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Adsorption of reactive blue 4 onto the chemically modified red seaweed *Amphiroa foliacea*: Equilibrium, kinetics and modeling studies

Siew-Ling Hii[1]*, Lesley-Lean Estrop[2] and Ching-Lee Wong[2,3]

[1]Department of Chemical Engineering, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia.
[2]Department of Bioscience, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia.
[3]Taylor's University Lakeside Campus, 47500 Subang Jaya, Selangor, Malaysia.

Indigenous red algae commonly found in Malaysian waters, *Amphiroa foliacea* was used as biosorbent for the removal of a reactive textile dye, Reactive blue 4 (RB4) from synthetic aqueous solution. Investigation on the effects of initial dye concentration on batch sorption of RB4 by *A. foliacea* was conducted, followed by the isothermic sorption and kinetic modeling of dye removal. Results revealed that biosorption of RB4 was greatly enhanced by using hydrochloric acid-treated seaweeds (94% of uptake), as compared to the unmodified and base-treated seaweed with 0% uptake of RB4. The sorption mechanism of acid-treated algal-RB4 system complied well with both Langmuir and Freundlich isotherms (R^2 > 0.97), with maximum adsorption capacity of 55.6 mg/g. This predominant chemisorption of RB4 by acid-treated red seaweed process was best described by the pseudo-second order kinetic model. Further analyses with the Weber-Morris model showed that boundary layer control, surface adsorption and intraparticle diffusion are the possible rate-limiting mechanisms during the sorption of RB4 by using acid-treated *A. foliacea*.

Key words: *Amphiroa foliacea*, seaweed, reactive blue 4, biosorption, modeling.

INTRODUCTION

Reactive dyes form a class of highly colored, water soluble organic substances, which are used extensively in the textile industry for dyeing of cellulosic fabric (cotton), wool and polyamide fibres. They differ from all other classes of dyes in that they bind to the textile fibres, such as cotton through covalent bonding, resulting in the formation of strong bond that resists fading effect (Aksu and Tezer, 2005). However, the reactions required to introduce the dye substances onto the fiber do not run to total completion due to the hydrolysis of dye during application (Stolz, 2001). Hence, the residues of reactive and hydrolysed dyes are left in the spent dyebath and disposed into the wastewater leaving the site.

Reactive blue 4 dye (Figure 1), a key dye used in the present study, is an anthraquinone-based chlorotriazine dye which is very important in textile industry for coloring cloth variants (Libra et al., 2004). This dye is normally known as cold brand dye because it requires milder alkaline conditions, and fixation occurs at the optimum temperature of 25 to 30°C. However, during reactive dyeing, high pH and high temperature cause hydrolysis of dyes due to the reaction of dichlorotriazinyl reactive group with water. Thus, effective and efficient methods for removal of anthraquinone reactive dyes and their decolorized products are needed (Libra et al., 2004).

Generally, textile dyes differ in their chemical composition and stability and thus, different approaches have been used to lower the dye content in water sources. Dye-based effluents are usually treated by

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*Corresponding author. E-mail: yvonne_hii@ymail.com. Tel: +603 41079802. Fax: +603 41079803.
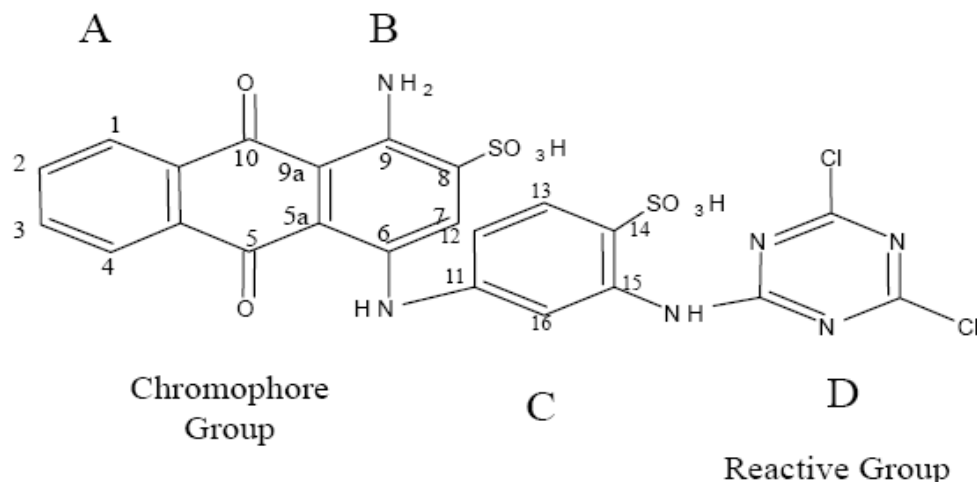
Figure 1. Molecular structure of RB4 dye.

physical, physicochemical, biological and chemical processes. Current methods found to be effective include chemical coagulation, flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation and adsorption (Ho and McKay, 1998; Mohan and Karthikeyan, 1999; Mohan et al., 2002; Aksu and Tezer, 2005; Aravindham et al., 2006). However, these procedures differ in their efficiency and the overall cost required in achieving the same level of sorption from the dye polluted water.

Studies on biological processes, such as biosorption (Ramakrishna and Viraraghavan, 1997; Bayramoğlu et al., 2006), bioaccumulation (Robinson et al., 2001) and bio-degradation (Chao and Lee, 1994; Fu and Viraraghavan, 2001) have become more popular in recent years owing to their efficiencies in the removal of pollutants from wastewater and other aqueous solutions. Among these, biosorption is reported to be more advantageous because of its simplicity in design, its use of inexpensive sorbent material, easy to handle and provides sludge-free cleaning operation (Chen et al., 2003; Garg et al., 2004; Wan Ngah and Hanafiah, 2008). However, most of the biomass, such as pomelo peel (Hameed et al., 2008), fly ash (Gupta et al., 2000), rice husk (Chuah et al., 2005), and weed (Aksu and Tezer, 2005) are needed in large quantities for real field application due to low adsorption capacities of these adsorbents (Aravindham et al., 2006).

