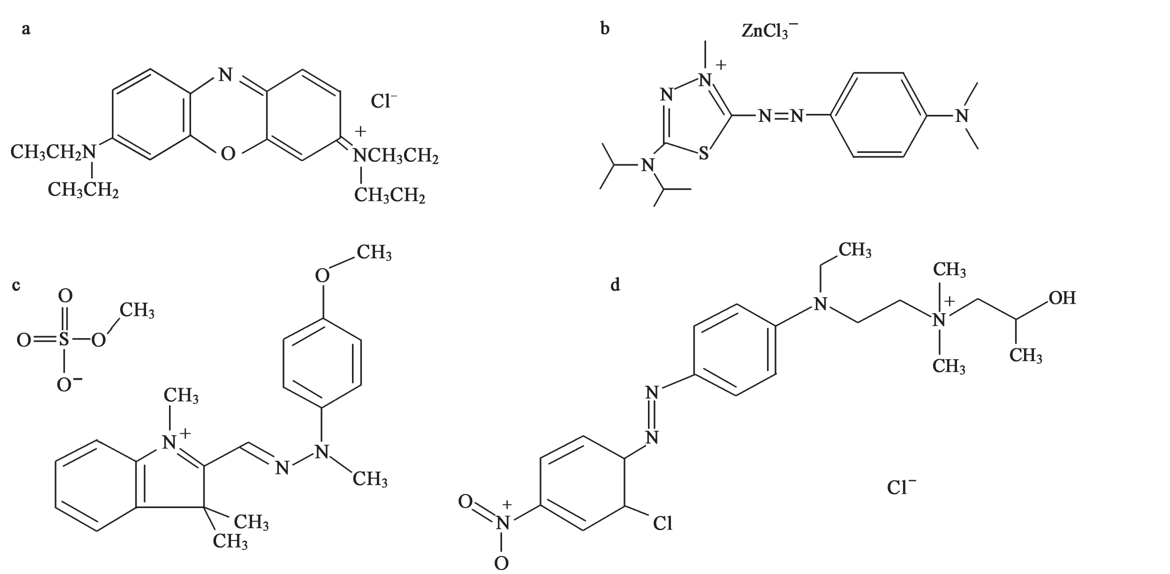

Fig. 1 Chemical structures of C.I. Basic Blue 159 (a), C.I. Basic Blue 3 (b), C.I. Basic Yellow 28 (c), and C.I. Basic Red 18:1 (d).

formed through a UV-Vis spectrophotometer, Spectronic® UV/Vis Helios Alpha with version 32 software V1.25. The dye concentrations of the solutions were determined spectrophotometrically at λ_{max} of 571, 521, and 400 nm for AB, AR, and AY, respectively.

1.2 Preparation of dried algae

Caulerpa lentillifera was collected from Banchong Farm, Chachoengsao Province, Thailand. The alga was firstly washed with water and dried at 80°C for 12 h. The alga was then ground with blender, sieved to S, M, and L sizes. S size is for the size range of 0.1–0.84 mm, M size is the range of 0.84–2 mm, and L size is larger than 2 mm. The dried, ground alga was subsequently stored in dessicator.

1.3 Adsorption experiments

The flask containing 0.5 g of alga and 30 ml of dye solution was placed in a shaker operating at 130 r/min. Experimental data were carried out at 25 ± 1°C by varying the concentration of dye in aqueous solution from 100 to 1,800 mg/L. This range of concentration was chosen to cover the actual range found in wastewater and up to the very high concentration to ensure an examination of more complete isotherm data. In the adsorption kinetic experiments, the initial dye concentration was fixed at 100 mg/L.

Samples were taken to measure the dye concentration at predetermined time intervals of 1, 3, 5, 10, 20, 30, 60, 120, and 180 min. The effect of pH was investigated by varying pH from 2 to 6 using S-size algal sorbent. The effect of salt on the adsorption capacity was done using NaCl (0%–10%, *W/V*). The alga was removed from the solution by filtering it through a screen fabric filter.

