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Biosorption of C.I. Reactive Black 5 from aqueous solution using acid-treated biomass of brown seaweed *Laminaria* sp.

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Abstract

The biosorption of C.I. Reactive Black 5 (RB5) from aqueous solution, using the brown seaweed, *Laminaria* sp., was investigated in both batch and column modes of operation. Protonation of the native *Laminaria* biomass, with 0.1 M HCl, considerably improved its RB5 biosorption capacity. Evidence from FT-IR spectra confirmed the participation of amine groups in the biosorption of RB5 and the mechanism was proposed to be electrostatic interaction between the positively charged amine groups and negatively charged RB5. At various initial RB5 concentrations (50–200 mg/l), batch sorption equilibrium was reached within 3 h, followed by slow attainment of equilibrium, and the kinetic data obtained were interpreted in terms of the pseudo-second order model. Biosorption isotherm experiments, under different pH and temperature conditions, revealed that decreasing the pH and increasing the temperature favored biosorption. The Langmuir, Freundlich and Redlich–Peterson models were used to describe the isotherm data; of which the Freundlich model described the isotherm data with high correlation coefficients and low percentage error values. According to the Langmuir model, the maximum RB5 uptake of 101.5 mg/g was observed at pH 1 and temperature of 40 °C. Various thermodynamic parameters, such as ΔG°, ΔH° and ΔS°, were calculated, which indicated that the present system was spontaneous and endothermic process. A 0.01 M NaOH solution successfully eluted all dye from the RB5-loaded *Laminaria* biomass. The feasibility of the brown seaweed for the continuous removal of RB5 from aqueous solution was examined in an up-flow packed column (1 cm ID and 12 cm height). With a bed height, flow rate and initial RB5 concentration at 10 cm, 1 ml/min and 50 mg/l, respectively, the *Laminaria* biomass exhibited an RB5 uptake and removal efficiency of 41.9 mg/g and 72.7%, respectively. The column was successfully eluted using 0.01 M NaOH, with an elution efficiency of 97.7%.

Keywords: Biosorption; Seaweed; Reactive Black 5; Waste-water treatment; Modeling; Packed column

1. Introduction

Synthetic dyes have wide industrial uses, such as rubber, textiles, plastics, paper and cosmetics etc., for the coloration of products. The effluents emanating from these industries are often colored and require treatment prior to discharge. Several strategies currently exist for the removal of color from industrial effluents, including physico-chemical and biological processes. Important physico-chemical processes include ozonation, adsorption, chemical precipitation and flocculation [1], but these are usually inefficient, costly and not adaptable to a wide range of dye wastewaters [2]. Conversely, biological processes, such as biodegradation, bioaccumulation and biosorption, offer attractive options for dye remediation [3,4]. However, the use of biodegradation and bioaccumulation can be unpredictable, cumbersome and sometimes difficult to operate on a large scale, as stringent conditions (pH, temperature and nutrient concentrations) have to be maintained to support microbial growth [4]. In contrast, biosorption processes are relatively easy to operate and possess several inherent advantages, including low cost, operation over a wide range of conditions and the possible reuse of biosorbents [5]. Biosorption can be defined as the uptake of contaminants, via various physico-chemical

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mechanisms, including ion-exchange, adsorption, complexation, chelation and microprecipitation etc., by inactive/dead biological materials [5]. The mechanism of binding depends upon the type of biomass, chemical nature of the pollutant and the environmental conditions (pH, temperature and ionic strength).

Reactive dyes, the removal of which is examined here, are widely used in many industrial uses due to their bright color, excellent colorfastness and ease of application [6]. Reactive dyes are typically azo-based chromophores combined with different reactive groups. More than 80,000 tonnes of reactive dyes are produced and consumed annually, making estimation of the total pollution caused by their use possible [7]. They differ from all other dye classes in that they bind to the textile fibre, such as cotton, through covalent bonds; and thus, are highly recalcitrant to conventional waste-water treatment processes [8].