In particular, algae represents a cheap source of biosorbent, as they are readily available in large quantities, therefore offering relatively high surface area and have been proven to be an effective biosorbent in the treatment of wastewater (Schiewer and Wong, 2000; Mohan et al., 2002; Aravindham et al., 2006; Marungrueng and Pavasant, 2006; Özer et al., 2006; Daneshvar et al., 2007; Cengiz and Cavas, 2008). Biosorption by using algae has mainly been attributed to the cell wall properties where both electrostatic attraction and complexation can play a role (Şatiroğlu et al., 2002).

Algal cell surface is naturally formed by various chemical groups, such as hydroxyl, carboxylate, amino and phosphate which are believed to be responsible for the sequestration of unwanted materials from effluents (Özer et al., 2006). Most of the reported studies proved that algae species possess impressive sorption capacities for a range of heavy metal ions, however, little attention has been paid to dye biosorption by algal biomass. The present study was therefore initiated to: (1) investigate the possibility of using red seaweed as a potential biosorbent for uptake of RB4; (2) evaluate the effects of chemical pretreatment on the structures of *Amphiroa foliacea* and hence the subsequent removal process of reactive dye; (3) assess the effect of different initial dye concentration on the sorption capacity of modified *A. foliacea*; (4) study the sorption pattern, kinetics and mechanism of RB4 onto chemically pretreated *A. foliacea*.

MATERIALS AND METHODS

Preparation of biosorbent

Adsorbent used in the present study is *A. foliacea*, red seaweed from Port Dickson, Malaysia. The seaweed was washed with generous amounts of distilled water to remove salt and some epiphytes. Washed seaweed was then air-dried at room temperature overnight and labeled as unmodified seaweed (UMS).

Modification process

The unmodified seaweed (UMS) was mixed with 1.0 M hydrochloric acid (HCl) and 1 M sodium hydroxide (NaOH), respectively. The mixture was agitated at a constant speed of 200 rpm until it was homogenous. The treated red seaweed was subsequently rinsed with distilled water until it becomes neutral and was dried at 50°C in a forced-air oven for 24 h. The final products were labeled as acid-treated seaweed (ATS) and base-treated seaweed (BTS), respectively. The samples were kept in a sealed plastic bag and refrigerated for further use.

Preparation of dye solutions

The textile dye, reactive blue 4 (abbreviation: RB4, CI number: 61205; molecular formula: $C_{23}H_{12}Cl_2N_6Na_2O_8S_2$) was purchased from Sigma Aldrich (Germany). The molecular structure of RB4 is presented in Figure 1. Stock solutions of 1000 mg/L RB4, without further purification, was prepared and dilutions were made for subsequent adsorption tests. Dye concentrations were measured by using a UV-Visible spectrophotometer (ThermoSpectronic Genesys 20) at the maximum wavelength of 595 nm.

Batch adsorption experiments

All the batch experiments were carried out in triplicate. Batch adsorption experiments were conducted in 250 ml Erlenmeyer flasks containing 100 ml of dye solutions and 1.0 g of seaweed biomass, unless otherwise stated. Flask with biosorbent in distilled water was prepared as control. The flasks were agitated at 130 rpm and 30°C in a rotary shaker (Copen Scientific, USA). Samples were taken at pre-determined time intervals for determination of residual dye concentration in the solution.

The percentage of dye removal was calculated as shown in Equation 1.

$$\text{Percentage of dye uptake} = \frac{C_o - C_e}{C_o} \times 100\% \qquad (1)$$

The sorption capacities of *Amphiroa* species, q_e (amount of dye sorbed per unit weight of seaweed biomass at equilibrium) was calculated from the mass balance Equation 2.

$$q_e = \frac{V(C_o - C_e)}{m} \qquad (2)$$

Comparative uptake of RB4 by natural and chemically modified seaweeds

A constant mass (1.0 g) of UMS, ATS and BTS were shaken in 100 ml of 100 mg/L of RB4 dye solution at room temperature, respectively. Samples were taken at regular time intervals and the dye content was analysed by using spectrophotometer. The seaweed with the highest percentage of uptake of RB4 and sorption capacity (q_e) was chosen for subsequent experiments.

Effect of initial dye concentration

A constant mass of seaweed (1 g) was put into a series of flasks containing 100 ml of RB4 dye solution. Initial concentrations of RB4 were made to vary from 100 to 1000 mg/L.

Sorption isotherm

Langmuir (Equation 3) and Freundlich (Equation 4) sorption isotherm equilibrium models (in linearised form) were used for the analysis of algal-dye sorption system.

$$\text{Langmuir equation: } \frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} \times \frac{1}{C_e} \qquad (3)$$

$$\text{Freundlich equation: } \log q_e = \log K_f + \frac{1}{n} \times \log C_e \qquad (4)$$

For Langmuir model (Equation 3), plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ yields a straight line with maximum adsorption capacity (q_m) and Langmuir constant (b) could be determined from the intercept and slope of the plot. Meanwhile, Freundlich's constants, $\frac{1}{n}$ and K_f values could be calculated from the slope and interception of the straight-line plot of $\log q_e$ versus $\log C_e$, respectively (Equation 4).

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L, which is defined as follows:

$$R_L = \frac{1}{1 + bC_0} \qquad (5)$$

Kinetics and modeling of sorption process

Biosorption kinetic of RB4 onto the *Amphiroa* spp. was analysed using pseudo-first and pseudo-second order kinetic models. In order to explore the kinetics involved in dye sorption, the experimental data were fitted into the Equations 6 and 7 (Ho and McKay, 1999, 2000). Predicted values of q_e are validated by the correlation coefficient (R^2) which should be close or equal to unity (≈ 1) (Nacèra and Aicha, 2006).