2 Results and discussion

2.1 Characteristics of algal sorbent

Recent works (Marungrueng and Pavasant, 2006) on the examination of the functional groups of the dried *C. lentillifera* were conducted using Fourier Transform Infrared (FT-IR) technique (1760X, Perkin Elmer, USA). They reported that the most abundant functional groups in dried alga *C. lentillifera* were hydroxyl (O–H), carboxyl (COOH), amine (NH_2), and sulfonyl (S=O). These functional groups could exhibit chemical binding affinity towards several positively charged ions. Similar phenomena have been observed in the biosorption of Remazol Black B on biomass (Aksu and Tezer, 2000), Congo Red on activated carbon (Namasivayam and Kavita, 2002), and Methylene Blue on perlite (Doğan *et al*., 2004). The pK_a of these functional groups were 9.5–13, 1.7–4.7, 8–11, and 1.3, respectively (Apiratikul and Pavasant, 2006). The effect of pH on the dissociation of functional groups could be explained in terms of pH_{zpc} (pH of zero-point charge) of the adsorbent. In this study, the pH_{zpc} of *C. lentillifera* was at the pH of 0.3. The surface areas, total pore volume, and pore diameter of the alga sizes L, M, and S (from the standard BET procedure, N_2 adsorption) are shown in Table 2. Specific surface area and total pore volume of M was greater than those of S and L. On the other hand, pore diameter of S was greater than those of L and M.

Table 2 BET surface areas, total pore volume, and average pore diameter for adsorbent particles with different sizes

Algae size	Surface area (m^2/g)	Total pore volume (ml/g)	Average pore diameter (0.1 nm)
L (> 2 mm)	3.2	6.2×10^{-3}	77.1
M (0.84–2 mm)	8.7	14.6×10^{-3}	44.8
S (0.1–0.84 mm)	5.0	11.6×10^{-3}	105.0

2.2 Kinetics of basic dyes

To investigate the mechanism of adsorption, two kinetic models are generally employed. Largergren pseudo first order kinetics has been widely used to determine the solute adsorption on various adsorbents. This pseudo first order kinetics equation can be written in a linear form as:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

The pseudo second order kinetic equation was proposed by Ho and McKay (1999):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{2}$$

where, q (mg/g) is the amount of dye adsorbed at time t (min), q_e (mg/g) is the amount of dye adsorbed at equilibrium time t (min), k_1 (min^{-1}) is the equilibrium rate constant of first order model, k_2 (g/(mg·min)) is the equilibrium rate constant of pseudo second order model.

The kinetic plots for the adsorption of the three basic dyes with *C. lentillifera* were shown in Fig.2. For all sizes of alga, the adsorption of the three dyes reached equilibrium within the first hour. At initial dye concentration of 100 mg/L, the adsorption capacity (q_e) of AB from kinetic experimental results was 5.4, 5.2, and 5.1 mg/g for adsorbent sizes S, M, L, respectively, and q_e for AR was 5.4, 5.3, and 5.2 mg/g, for AY was 4.7, 4.4, and 3.7 mg/g, respectively.

The parameter fittings demonstrated that the data fitted better with the pseudo second order than the pseudo first order models. Kinetics parameters were obtained using linear regressive method with least sum of squares of difference where kinetic parameters from pseudo first order and pseudo second order model are reported in Table 3. This finding was similar to the results of other studies on the biosorption of several other basic dyes. For instance, the pseudo second order kinetics were successfully applied for the biosorption of Rhodamine B on anerobic sludge (Wang *et al*., 2006), the adsorption of Remazol black B, red and golden yellow on *Chlorella vulgaris* (Aksu, 2005), and Basic Green 4 (Malachite Green) on cyclodextrin-based (Crini *et al*., 2007). Azizian (2004) suggested that the pseudo second order kinetic model was the best to describe the adsorption at low initial concentration (when compared to the weight of sorbent) which could be the case for this work. Table 3 also illustrates that the adsorption capacity and k_2 slightly increased when the alga was

Table 3 Kinetic parameters for all basic dyes at initial dye concentration of 100 mg/L