Marine algae, apart from in very few cases [9,10], have not been utilized for the removal of dyes. They are well established metal biosorbents and are abundantly available in many of the world's oceans. Marine algae, in particular brown seaweed, have been identified as potent metal biosorbents due to the presence of binding sites, such as carboxyl, sulfonate, amine and hydroxyl groups [11]. They also offer advantages in biosorption as their macroscopic structures impart a convenient basis for the production of biosorbent particles suitable for application to the sorption process [12].

In this work, attempts were made to utilize the potential of the brown seaweed, *Laminaria* sp., as a biosorbent for the removal of C.I. Reactive Black 5 from aqueous solution in both batch and column modes of operation. The influences of pH and temperature were studied, and the isotherms were described using several models. Dye desorption was attempted using several elutants. An up-flow packed column was also employed to study the continuous removal of C.I. Reactive Black 5 from aqueous solution.

2. Materials and methods

2.1. Dye and biosorbent

C.I. Reactive Black 5 (RB5) of purity 55%, was purchased from Sigma-Aldrich Korea Ltd. (Yongin, Korea). The brown seaweed, *Laminaria* sp., was collected along the seashore of Pohang (Korea). After washing with de-ionized water, the samples were sun-dried and then ground to an average particle size of 0.4–0.6 mm. Protonation of biomass involved bringing into contact 10 g/l of algae with 0.1 M HCl for 3 h. The resultant biomass was then washed in de-ionized water and dried overnight at 60 °C.

2.2. Batch experimental procedure

Batch biosorption experiments, to obtain isotherm and kinetic data, were performed in 50 ml plastic bottle (high-density polyethylene) containing various concentrations (50–1000 mg/l) of 40 ml RB5 solution adjusted to desired pH using 0.1 M HCl or NaOH. A known quantity of biosorbent (0.1 g) was added to each bottle, and agitated at 160 rpm at the desired temperature. The pH of reaction mixture was controlled at the desired value by the addition of 0.1 M HCl or NaOH during the biosorption experiments. After 12 h, the slurries were centrifuged at 3000 rpm for 5 min to remove the biosorbent from the solution. The resultant solutions were then analyzed, after appropriate dilution, using a spectrophotometer (UV-2450, Shimadzu, Kyoto, Japan) at 597 nm. The amount of dye sorbed by the biosorbent was calculated from the differences between the initial quantity of dye added and that left in the supernatant, using the following equation:

$$Q = V(C_0 - C_f)/M \tag{1}$$

where Q is the dye uptake (mg/g), C_0 and C_f the initial and equilibrium dye concentrations in the solution (mg/l), respectively, V the solution volume (l) and M the mass of biosorbent (g).

The dye-loaded biosorbent, exposed to 200 mg/l of RB5 solution at a pH of 1 and temperature of 25 °C, was separated from the solution by centrifugation. The biosorbent was then brought into contact with 20 ml of several individual desorbents on a rotary shaker at 160 rpm. The remaining procedure was the same as that employed for the biosorption equilibrium experiments. The elution efficiency was determined from the ratio of the dye mass in the solution after desorption to that initially bound to the biosorbent.

2.3. Models to fit batch experimental data

Three equilibrium isotherm models were used to fit the experimental data, as follows:

Langmuir model

$$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \tag{2}$$

Freundlich model

$$Q = K_F C_f^{1/n} \tag{3}$$

Redlich–Peterson model

$$Q = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{\beta_{RP}}} \tag{4}$$

where $Q_{\max}$ is the maximum dye uptake (mg/g), b the Langmuir equilibrium constant (l/mg), K_F the Freundlich constant $(\mathrm{l/g})^{1/n}$, n the Freundlich constant, K_{RP} the Redlich–Peterson isotherm constant (l/g) and a_{RP} the Redlich–Peterson isotherm constant $(\mathrm{l/mg})^{\beta}_{RP}$; where β_{RP} is the Redlich–Peterson model exponent. All the model parameters were evaluated from a non-linear regression using the Sigma Plot (version 4.0, SPSS, USA) software.

The average percentage error between the experimental and predicted values was calculated using:

$$\varepsilon(\%) = \frac{\sum_{i=1}^{N} \left(Q_{\exp,i} - Q_{\mathrm{cal},i}/Q_{\exp,i}\right)}{N} \times 100 \tag{5}$$

where Q_{exp} and Q_{cal} represent the experimental and calculated dye uptake values, respectively, and N the number of measurements.