Pseudo-first order equation of Lagergren:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (6)$$

Pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (7)$$

The values of q_e, k_2 and h against C_o in the corresponding linear plots of the pseudo-second order equation were regressed to obtain expressions for these values in terms of initial dye concentration. Ho and McKay (2000) reported that each of these parameters can be expressed as a function of C_o for RB4, as shown in Equations 8 to 10.

$$q_e = \frac{C_o}{A_q C_o + B_q} \qquad (8)$$

$$k_2 = \frac{C_o}{A_k C_o + B_k} \qquad (9)$$

$$h = \frac{C_o}{A_h C_o + B_h} \qquad (10)$$

Weber-Morris model (intraparticle diffusion)

The intraparticle diffusion model (Equation 11) as proposed by Weber and Morris (1963) was applied to study the diffusion mechanism of RB4 onto the red seaweed.

$$q_t = k_w t^{0.5} \tag{11}$$

Spectroscopic analysis

Fourier transform infrared (FTIR)

Fourier transform infrared spectroscopy was conducted to investigate the changes of vibration frequency in the functional groups of the biosorbents. The spectra were collected by Perkin-elmer RXI spectrometer within the range of wavenumber of 400 to 4000 cm^{-1}. Specimens of various biosorbents were first mixed with KBr and then ground in an agate mortar (Merck, for spectroscopy) at an approximate ratio of 1/100 for the preparation of pellets. The resulting mixture was pressed at 20 ton for 1 min. The background obtained from scanning of pure KBr was automatically subtracted from the sample spectra.

Scanning electron microscope (SEM)

Surface morphology of the biosorbents was visualized by a scanning electronic microscope (JEOL, JSM- 6400 attached with Oxford Inca Energy 200EDX). Prior to the observation, the surface of the samples was coated with a thin, electric conductive gold film.

Statistical analysis

Mean values obtained were analyzed with statistical analysis software, SPSS (version 16.0). One-way analysis of variance (ANOVA) was used to detect significant differences between parameters with $p < 0.05$. The data was also subjected to homogeneity (Post Hoc Test) and normality analysis.

RESULTS AND DISCUSSION

Batch adsorption

Comparative uptake of RB4 by *Amphiroa* spp.

As observed from the present study, the unmodified and base-treated *A. foliacea* has no affinity towards RB4 as no sorption of dye was recorded (data not shown). On the other hand, the acid-treated seaweed exhibited significantly high percentage of RB4 removal (94.0% of uptake), when compared with UMS and BTS. In view of this, ATS was selected as key sorbent for the subsequent experiment.

Chaisena and Rangsriwatananon (2005) and Al-Qodah (2000) mentioned that the pretreatment process was found able to modify and increase the porosity of the biosorbent's surface which resulted in the interaction of some new functional groups with the dyes. In addition, nitrogen and hydroxyl containing functional groups in the biomass will be protonated under acidic condition and the

biomass will have a net positive charge (Won et al., 2005). Thus, such positively charged groups are likely to be the binding sites for negatively charged dye molecule.

In the present study, it is believed that the hydrogen ions from the HCl were introduced onto the surface of the seaweed during the modification process, which then acted as bridging ligand between the seaweed cell wall and the dye molecules (Vijayaraghavan and Yun, 2008). According to Namasivayam and Kavitha (2002), the RB4 dye contains sulphonic groups which release colored negatively charge dye ions into the solution and thus, can be sorbed by the ATS due to the positively charged cell wall. Meanwhile, modification of *A. foliacea* with NaOH induced negative charges to the surface of seaweed which in turn increased the number of negative charges at the sorption sites (Namasivayam and Kavitha, 2002). Thus, this hampered or interfered with the ability of the seaweed to adsorb the negatively charged dye (RB4) used in this study.

Spectroscopy analysis

FTIR spectroscopy analysis was conducted to investigate the types of functional groups existing on the surface of unmodified and pre-treated *A. foliacea*. As observed from Figure 2, the unmodified seaweed (UMS) exhibits four peaks in broad region around 3421, 2363, 1420 and 1087 cm^{-1}. The broad region around 3421 cm^{-1} can be assigned to overlapping of -OH stretch and -NH functional groups. The peak at 2363 cm^{-1} could be the H_3O^+ stretch. The peak at wavenumber 1420 cm^{-1} represents the carboxylate salt COO-M, where M denotes the metal cations, such as Na^+, K^+, Mg^{2+} and Ca^{2+} that may naturally exist in unmodified *A. foliacea* (Yang and Chen, 2008). The phosphonate groups show some characteristics adsorption peaks around 1087 cm^{-1} (P-OH stretching). The FTIR spectra of unmodified *A. foliacea* indicated the presence of hydroxyl, carboxyl, amide and phosphate groups which are important sorption sites.

As for base-treated *A. foliacea* (BTS), a new peak appeared at region 2529 cm^{-1} and disappeared at region 1087 cm^{-1}. In addition, the spectrum also showed that the band caused by overlapping -OH and -NH shifted from 3421 cm^{-1} to 3403 cm^{-1}; suggesting addition of hydroxyl group from NaOH. A new peak appears around 2529 cm^{-1} which might be due to the formation of C-H stretch. Interestingly, the spectrum of BTS is almost similar with the UMS spectrum (Figure 2).