Basic dye	Particle size	$q_{e,exp}$ (mg/g)	Pseudo first order rate constant		Pseudo second order rate constant		
			k_1 (min^{-1})	R^2	k_2 (g/(mg·min))	$q_{e,cal}$ (mg/g)	R^2
AB	L (> 2 mm)	5.1	9.12×10^{-3}	0.9499	7.80×10^{-2}	5.2	0.9999
	M (0.84–2 mm)	5.2	1.11×10^{-2}	0.9898	8.30×10^{-2}	5.3	0.9999
	S (0.1–0.84 mm)	5.4	1.12×10^{-2}	0.9860	11.9×10^{-2}	5.5	0.9999
AR	L (> 2 mm)	5.2	1.09×10^{-2}	0.9373	14.0×10^{-2}	5.3	0.9999
	M (0.84–2 mm)	5.3	9.86×10^{-3}	0.9873	15.0×10^{-2}	5.3	0.9999
	S (0.1–0.84 mm)	5.4	1.16×10^{-2}	0.9947	16.3×10^{-2}	5.4	0.9999
AY	L (> 2 mm)	3.7	1.35×10^{-2}	0.9867	10.0×10^{-2}	3.8	0.9985
	M (0.84–2 mm)	4.4	1.51×10^{-2}	0.9908	12.5×10^{-2}	4.5	0.9999
	S (0.1–0.84 mm)	4.7	1.83×10^{-2}	0.9148	15.7×10^{-2}	4.7	0.9997

AB: Astrazon® Blue FGRL; AR: Astrazon® Red GTLN; AY: Astrazon® Golden Yellow GL-E. $q_{e,exp}$ is the amount of dye adsorbed at equilibrium from experiments; $q_{e,cal}$ is the amount of dye adsorbed at equilibrium, calculated from the pseudo second order model; R^2 means the linear regression coefficient of determination.

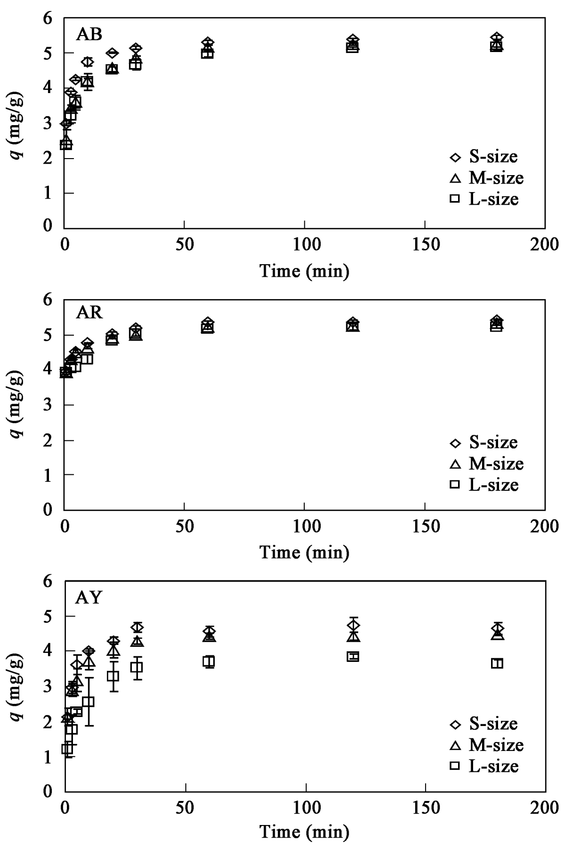

Fig. 2 Kinetics plots of the adsorption of basic dyes with *Caulerpa lentillifera*. Conditions: adsorbent dose 0.5 g; initial pH 7.0; 130 r/min; temperature 25°C.

ground to smaller size. This could be due to two reasons. Firstly the smaller alga had more binding sites available for adsorption, secondly the binding sites in the small alga were easier to access. This was explained in more detail in the next section.

2.3 Adsorption isotherms

Sorption isotherm is the relationship between concentration and adsorption capacity at each particular temperature. In this study, Langmuir and Freundlich isotherm equations were employed to describe the isotherm of the adsorption of basic dyes where:

$$\text{Langmuir isotherm} \quad q = \frac{x}{m} = \frac{q_m b C_e}{1 + bC_e} \tag{3}$$

$$\text{Freundlich isotherm} \quad q = \frac{x}{m} = K_f C_e^{1/n} \tag{4}$$

where, x (g) is the amount of sorbed dye, m (g) is the mass of sorbent used, q_m (mg/g) is the maximum adsorption capacity of sorbent, b (L/mg) is the Langmuir isotherm constant, C_e (mg/L) is the liquid phase dye concentration at equilibrium, K_f (L/g) is the Freundlich isotherm constant, n is the Freundlich isotherm exponent.