2.4. Fourier transform infrared analysis

The infrared spectra of the biomass samples in KBr discs were analyzed using a Fourier transform infrared spectrometer (MB 100, ABB Bomem, Canada), within the range 400–4000 cm^{-1}, to identify the functional groups responsible for the biosorption.

2.5. Column experimental procedure

Continuous biosorption experiments were conducted in a glass column (1 cm ID and 12 cm height), packed with 3.8 g of seaweed to yield an initial bed height of 10 cm. RB5 solution (50 mg/l at pH 1) was pumped upwards through the column, at 1 ml/min, using a peristaltic pump. Effluent samples were collected at different time intervals as they left the column, and the dye concentration analyzed. All the column studies were performed at room temperature of 25 °C.

The total quantity of dye mass biosorbed in the column (m_{ad}) was calculated from the area above the breakthrough curve (outlet dye concentration vs. time) multiplied by the flow rate. Dividing the dye mass (m_{ad}) by that of the biosorbent (M) allowed the uptake capacity (Q) of the biomass to be obtained. The total dye mass sent to the column can be calculated from the following equation:

$$m_{\mathrm{total}} = \frac{C_0 F t_{\mathrm{e}}}{1000} \tag{6}$$

where C_0 is the inlet dye concentration (mg/l), F the volumetric flow rate (l/h) and t_{e} the exhaustion time (h).

The total dye removed (%) with respect to flow volume can be calculated from the ratio of dye mass adsorbed (m_{ad}) to the total amount of dye mass sent through the column (m_{total}), as follows:

$$\text{Total dye removal }(\%) = \frac{m_{\mathrm{ad}}}{m_{\mathrm{total}}} \times 100 \tag{7}$$

After exhaustion of the column, the desorption process was carried out by pumping a known concentration of elutant upwards, at a flow rate of 1 ml/min, through the column. The dye mass desorbed (m_{d}) can be calculated from the area below the elution curve (outlet RB5 concentration vs. time) multiplied by the flow rate. The elution efficiency can be calculated from the following equation

$$E(\%) = \frac{m_{\mathrm{d}}}{m_{\mathrm{ad}}} \times 100. \tag{8}$$

3. Results and discussion

3.1. Effect of pH and mechanism of dye biosorption

The sorption of dye as a function of equilibrium pH (Fig. 1) clearly showed that pH played an important role in the biosorption of RB5 by *Laminaria* biomass. Initial experiments were conducted with native *Laminaria* biomass, which exhibited a RB5 uptake of 39.4 mg/g at pH 1. The acid-washed *Laminaria* biomass exhibited a superior RB5 uptake of 53.8 mg/g at the same pH. An increase in solution pH resulted in a decrease in the biosorption performance, in the case of both raw and protonated biomasses. Apart from structural modification of the biomass, the action of mineral acids may also be attributed to the protonation of the functional groups responsible for the biosorption.

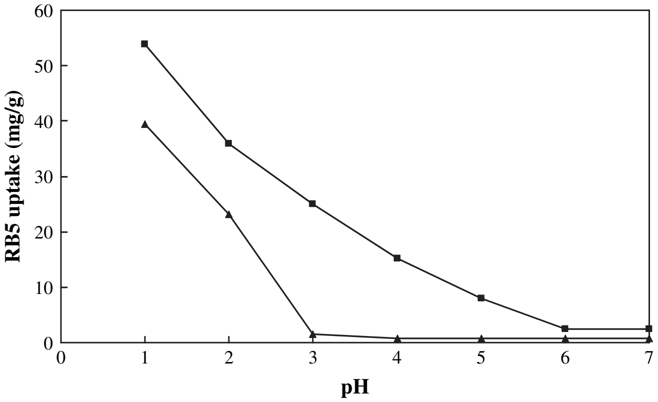

Fig. 1. The effect of solution pH on the RB5 uptake capacity of *Laminaria* biomass (initial dye concentration = 200 mg/l; temperature = 25 °C; agitation rate = 160 rpm); biomass: (▲) raw; (■) protonated.