As observed from Figure 2, upon contact with 1.0 M hydrochloric acid solution, the band caused by -OH and -NH for acid-treated seaweed (ATS) is slightly broaden and shift towards lower wavenumber of 3402 cm^{-1} as compared to spectrum of UMS. In addition, two new peaks appeared in the ATS spectra at around regions 2926 and 1654 cm^{-1} which corresponds with C-H and C=O stretch, respectively (Yun et al., 2001). The peak at
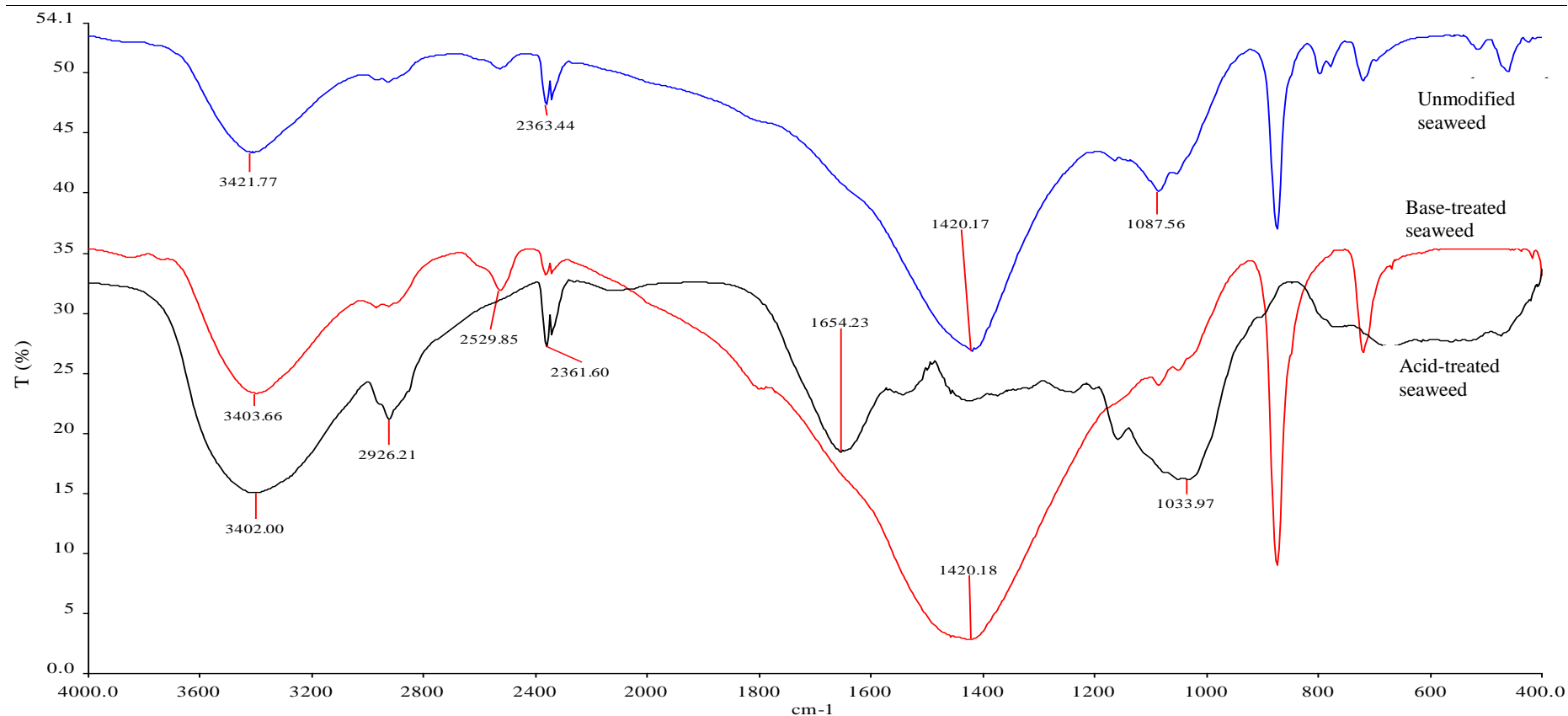
Figure 2. Fourier transform infrared spectra of *Amphiroa* spp., before and after the treatment process. Symbols: (blue), natural seaweed; (black), acid-treated seaweed; (red), base-treated seaweed.

peak at region 1420 cm^{-1} of UMS did not appear in the ATS spectra, suggesting that protonation process might have displaced the light metal ions from the binding sites of carboxylic, sulfonic, etc. According to Huang and Huang (1996), acid-treated biomass contained a higher percentage of surface nitrogen. The treatment process may dissolve polysaccharide compounds in the outer

layer of the cell wall and therefore produce additional binding sites. Moreover, acid treatment also could have resulted in a clean-up of the surface impurities; stabilisation of the surface compounds, and increases the surface area by opening the available sites for dye adsorption (Popuri et al., 2007).