Different adsorbent sizes (S, M, and L) were examined for their effects on adsorption isotherms. Langmuir and Freundlich plots are shown in Fig.3 and their corresponding isotherm parameters obtained by linear regression method are summarized in Table 4. The high R^2 for both models suggested that the equilibrium data were well represented by both equilibrium models. The applicability of these models to this dye-algal sorbent system implied the possibility that both monolayer biosorption and heteroge-

Table 4 Constants of Langmuir and Freundlich isotherms

Basic dye	Sorbent size	Langmuir constant			Freundlich constant		
		q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2
AB	L (> 2 mm)	68.0	4.0×10^{-3}	0.9256	0.6	1.4	0.9736
	M (0.84–2 mm)	70.4	3.9×10^{-3}	0.9752	0.8	1.5	0.9915
	S (0.1–0.84 mm)	80.7	5.8×10^{-3}	0.9689	0.9	1.4	0.9776
AR	L (> 2 mm)	78.7	3.4×10^{-3}	0.9584	0.6	1.2	0.8634
	M (0.84–2 mm)	76.9	7.0×10^{-3}	0.8997	1.6	1.5	0.7899
	S (0.1–0.84 mm)	113.6	4.6×10^{-3}	0.9139	0.3	1.4	0.8952
AY	L (> 2 mm)	26.9	4.5×10^{-3}	0.9124	0.7	1.9	0.9457
	M (0.84–2 mm)	27.4	4.1×10^{-3}	0.9573	0.8	2.0	0.9434
	S (0.1–0.84 mm)	35.5	7.4×10^{-3}	0.9164	2.1	2.4	0.8977

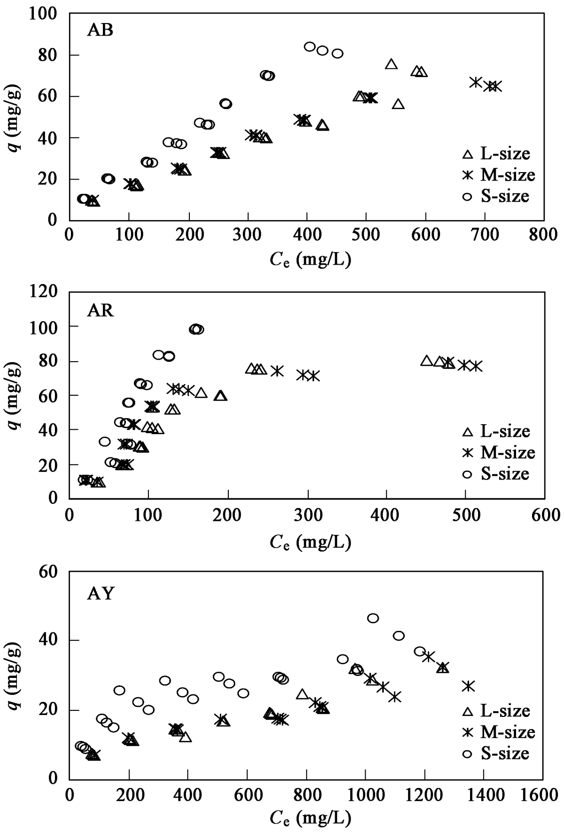

Fig. 3 Isotherms plots of the adsorption of basic dyes with *Caulerpa lentillifera*. Conditions are the same as that in Fig.2.

nous surface conditions could exist under the experimental condition (Dönmez and Aksu, 2002). It could be that the range of initial dye concentrations employed in this work was still too narrow, and not adequate for the complete isotherm curve. However, a dye concentration above 1,800 mg/L was far beyond the level found in industrial effluent, which was only approximately 100 mg/L (USEPA, 1996). Hence, increasing initial concentrations above this point was not included in the scope of this work. In addition, the dye solution at above 1,000 mg/L was highly viscous and quite difficult to handle. The maximum adsorption capacities (q_m) calculated by Langmuir model for AB, using the L, M, and S size adsorbent, were 68.0, 70.4, and 80.7 mg/g; AR 78.7, 76.9, and 113.6 mg/g; AY 26.9, 27.4, and 35.5 mg/g, respectively. The results showed that smaller sized alga gave more adsorption capacity to the removal of basic dyes than the alga of larger sizes.