To better understand the nature of the functional groups responsible for the biosorption of RB5, the FT-IR spectrum of protonated biomass was obtained (Fig. 2). The broad absorption band around 3390 cm^{-1} indicated the existence of –OH groups of glucose and –NH groups of proteins [13]. The strong absorption band at 2930 and that at 1740 cm^{-1} can be assigned to –CH stretching of carboxyl groups [14]. The absorption peaks at 1650 and 1540 cm^{-1} can be attributed to the amide I and amide II bands of the protein peptide bonds [15]. The bands at 1160 and 1040 cm^{-1} can be assigned to the –CN stretching vibration of the protein fractions [16].

In order to elucidate the biosorption of RB5, the FT-IR spectrum of RB5-loaded biomass was compared with that of

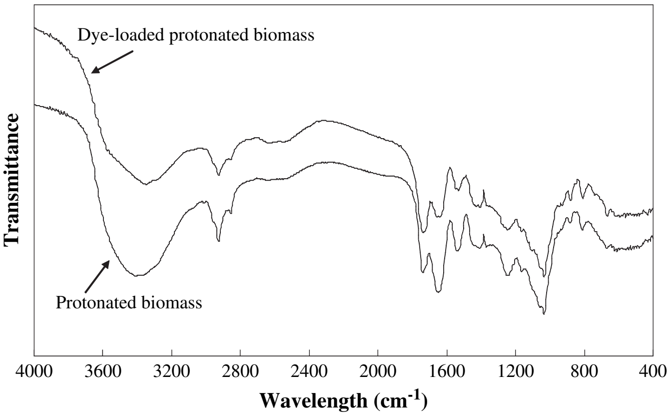

Fig. 2. FT-IR spectra of protonated and dye-loaded protonated *Laminaria* biomasses.

the protonated biomass (Fig. 2). In the RB5-loaded biomass, the peaks around 1650 and 1540 cm^{-1}, corresponds to −NH bending, became smaller. Although the peak at 1650 cm^{-1} can be attributed to carboxyl groups, the change in the peak intensity at 1540 cm^{-1} confirmed the involvement of amino groups in the biosorption. The negatively charged RB5 would be able to electrostatically interact with the amino groups of the *Laminaria* biomass. Although slight changes in the absorption at other frequencies were also observed, it was difficult to interpret their participation in the biosorption of RB5.

The enhancement of reactive dye uptake under strongly acidic conditions (Fig. 1) may be explained in terms of the electrostatic interactions between the biomass and the dye particles [6]. Seaweeds contain mainly carboxyl, sulfate and amine groups [11,17]. Thus, it would be expected that the nitrogen-containing functional groups in the biomass will be protonated under acidic conditions; and thus, the biomass will have a net positive charge. Conversely, reactive dyes release colored negatively charged dye ions into solution, which will exhibit electrostatic attraction towards the positively charged cell surface. In general, hydrogen ion acts as a bridging ligand between the algal cell wall and the dye molecule. However, it should be noted that the pK_a value of amine groups is usually around 8.5; meaning the amine groups will be completely protonated at a pH less than approximately 7 [18]. In contrast, the experimental results implicate no significant biosorption at pH 7. This may be due to other functional groups, such as carboxyl, which are negatively charged and will exhibit repulsion towards the negatively charged RB5. The pK_a value of the carboxylic groups in brown seaweed is usually within the range 3.6–4.5 [19–21]. Therefore, the carboxyl groups will have negative charge at a pH higher than approximately 4, which will electrostatically hinder access of the RB5 to the seaweed biomass.

3.2. Biosorption kinetics

Fig. 3 presents a typical set of kinetic experimental results for the biosorption of RB5 onto *Laminaria* biomass with different initial concentrations (50–200 mg/l). 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. Hence, the uptake of dye increases with increase in the initial dye concentration. On changing the initial RB5 concentration from 50 to 200 mg/l, the amount of biosorption increased from 20 to 53.9 mg/g. However, the RB5 removal efficiency decreased from 100 to 67.3% with an increase in the dye concentration from 50 to 200 mg/l. This is because at the lower concentration, the ratio of the initial moles of dye compared to the available surface area is low; therefore, the subsequent fractional sorption becomes independent of the initial concentration. However, at the higher concentration the available sites for sorption will be fewer than the moles of dye present; hence, the percentage RB5 removal is dependent on the initial dye concentration [22]. It was observed that 50% of the dye molecules were removed within 90 min of contact at all concentrations examined, after which, the rates of uptake slowed, with equilibrium finally was reached at around 360–540 min. The higher sorption rate during the initial period may have been due to an increase in the number of vacant sites initially available, resulting in an increased concentration gradient between the sorbate in the solution and that at the biosorbent surface. With increasing time, this concentration gradient was reduced due to the sorption of RB5 molecules onto the vacant sites, leading to decreased sorption during the later stages.