The surface morphology and changes in the

surface microstructures of *A. foliacea* was further observed by scanning electron microscope (SEM) (Figure 3a, b and c). The unmodified *A. foliacea* appears as thick cell wall and surface protube-rance could be observed (Figure 3a).Considerable number of small particles was found to   adhered to the surface of unmodified *A. foliacea*, which might be due to deposition of calcium and other
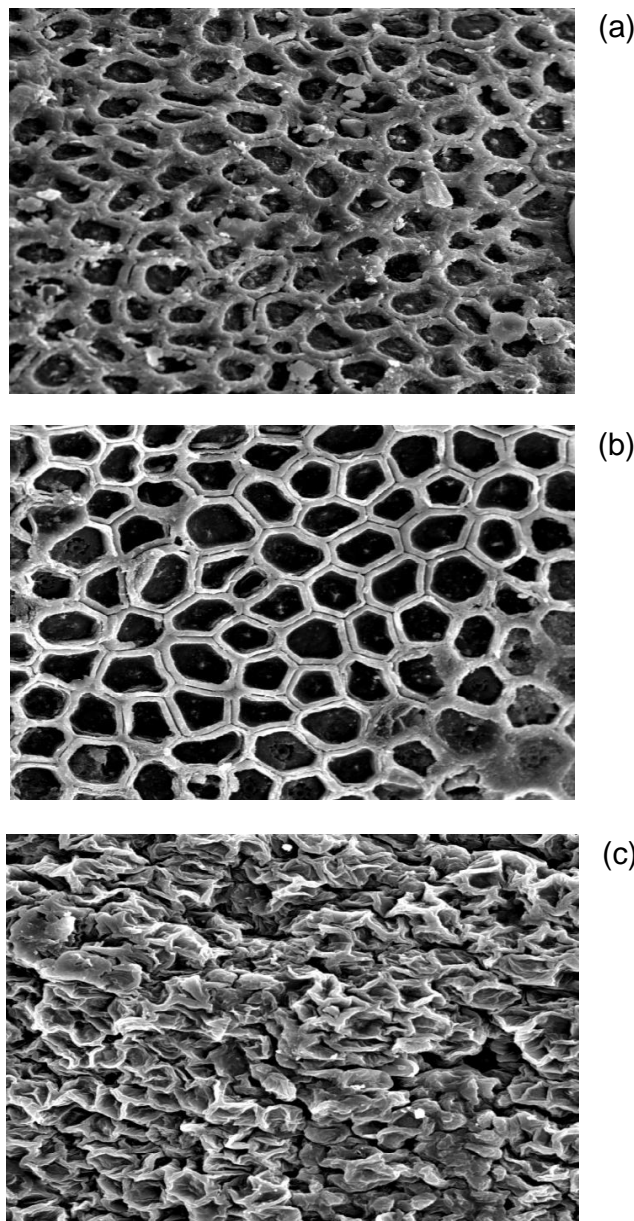
Figure 3. Scanning electron micrographs of (a) unmodified *Amphiroa* spp., (b) base-treated *Amphiroa spp.* and (c) acid-treated *Amphiroa* spp.

salt crystalloids (Yang and Chen, 2008). The microstructures of unmodified *Amphiroa* spp. were further developed and became deeper after the modification with NaOH, as illustrated in Figure 3b. Well-defined cell structures with a clear view of middle lamella (diameter of about 2 μm) could be observed from SEM micrograph of these two samples.

The effect of acid treatment on *A. foliacea* is however quite interesting. After being in contact with hydrochloric acid, the cell structure deteriorates and clearly showing that the cell wall of *A. foliacea* became ruptured, thus losing their defined shape making the protuberance less obvious and resulting in irregular shape of ATS (Figure 3c). These effects of modification might be due to the higher corrosive properties of hydrochloric acid. In contrast with ATS, the UMS and BTS appeared as separate particles with clear structures.

Effect of initial dye concentration

It is understood that the initial dye concentration possess
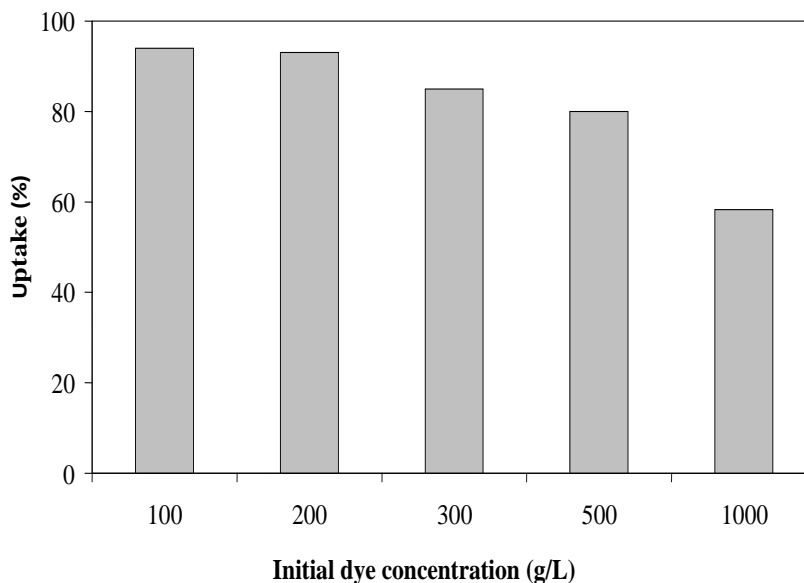
Figure 4. Percent uptake of RB4 (at equilibrium) in various initial dye concentrations.

significant influence on the amount of dye being adsorbed onto the sorbent because there is large difference in concentration between the sorbent surface and the solution (Özer et al., 2006). As observed from Figure 4, percentage of RB4 removal by ATS at equilibrium decreased from 94 to 58.3% with increasing the initial dye concentration from 100 to 1000 mg/L. According to Padmesh et al. (2005), the ratio of the initial moles of dye molecules to the available surface area is low at lower concentration and subsequently the fractional sorption becomes independent of the initial concentration. In other words, the binding sites available on the surface of ATS are sufficient to bind all the dye molecules of RB4 at low initial concentration of RB4. Same phenomena were reported by Hema and Arivoli (2007) by using acid activated carbon. As shown in Figure 4, at initial concentration of 1000 mg/L, the percentage of dye removal was lower than that with dye concentration of 500 mg/L. This phenomenon indicated that the sorption sites on the ATS could not accommodate more dye molecule with the increase of RB4 concentration and it is believed that the system had reached saturation point. At higher concentration, the available sites of sorption became fewer as compared to the moles of dye present and hence the percentage of dye removal is dependent upon the initial dye concentration (Padmesh et al., 2005). In other words, the abundant dye molecules of RB4 available in the solution were found to compete for the limited binding sites on the surface of ATS at high initial concentration, suggesting that the available sites on the ATS is one of the limiting factors for RB4 sorption.