From the BET analysis reported in Table 2, the alga with size M, unexpectedly, had the largest surface area and total pore volume, followed by S and L. However, the pore diameter of alga size M was the lowest among the three. The effects of sorbent size on the adsorption capacity are discussed as follows. Firstly, the smaller particle, M and S size sorbents, had more surface area and total pore volume available for the removal of basic dyes than the larger ones. As a result, the adsorption capacity acquired from the L-size sorbent was the lowest in all experimental conditions. Secondly, the pore diameter was believed to also exert significant impacts on adsorption capacity where a larger pore diameter allowed an easier access of the dye molecule into the sorbent structure resulting in a higher adsorption capacity. For the sorbent of S size, it was shown that this did not only possess high surface area, but also had the largest pore diameter. Consequently, it gave the highest adsorption capacity. In case of M size, the sorbent had the largest surface area, but smallest pore diameter. Therefore, basic dyes molecules could hardly enter the pore and the access to the binding sites inside the pore became difficult. It was also possible that there was a clog in the pore. The adsorption capacity was therefore controlled by two contradicting mechanisms, surface area and pore diameter. The fact that the alga with size M had lower adsorption capacity for removal of basic dye than the S size suggested that the effect of pore diameter was more significant than the effect of surface area.

2.4 Effect of pH

pH is an important factor influencing the adsorption of basic dyes on the algal biomass. It had been proven that the adsorption system depended on the degree of ionization of the dye solution and the dissociation of functional groups on the active sites of the adsorbent which varied at different pH. In most cases, the adsorption of basic dyes decreased at lower pH due to the occurrence of proton in acidic mediums (Kumar *et al.*, 2005; Crini *et al.*, 2007). To search for the optimal pH, the adsorptions of basic dyes (AB, AR, and AY) were conducted at various pH levels (2, 4, 6), whereas the uncontrolled experiment was conducted at pH 7+1 (unctrl). There were no attempts to examine the adsorption at basic conditions (pH > 7) as the dyes could not be dissolved completely. Fig.4 displays the results from this experiment where isotherm parameters are summarized in Table 5.

The maximum adsorption capacities (q_m) at pH 2, 4, 6, and the uncontrolled pH conditions, estimated from Langmuir model for AB were 74.1, 94.3, 93.5, and 80.7 mg/g; AR 97.1, 100.0, 105.3, and 113.6 mg/g; and AY 31.9, 30.4, 32.9, and 35.5 mg/g, respectively (Table 5). From the results, the conditions at pH 6 and uncontrolled pH seemed to give the highest adsorption capacity for the removal of all basic dyes, and in most cases, the adsorption capacity decreased with a drop in pH. For AB and AR, the effect of pH was significant and the adsorption capacity could drastically change from 74.1 to 93.5 mg/g and 97.1 to 113.6 mg/g with an increase in the pH from 2 to 6. However, the pH effects on the adsorptions of AY were not quite strong and the adsorption capacity only varied in a narrow range. As the error from the measurement by spectrophotometer was about ±2.5%, the differences in q_m of AY which were less than 5% was considered not significant (Table 5).