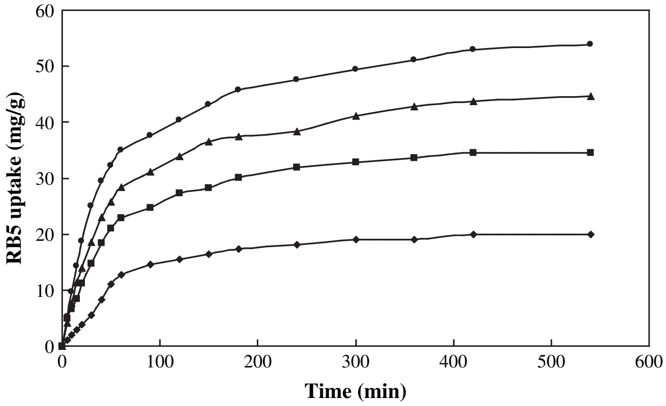

Fig. 3. The effect of initial concentration on the biosorption of RB5 onto *Laminaria* biomass (pH = 1; temperature = 25 °C; agitation rate = 160 rpm). Initial RB5 concentration: (◆) 50 mg/l; (■) 100 mg/l; (▲) 150 mg/l; (●) 200 mg/l.

The experimental biosorption kinetic data were modeled using pseudo-second order kinetics. The linearized form of the pseudo-second order model [23] can be represented as:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \tag{9}$$

where Q_e is the amount of dye sorbed at equilibrium (mg/g), Q_t the amount of dye sorbed at time t (mg/g) and K_2 the pseudo-second order rate constant (g/mg min).

The pseudo-second order model is based on the sorption capacity onto the solid phase, which predicts the sorption behavior over the whole range studied [24], which was consistent with the better results obtained with the pseudo-second order model (Table 1). All the correlation coefficients were greater than 0.994, and the predicted equilibrium sorption capacities values showed reasonably good agreement with those obtained experimentally.

Table 1
Pseudo-second order model kinetic parameters at different initial RB5 concentrations

Initial concentration (mg/l)	Experimental Q_e (mg/g)	$K_2 \times 10^4$ (g/mg min)	Predicted Q_e (mg/g)	R^2
50	20.0	5.03	23.9	0.994
100	34.6	5.98	37.7	0.999
150	44.7	4.14	48.5	0.999
200	53.8	3.78	57.8	0.999

3.3. Biosorption isotherms

As the solution pH, especially low values, has a significant effect on the uptake of RB5, biosorption isotherm experiments were conducted under different pH conditions (pH 1–2). In addition, biosorption isotherms were also studied at different temperatures (25–40 °C). The initial RB5 concentration was varied from 50 to 1000 mg/l to obtain biosorption isotherms. From Fig. 4 it can be clearly seen that a low pH (pH 1) and high temperature (40 °C) favored biosorption. A steep initial isotherm slope (which is the measure of the sorbent–solute affinity), with an eventual highest uptake value of 100 mg/g was observed under these conditions. Under all the conditions examined, the uptake of RB5 increased with increasing dye concentration, reaching saturation at a higher equilibrium concentration. From Fig. 4, it can also be observed that the biosorption performance increased with increasing temperature; showing the endothermic character of biosorption. This increase in uptake could be due to the increased surface activity and kinetic energy of the dye molecules [8].