The adsorption capacity (q_e) increased exponentially

from 9.4 to 58.3 mg/g with further increase of initial dye concentration (Figure 5). ANOVA analysis revealed that there were significant differences between variable initial dye concentrations with $p < 0.05$. As stated by Vijayaraghavan and Yun (2008), the initial dye concentration provides an important driving force to overcome all the mass transfer resistances of the dye between the aqueous and solid phases. Therefore, the sorption capacity increases with increasing initial dye concentration. In this study, initial concentration of RB4 above 1000 mg/L was not conducted because it was far beyond the level found in the industrial wastewater effluxent (Steekeen-Richter and Kermer, 1992; Vanderviere et al., 1998).

Adsorption isotherm analysis

Adsorption equilibrium is established when the amount of solute being adsorbed on to the sorbent is equal to the amount being desorbed (Aravindham et al., 2006). At this point, the equilibrium solution concentration remains constant. In the present study, the equilibrium adsorption isotherm of ATS towards RB4 was evaluated at 30°C, using different initial dye concentrations from 100 to 1000 mg/L. The experimental results were analysed within the context of two common adsorption models: the Langmuir and Freundlich adsorption isotherms. Langmuir and Freundlich isotherms are widely used in analysis of adsorption process as they reflect the feature of sorbent and are used to compare the biosorption performance (Lodeiro et al., 2004). According to Akar et al. (2008), Langmuir isotherm assumes a homogeneous type of
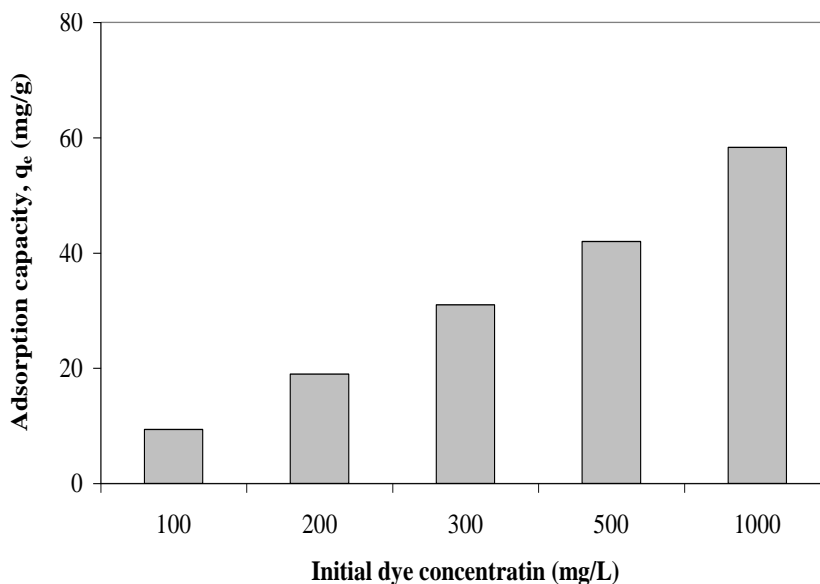
Figure 5. Sorption capacities of ATS (at equilibrium) in various initial dye concentrations.

biosorption within the biosorbent, that is, once a dye molecule occupies a site, no further biosorption can take place at that site. The isotherm further explained that all the sorption sites are energetically identical and sorption occurs on a structurally homogeneous sorbent (Hameed et al., 2008). In addition, the Langmuir isotherm served to estimate the maximum dye uptake values when the values could not be experimentally obtained (Vijayaraghavan and Yun, 2008). The Freundlich isotherm was constructed with different assumption from Langmuir isotherm. Freundlich adsorption isotherm was used to study the non-ideal adsorption involving heterogeneous adsorption phenomena (Mohan et al., 2008) and with the presence of different classes of adsorption sites (Aravindham et al., 2006). According to Marungrueng and Pavasant (2006), the different classes of adsorption sites as described by Freundlich isotherm could be advantageous in describing the adsorption of a low strength solution.

As observed from Table 1, the maximum adsorption capacity (q_m) of acid-treated *A. foliacea* was 55.6 mg/g at 30°C while the Langmuir constant b was 0.034 L/mg. As stated by Greluk and Hubicki (2010), the constant b indicates the affinity of biosorbents for the binding of dyes and the large value of b reflects large affinity of the biosorbents for the dyes, resulting in a stable adsorption product. In addition, the values of R_L for all systems under investigation were found to be between 0 and 1 (Table 2), which indicates favorable adsorption of acid-treated *A. foliacea* towards RB4. It has been established that (1) $0 < R_L < 1$ indicates a favorable adsorption, (2) $R_L > 1$ suggests an unfavorable adsorption, (3) $R_L = 1$ for linear adsorption and (4) $R_L = 0$ for irreversible adsorption

(Crini, 2008).

The linearised forms of Freundlich isotherm model for RB4 adsorption on ATS are found to be linear over the whole concentration range studied. According to Ho and McKay (1998) and Basha and Murty (2007), values of n between 1 and 10 represent favourable adsorption. As shown in Table 1, the Freundlich exponent, n, value of 2.049, indicates that RB4 dye is favorably adsorbed onto ATS at all initial dye concentrations investigated.

Further, the high correlation coefficient values of both isotherm models ($R^2 > 0.95$) confirm that it is appropriate to use both Langmuir and Freundlich isotherms to describe sorption of RB4 by acid-treated *A. foliacea* (ATS). The applicability of both Langmuir and Freundlich isotherms to the current sorption study implies that the *A. foliacea* might exhibit both monolayer adsorption and heterogeneous surface conditions, which can be considered as a normal phenomenon with system using biological adsorbent (Kumari and Abraham, 2007).

Kinetics and modeling of sorption process

The adsorption kinetics for RB4 on acid-treated *A. foliacea* were analyzed and stimulated by using the pseudo-first (Equation 6) and pseudo-second order (Equation 7) kinetic models. Pseudo-first order kinetic indicates that the process of biosorption occurs at a rate proportional to dye concentration, which is particularly suitable for low concentration (Bayramoğlu et al., 2006). Pseudo-second order model is based on the sorption capacity on the solid phase and the model predicts the behavior over the whole range of adsorption (Aksu and

Table 1. Equilibrium constants for sorption of RB4 by acid-treated seaweed.