The pH_{zpc} of the adsorbent is the pH where the surface charge remains neutral. The surface charge of the adsorbent is positive when the media pH is below the pH_{zpc} while it is negative at pH greater than pH_{zpc}. In this study, *C. lentillifera* had pH_{zpc} of 0.3 and the negative zeta potential increased at pH higher than pH_{zpc}, and remained constant after pH 7. Therefore the alga had less negative charges on its surface at acidic medium and

Table 5 Constants of Langmuir and Freundlich isotherms for the adsorption of basic dyes with S size algae

Basic dye	pH	Langmuir constant			Freundlich constant		
		q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2
AB	2	74.1	7.0×10^{-3}	0.9693	1.5	1.6	0.9823
	4	94.3	3.8×10^{-3}	0.9711	0.7	1.3	0.9916
	6	93.5	4.9×10^{-3}	0.9731	0.8	1.3	0.9771
	unctrl*	80.7	5.8×10^{-3}	0.9689	0.9	1.4	0.9776
AR	2	97.1	6.4×10^{-3}	0.9302	0.2	0.7	0.8966
	4	100.0	4.2×10^{-3}	0.9357	0.2	0.8	0.9138
	6	105.3	3.9×10^{-3}	0.9186	0.2	0.8	0.9186
	unctrl*	113.6	4.6×10^{-3}	0.9139	0.3	1.4	0.8952
AY	2	31.9	3.0×10^{-3}	0.9381	0.6	1.9	0.9579
	4	30.4	4.6×10^{-3}	0.9630	1.2	2.2	0.9689
	6	32.9	5.1×10^{-3}	0.9530	1.1	2.1	0.9638
	unctrl*	35.5	7.4×10^{-3}	0.9164	2.1	2.4	0.8977

* pH 7±1.

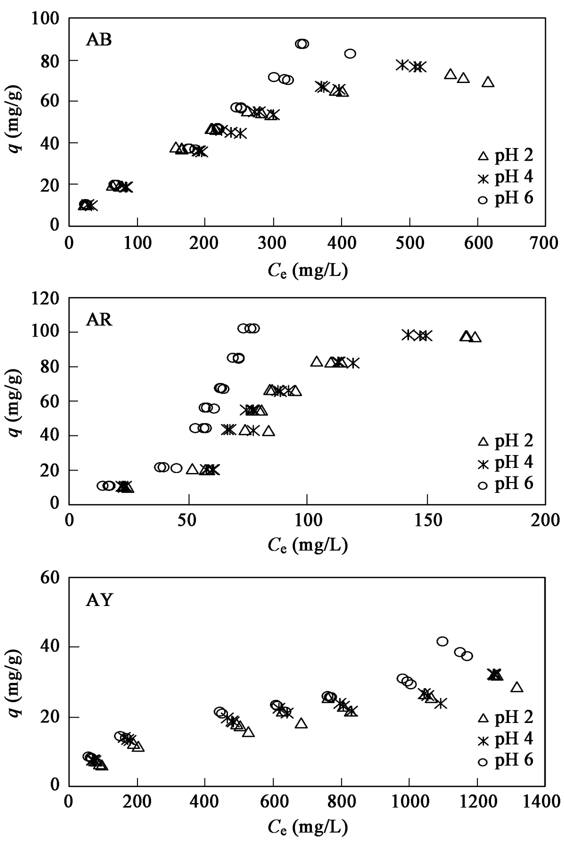

Fig. 4 Isotherms plots of the adsorption of basic dyes with *Caulerpa lentillifera*. Conditions: adsorbent dose 0.5 g; control pH 2–6; 130 r/min; temperature: 25°C.

had the highest negative charge at neutral pH due to the protonation in acidic solution. From the results in Section 2.1, the possible functional group that could change the charge within the pH range from 2 to 6 was carboxyl which had the pK_a at around 1.7–4.7. At pH higher than 1.7–4.7, carboxyl became deprotonated and therefore attracted positive charged compounds such as basic dye. However, pH only did have significant effect on the adsorption of AB and AR, therefore this carboxyl group was expected to be mainly responsible for the adsorption of AB and AR. The adsorption mechanisms for AY should be different from AB and AR, and none of the functional groups examined above could be reasonably responsible for such adsorption. In case of AY, the adsorption mechanism for the cationic dyes and adsorbent might be due to a weak electrostatic interaction between dyes and electron-rich sites of the surface of algae which might not be affected significantly from the change in pH.