The biosorption isotherm was studied using three models: the Langmuir, Freundlich and Redlich–Peterson models. The model constants, along with correlation coefficients (R^2) and percentage error values obtained for the three isotherm models, are listed in Table 2. The Langmuir sorption model served to estimate the maximum dye uptake values when these could not be experimentally obtained. The constant b represents the affinity between the sorbent and sorbate. The Langmuir model parameters were largely pH and temperature dependent. Maximum dye uptake, $Q_{\max}$, and the Langmuir equilibrium constant, b, increased with decreasing solution pH and increasing temperature. High b values are reflected in the steep initial slope of a sorption isotherm, indicating a desirable high affinity. Thus, for good general biosorbents, a high $Q_{\max}$ and steep initial isotherm slope (i.e. high b) are desirable [11]. The relationship between the dye uptake capacity (Q) of an algae and the residual dye concentration (C_f) at equilibrium can also be described using the Freundlich equation. From Table 2, it was obvious that maximum K_F and n values were obtained at a pH of 1 and temperature of 40 °C. High K_F and n values indicate that the binding capacity has reached its highest value; the affinity between the biomass and dye molecules was also higher. The experimental n values were greater than unity in all cases, indicating favorable biosorption, with repulsive forces between the sorbed molecules [25].

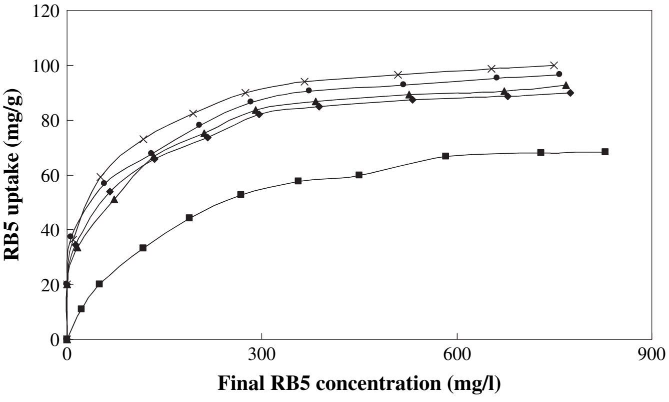

Fig. 4. RB5 biosorption isotherms for *Laminaria* biomass under different conditions (agitation rate = 160 rpm). pH and temperature: (◆) 1 and 25 °C; (■) 2 and 25 °C; (▲) 1 and 30 °C; (●) 1 and 35 °C; (×) 1 and 40 °C.

The Redlich–Peterson model incorporates the features of both the Langmuir and Freundlich isotherms into a single equation, as shown in Eq. (4). There are two limiting behaviors: the Langmuir form for $\beta_{RP} = 1$ and the Henry's law form for $\beta_{RP} = 0$. The isotherm constants (K_{RP} and a_{RP}) and model exponent (β_{RP}) increase with decreasing pH and increasing temperature (Table 2). High Redlich–Peterson constant values were observed under optimum conditions (pH 1 and temperature 40 °C). In general, based on the correlation coefficients and % error values, the Freundlich model described the biosorption isotherm data well compared to other model equations examined.

3.4. Thermodynamic parameters of biosorption

The biosorption isotherm data obtained at different temperatures were used to calculate potentially important thermodynamic properties, such as changes in the standard Gibbs free energy (G°), standard enthalpy (H°) and standard entropy (S°). The Langmuir constant, b (l/mg), was used to calculate the change in the standard Gibbs free energy (G°) according to the following equation:

$$\Delta G^\circ = -\mathrm{R}T \ln b \tag{10}$$

where R is the gas constant (8.314 J/mol K) and T the absolute temperature (K). The changes in the standard enthalpy and entropy were obtained from the plot of ln b vs. $1/T$; the equations are as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{11}$$

From Eqs. (10) and (11), we get,

$$\ln b = -\frac{\Delta H^\circ}{\mathrm{R}T} + \frac{\Delta S^\circ}{\mathrm{R}} \tag{12}$$

ΔG° values of −25.1, −25.7, −26.3 and −27.0 kJ/mol were obtained at 25, 30, 35 and 40 °C, respectively. The negative free energy change value indicates the feasibility of the RB5 biosorption process and confirms the affinity of the biosorbent towards the sorbate. The ΔH° and ΔS° values obtained from the plot of ln b vs. $1/T$ ($R^2 = 0.997$) were 12.3 kJ/mol and 0.125 kJ/mol K, respectively. The positive enthalpy value indicates that the RB5 biosorption process is endothermic, as the process usually favored by an increase in temperature as this will activate the sorption sites. The positive entropy value indicates the increasing randomness at the solid/liquid interface during the biosorption process [26].