Langmuir constant			Freundlich constant		
q_m (mg/g)	b (L/mg)	R^2	n	K_f	R^2
55.556	0.0340	0.972	2.049	0.633	0.980

Table 2. Langmuir isotherm of dimensionless constant at various initial concentrations.

Initial dye concentration (mg/L)	100	200	300	500	1000
R_L	0.227	0.128	0.089	0.056	0.029

Table 3. Sorption capacities and correlation coefficients of pseudo-first and pseudo-second kinetics.

Initial concentration (mg/L)	Experimental sorption capacities($q_{e,exp}$) (mg/g)	Pseudo-first order		Pseudo-second order	
		Calculated sorption capacities($q_{e,cal}$) (mg/g)	R^2	Calculated sorption capacities($q_{e,cal}$) (mg/g)	R^2
100	9.40	9.59	0.999	9.8039	0.998
200	18.50	15.67	0.998	19.2308	0.998
300	26.00	16.60	0.816	27.7778	0.993
500	42.00	49.09	0.885	47.6190	0.971
1000	56.00	12.65	0.092	71.4286	0.945

Table 4. Empirical parameters for predicted q_e, k_2 and h from C_o.

Dye	A_q(g/mg)	B_q(g/L)	A_k (mg min/g)	B_k (mg^2 min/g L)	A_h (g min/mg)	B_h (g min/L)
RB4	0.002	9.902	3175	-38975	0.849	-10.9

Tezer, 2005) which is in agreement with the chemi-sorptions mechanism being the rate-controlling step (Ho and McKay, 1998).

As shown in Table 3, pseudo-first order equation did not fit well for most of the range of concentrations under study with lower correlation coefficient (R^2) as compared to those of the second order model for the dye studied. Moreover, the calculated equilibrium sorption capacities (q_e) based on first-order kinetic model does not agree well with those determined experimentally. The reason for the discrepancies in q_e values is that there is a time lag, probably resulting from the presence of boundary layer or external resistance controlling at the beginning of the sorption process (Ho and McKay, 1998). For this reason, the Lagergren expression cannot be applied for the entire process of adsorption of RB4 onto ATS.

On the other hand, the pseudo-second order plot ($\dfrac{t}{q_t}$ versus time, t) revealed a good compliance with extremely high correlation coefficients ($R^2 > 0.94$) for all the experimental data. Furthermore, the calculated adsorption capacities (q_e) were with good accuracy with those determined experimentally (Table 3). The results indicated that the rate limiting step may be chemical sorption or chemisorptions involving valency forces through sharing or exchange of electron between sorbent and sorbate, as suggested by Ho and McKay (2000).

The corresponding linear plots of the value q_e, k_2 and h against C_0 (Equations 8, 9 and 10) were regressed to obtain expression of these values in terms of initial dye concentration (Table 4). Substituting the values of these constants from the Table 4, a generalized predictive model for RB4 sorbed at any contact time and initial concentration within the given range with relationship of q_e, C_0 and t is shown in Equation 12.

Proposed model

$$q_{t(calc.)} = \frac{C_0 t}{0.849 C_0 - 10.9 + (0.002 C_0 + 9.902)t} \qquad (12)$$

This equation can be used to derive the removal of RB4 at any given initial dye concentration (C_0) and reaction
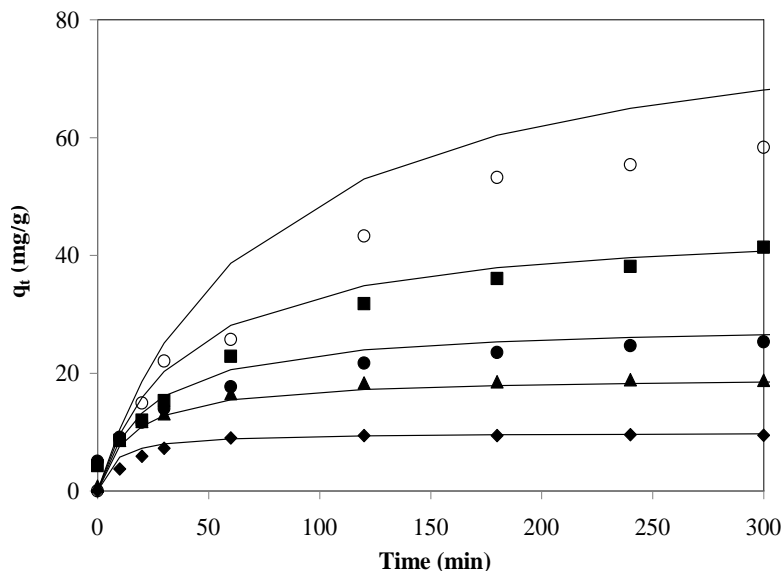
Figure 6. Comparison between the experimental and pseudo-second order modeled time profiles for RB4 sorption onto ATS. Symbols: (♦), 100 mg/L; (▲), 200 mg/L; (●), 300 mg/L; (■), 500 mg/L; (O), 1000 mg/L. Solid lines represent data calculated according to Equation 12.

time (t), as shown in Figure 6 (solid lines). The calculated adsorption capacities ($q_{t(calc.)}$) showed very good compliance with experimental adsorption capacities (q_e), of which concentration up to 500 mg/L can be observed. Deviation was observed with initial dye concentration of 1000 mg/L, suggesting that further modification of current model (Equation 12) is required for mechanism of biosorption involving dye concentration at and higher than 1000 mg/L.