2.5 Effect of salt concentration

The effect of salt concentration was studied using NaCl solution. The NaCl concentration ranged from 0 to 10% (*W/V*). Langmuir and Freundlich models were used to describe adsorption isotherms of the basic dyes. The effect of salt concentration on the adsorption of AB and AY using initial dye concentration of 100–1,800 mg/L are shown in Fig.5. AR could not be dissolved in saline water, therefore was not investigated here. The results clearly demonstrated that increasing in salt concentration from 0 to 10% (*W/V*) led to a significant decrease in adsorption capacity of AB. The maximum adsorption capacity (q_m) of AB at 0, 5%, and 10% (*W/V*) salt concentration were 80.7, 78.7, and 38.3 mg/g, respectively. This corresponded to an almost 50% decrease in the adsorption capacity for the range of salt concentration. The isotherm parameters of Langmuir and Freundlich models were shown in Table 6. The results suggested that q_m decreased with an increase

Table 6 Constants of Langmuir and Freundlich isotherms of basic dyes at various salt concentrations using algal S size

Basic dye	NaCl (%, *W/V*)	Langmuir constant			Freundlich constant		
		q_m (mg/g)	b (L/mg)	R^2	K_f	n	R^2
AB	0	80.7	5.8×10^{-3}	0.9689	0.94	1.4	0.9796
	5	78.7	3.8×10^{-3}	0.9333	0.49	1.3	0.9606
	10	38.3	11.2×10^{-3}	0.9839	1.98	2.1	0.9803
AY	0	35.5	7.4×10^{-3}	0.9164	2.10	2.4	0.8977
	5	27.9	5.4×10^{-3}	0.9745	1.17	2.2	0.9852

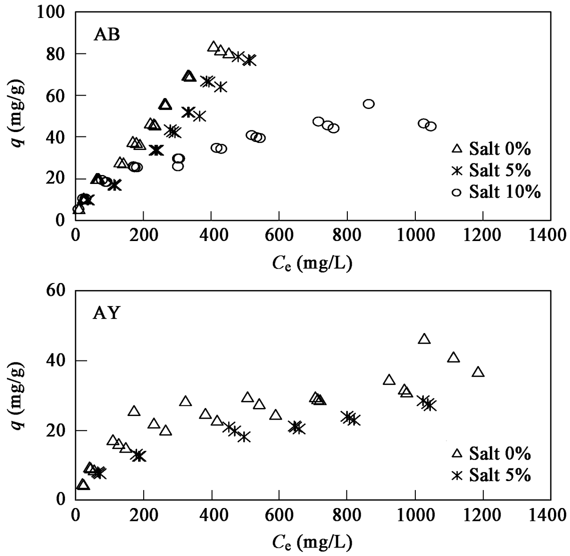

Fig. 5 Isotherms plots of the adsorption of basic dyes with *Caulerpa lentillifera*. Conditions are the same as those in Fig.2.

in NaCl concentration. The same finding was found for the adsorption of AY. However, the solubility of AY at high salt concentration (10% NaCl, *W/V*) was relatively low, therefore the experiment could not be conducted in such condition. The maximum adsorption capacities (q_m) of AY at 0 and 5% (*W/V*) salt concentrations were 35.5 and 27.9 mg/g, respectively.

It was demonstrated clearly that salinity had significant impact on the adsorption of basic dyes. The ion strength became large at high salt concentration, and this reduced the active concentration of dyes and active binding sites at the adsorbent surface, thus reducing the adsorption capacity. Past research showed that an increase in salinity or ionic strength (Na^+ or Ca^{2+}) of the solution could cause a sharp decrease in maximum adsorption capacity of Methylene Blue on chaff (Han *et al.*, 2006). This could be attributed to the competition between ions of similar charge. For this study, the decrease in adsorption capacity might be due to the competition of basic dyes (which also possessed cationic properties) and Na^+ for the adsorption sites on algal surface. In addition, the presence of salinity generated the electrical double layer (Gong *et al.*, 2007; Eren and Afsin, 2006; Anirudhan and Ramachandran, 2006). According to surface chemistry theory (Shaw, 1980), most substances acquired a surface electric charge when contact with a polar medium in aqueous phase. This surface charge influenced the distribution of nearby ions in the polar medium. Ions of opposite charge (counter-ions) were attracted towards the surface and less important ions of the same charge (co-ions) were repelled away from the surface. At this point, they were surrounded by an "electrical double layer" owning to electrostatic interaction.