Table 2
Langmuir, Freundlich and Redlich–Peterson model parameters under different pH and temperature conditions

pH	T (°C)	Langmuir model				Freundlich model				Redlich–Peterson model				
		Q_{max} (mg/g)	b (l/mg)	R^2	ε (%)	K_F(l/g)$^{1/n}$	n	R^2	ε (%)	K_{RP} (l/g)	a_{RP} (l/mg)$^{\beta RP}$	β_{RP}	R^2	ε (%)
1.0	25	92.3	0.026	0.939	11.6	24.7	5.0	0.983	1.6	7.9	0.24	0.84	0.955	9.7
2.0	25	73.2	0.009	0.971	6.5	23.3	5.1	0.981	1.7	7.1	0.21	0.63	0.975	6.4
1.0	30	93.1	0.027	0.939	9.3	25.9	5.1	0.973	0.7	9.1	0.25	0.85	0.941	4.0
1.0	35	97.8	0.029	0.908	13.6	27.6	5.2	0.990	1.5	10.8	0.28	0.86	0.953	10.7
1.0	40	101.5	0.033	0.944	12.1	28.3	5.3	0.988	0.8	11.4	0.29	0.86	0.965	9.7

R^2 = correlation coefficient; ε = error.

3.5. Batch desorption

Desorption of the RB5 from the dye-loaded *Laminaria* biomass was attempted using several chemical agents, including HCl, NaOH, Na_2CO_3, EDTA (disodium salt) and methanol. The performances of these elutants in the desorption of RB5 are illustrated in Fig. 5. The 0.1 M HCl solution, as expected, did not performed well in the biosorption of RB5, as an acidic pH is favored for the biosorption of RB5; therefore, reverse equilibrium (desorption) would not be expected under acidic conditions. Furthermore, the performance of 0.01 M EDTA solution was mediocre, with an elution efficiency for RB5 of only 22%. It was also found that washing the dye-laden biomass with 2% methanol did not result in considerable release of RB5 molecules. However, the alkaline elutants, 0.01 M NaOH and Na_2CO_3 solutions, performed very well in the desorption of RB5, and also exhibited very high elution efficiencies. Under strong basic conditions, the number of negatively charged sites increases. These negatively charged sites on the sorbent surface favor desorption of the dye anions as a result of electrostatic repulsion [27]. Due to its high elution performance, 0.01 M NaOH solution was selected as the elutant for further studies.

3.6. Column studies

The results from the batch experiments allowed the fundamental information with regard to the biosorbent behavior and dye biosorption performance to be studied. However, these results do not afford accurate scale-up data for industrial treatment systems where a continuous flow system is normally employed [28]. Hence, experiments, using an up-flow packed column, were carried out to study the performance of *Laminaria* biomass in the biosorption of RB5.

The breakthrough curve for the biosorption of RB5 onto *Laminaria* biomass followed the typical S-shaped curve that is favorable for a column operation (Fig. 6). The column breakthrough (when the dye concentration reached 1 mg/l) appeared at 18.3 h; thereafter, the *Laminaria* bed became progressively saturated with RB5, with column exhaustion (when the dye concentration reached 49.2 mg/l) observed at 73 h. The batch biosorption kinetics for RB5 was observed to be rapid, indicating minimal mass transfer resistance, which was also reflected by the very good biosorption performance that was observed during the column operation. The uptake and removal efficiency of RB5 in the column were 41.9 mg/g and 72.7%, respectively. The total volume of RB5 solution treated during the column operation was 4.38 l.