Intraparticle diffusion analyses with Weber-Morris model

Since neither the pseudo-first order nor the second-order model could identify the diffusion mechanism, the kinetic results were further analyzed by the intraparticle diffusion model to elucidate the diffusion mechanism and the model is expressed as in Equation 11. According to the model, the plot of q_t versus $t^{0.5}$ should be a straight line from the origin if in the adsorption process, film diffusion is negligible and intraparticle diffusion is the only rate limiting step. However, if the data exhibit multi-linear plot, then the process is governed by two or more steps (Kannan and Sundaram, 2001; Bhattacharyya and Sharma, 2004; Yalcin et al., 2004; Ho, 2006).

The amount of RB4 adsorbed (q_t) at time (t) was plotted against the square root of contact time ($t^{0.5}$) according to Equation 11. As observed from Figure 7, there are two separate zones: (1) first linear portion (phase I) representing surface adsorption and immediate utilization of the most readily available sorption sites on the surface

of adsorbent (Chang et al., 2003); (2) second linear part (phase II) illustrating the very slow diffusion of the adsorbate from the surface site into the inner pores (Chang et al., 2003; Mohan et al., 2008). The present study indicates that the initial portion of RB4 adsorption by ATS may be governed by the initial intraparticle transport of RB4, controlled by surface diffusion process and the later part controlled by pore diffusion.

Figure 7 shows that the intercept of the lines fail to pass through the origin, which indicated the existence of some degree of boundary layer control, and the difference in the rate of mass transfer in the initial and final stages of adsorption (Akar et al., 2008). Such deviation of the straight lines from origin reveals that the pore diffusion is not the only rate-limiting step, but other kinetic models which may be operating simultaneously and thus control the overall rate of adsorption (Ho and McKay, 2003; Akar et al., 2008).

Conclusion

Batch mode of RB4 removal from aqueous solution by using indigenous red seaweed as biosorbent was conducted in the present study. The study confirms the effectiveness of acid-treated *A. foliacea* (ATS) with higher sorption capacity towards RB4 when compared with unmodified and base-treated seaweed. The batch sorption experiments revealed that the highest removal efficiency of 94% was achieved by using 1 g of ATS in the solution with 100 mg/L of RB4. In addition, the sorption capacity of ATS increased with an increase in
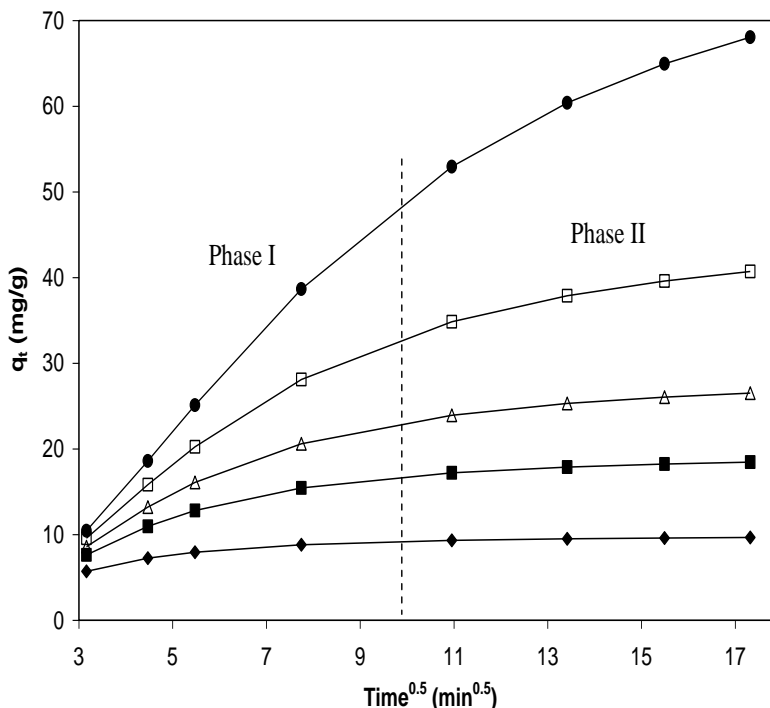
Figure 7. Intraparticle diffusion for adsorption of RB4 by acid-treated *Amphiroa* spp. (ATS). Symbols: (♦), 100 mg/L; (■), 200 mg/L; (△), 300 mg/L; (□), 500 mg/L; (●), 1000 mg/L.

initial dye concentration. The equilibrium data conformed to both Langmuir and Freundlich isotherms. The kinetics sorption of all initial concentration was best described with pseudo-second order kinetic model, which provides a better correlation coefficient of the experimental data. From the present study, we suggest that the sorption of 100 to 1000 mg/L of RB4 from aqueous onto seaweed was a rather complex process, involving boundary layer, surface adsorption and intraparticle diffusion mechanisms.

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Abbreviations: C_o, Initial dye concentration in liquid phase (mg/L); **C_e,** liquid phase dye concentration at equilibrium (mg/L); **q_e,** amount of dye sorbed at equilibrium per unit amount of the biomass (mg/g); **V,** volume of dye solution used (L); **m,** mass of sorbent used (g); **q_m,** maximum amount of dye sorbed per unit weight of biomass (mg/g); **b,** energy of adsorption (L/mg); **K_f,** Freundlich constants indicating sorption capacity, $\dfrac{1}{n}$, Freundlich constants indicating intensity; q_t, amount of dyes absorbed at time t (mg/g); k_1, rate constant of pseudo-first order sorption (L/min); $h = k_2 q_e^2$, the initial sorption rate (mg/g/min); k_2, rate constant of pseudo-second order kinetics (g/mg/min); **(A_q, B_q, A_k, B_k, A_h and B_h),** constants related to the respective equations; **$q_{t(calc.)}$,** calculated adsorption capacities; **k_w,** intraparticle diffusion rate constant (mg/g.min$^{-0.5}$).

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