If the adsorption mechanism was significantly influenced by the electrostatic attraction, adsorption decreased with an increase in salt concentration and ionic strength (Han *et al.*, 2006). The theory of the electrical double layer dealing with the distribution of ions on the surface of the adsorbent can be illustrated using Eq.(5) (Shaw, 1980):

$$\frac{1}{\delta} = \left(\frac{2e^2 N_A c z^2}{\in kT}\right)^{1/2} \quad (5)$$

where, δ is the thickness of the charged layer (or electrical double layer), N_A is the Avogadro's constant (6.02×10^{23} mol^{-1}), c is the electrolyte concentration, z is the electrolyte charged number, ∈ (C^2/(J·m)) is the permittivity constant, e the electron volt (1.6×10^{-19} J), k is the Boltzmann constant (1.38×10^{-23} J/K), and T the temperature (K). For an aqueous solution of a symmetrical electrolyte at 25°C, Eq.(5) becomes permittivity constant.

$$\frac{1}{\delta} = 0.329 \times 10^{10} c^{1/2} z \quad (6)$$

The thicknesses (δ) at 5%, 10% NaCl (*W/V*) were 3.29×10^{-10} and 2.32×10^{-10} m, respectively. This equation shows that an increase in salt concentration or ionic strength caused a compression of electrical double layer. At this point, the charge density (σ_0, C/m^2) at the surface increased according to the Poisson-Boltzmann distribution where, at low potential at 25°C:

$$\sigma_0 = \frac{\in \psi_0}{\delta} \quad (7)$$

where, ∈ is the permittivity constant (approximately 4.56×10^{-13} C^2/(J·m) for an aqueous solution of a symmetrical electrolyte at 25°C), Ψ_0 (J/C) is the potential of algae surface at pH 7 which was 60×10^{-3} J/C. The charge density values of 5%, 10% NaCl (*W/V*) at algal surface were approximately 8.32×10^{-5} and 11.77×10^{-5} C/m^2.

From the above description, a decrease of adsorption capacity with an increase in salt concentration might be due to two main reasons: (1) the competition with Na^+ with the dye cations to access the binding site on algal surface, and as a result, reduced the electric potential at the surface of adsorbent; and (2) the increase in NaCl concentration or ionic strength (c or z) led to the compression of electric double layer at 25°C (1/δ increased from Eq.(6)) which propelled away the positive charged dye molecules. Both effects deteriorated the removal efficiency of the basic dyes. These effects could be described diagrammatically as shown in Fig.6.

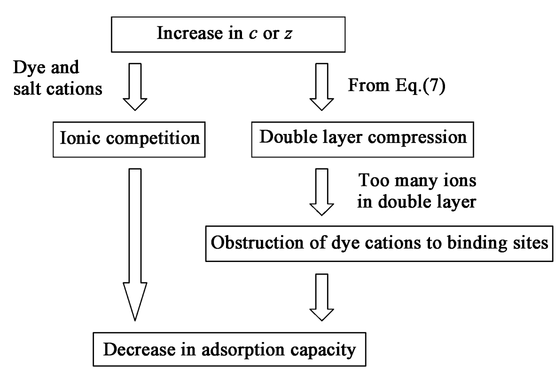

Fig. 6 Effect of salt concentration and ionic strength to adsorption capacity.

3 Conclusions

The management of waste has been a subject of concerns particularly in this new era where the consumption of natural resources is perhaps greater than the sustainable rate. Turning wastes into something useful is one of the potential alternatives capable of reducing the resource depletion rate. In this work, the unwanted dry biomass of *C. lenttilifera* was proven to be useful as biosorbent which was able to uptake several types of basic dyes. The experimental data showed that the adsorption capacities were a function of contact time, sorbent size, pH solution, and salt concentrations. The adsorption equilibrium could be explained by both Freundlich and Langmuir isotherms whereas the kinetics followed the pseudo second order model. The influence of salinity on the adsorption of the dyes was quite significant due to two main reasons, i.e. ion competition and electrical repulsion. Comparison between the adsorption capacities of this alga with other sorbents as given in Table 1 emphasized that the alga had a reasonably high adsorption capacities for the basic dyes. This validates the application of this alga for the color removal especially in textile industry.

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