The elution curve for RB5 through the *Laminaria* column is presented in Fig. 6. The 0.01 M NaOH solution performed well in the elution of RB5 from the biomass, with an elution efficiency of 97.7%. From the elution curve, the RB5 concentration of the effluent was observed to increase sharply during the initial stage, reaching a maximum (696 mg RB5/l) at around 4 h. A gradual decrease in the RB5 concentration was then observed, with the elution process completed at 11 h. During the elution

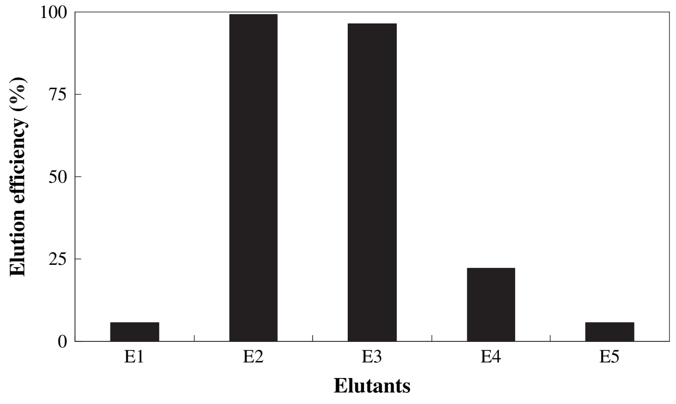

Fig. 5. Desorption of RB5 from dye-loaded *Laminaria* biomass using different elutants (RB5 loading on *Laminaria* biomass = 53.8 mg/g; volume of elutant = 20 ml). Elutants: (E1) 0.1 M HCl; (E2) 0.01 M NaOH; (E3) 0.01 M Na_2CO_3; (E4) 0.01 M EDTA; (E5) 2% CH_3OH.

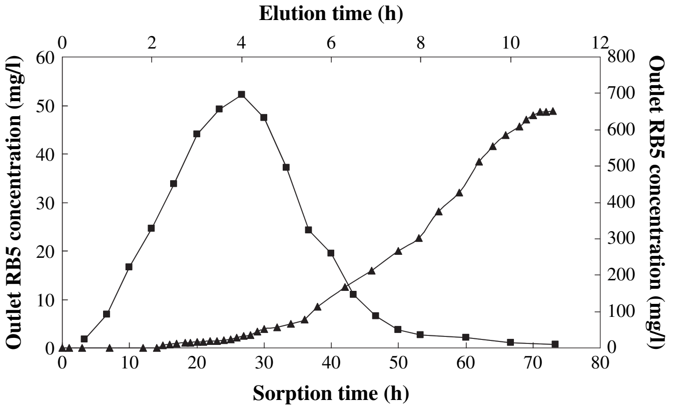

Fig. 6. RB5 sorption and elution breakthrough curves (initial RB5 concentration = 50 mg/l; bed height = 10 cm; flow rate = 1 ml/min; RB5 influent pH 1; elutant = 0.01 M NaOH). Breakthrough curves: (▲) sorption; (■) elution.

process, *Laminaria* biomass showed the tendency to swell because of the alkaline environment. However, the biomass leaching is minimal because of the low concentration of alkaline solution and less contact time. Therefore, no interference in RB5 analysis and no significant rise in column pressure were observed. The concentration factor [5], defined as the ratio of the total volume of dye solution treated to the total volume of desorbent used, was found to be 6.6. A high concentration factor value is always preferable as the eventual recovery of dye will; thus, become more feasible [17,29].

4. Conclusion

Biosorption by seaweed has been demonstrated to be a practical alternative to conventional systems for the removal of Reactive Black 5 in solution. Species of *Laminaria* were abundant in many parts of world oceans and can serve as a cheap source for the production of biosorbent. To our knowledge, a brown algae has been firstly employed in this study for reactive dye biosorption. Also, this study provides evidence of the participation of amine groups in the uptake of RB5 by *Laminaria* biomass. The batch experiments showed the importance of solution pH and temperature in the biosorption of RB5. With respect to eluents, 0.01 M NaOH solution was found to offer the possibility of recovering RB5 from dye-loaded biomass. The breakthrough curve, obtained at a pH of 1, temperature of 25 °C and an initial RB5 concentration of 50 mg/l, followed the typical S-shaped curve, with breakthrough and exhaustion appeared at 18.3 and 73 h, respectively. The column was successfully eluted with 0.01 M NaOH, which opens up the possibility of column regeneration. Considering the data and analysis presented in this paper, it is suggested that *Laminaria* sp. would be well suited for the detoxification of reactive dye-bearing industrial effluents.

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