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Montra Chairat

Walailak University, cmontra@yahoo.com

John B. Bremner

University of Wollongong, jbremner@uow.edu.au

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Abstract

The hypothesis that the dried, ground biomass of the red marine alga *Gracilaria tenuistipitata* could be used for the efficient removal of lac dye from aqueous solution was assessed in this work. The effects of parameters such as initial pH, biosorbent dosage, contact time, initial dye concentration, and temperature on the biosorption capacity of the dye were investigated. Equilibrium data were analysed using Langmuir, Freundlich, and Temkin isotherm models, and the Freundlich model provided the highest coefficient of determination values. Biosorption kinetic data were successfully described with a pseudo-second-order model at initial dye concentrations of 50, 80, 100, and 120 mg l⁻¹. The thermodynamic parameters of biosorption - enthalpy change ($\Delta H^\circ = -30.64 \text{ kJ mol}^{-1}$), free energy change ($\Delta G^\circ = 4.32 \text{ kJ mol}^{-1}$ at 303 K to 7.78 kJ mol⁻¹ at 333 K), and entropy change ($\Delta S^\circ = -115.38 \text{ J mol}^{-1} \text{ K}^{-1}$) - were determined. The negative value of the enthalpy change and positive values of the free energy change indicate that the biosorption process is exothermic and non-spontaneous. The negative value of the entropy change is consistent with decreased randomness at the solid-liquid interface with dye biosorption. Attenuated total reflectance-Fourier transform infrared spectroscopic analysis confirmed the presence of lac dye on the *G. tenuistipitata* material. The efficiency of lac dye removal by this biomass material at 20 g l⁻¹ and with an initial dye concentration of 50 mg l⁻¹ in acidic solution was 71%, which indicated its potential usefulness as a new dye biosorbent.

Keywords

gracilaria, parameters, dye, thermodynamic, red, tenuistipitata:, kinetics, isotherms, marine, lac, alga, biosorption

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Biosorption of lac dye by the red marine alga *Gracilaria tenuistipitata*:

Biosorption kinetics, isotherms and thermodynamic parameters

Montra Chairat^{1,*} and John B. Bremner²

¹*Division of Chemistry, School of Science, Walailak University, Nakhon Si Thammarat*

80160, Thailand

²*School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia*

*Corresponding author: cmontra@yahoo.com

Running title: Removal of lac dye by *Gracilaria tenuistipitata*

Abstract

The hypothesis that the dried, ground biomass of the red marine alga *Gracilaria tenuistipitata* could be used for the efficient removal of lac dye from aqueous solution was assessed in this work. The effects of parameters such as initial pH, biosorbent dosage, contact time, initial dye concentration, and temperature on the biosorption capacity of the dye were investigated. Equilibrium data were analysed using Langmuir, Freundlich, and Temkin isotherm models and the Freundlich model provided the highest coefficient of determination values. Biosorption kinetic data were successfully described with a pseudo-second-order model at initial dye concentrations of 50, 80, 100, and 120 mg l⁻¹. The thermodynamic parameters of – enthalpy change ($\Delta H^\circ = -30.64$ kJ mol⁻¹), free energy change ($\Delta G^\circ = 4.32$ kJ mol⁻¹ at 303 K to 7.78 kJ mol⁻¹ at 333 K) and entropy change ($\Delta S^\circ = -115.38$ J mol⁻¹ K⁻¹) – were determined. The negative value of the enthalpy change and positive values of the

free energy change indicate that the biosorption process is exothermic and non-spontaneous. The negative value of the entropy change is consistent with decreased randomness at the solid-liquid interface with dye biosorption. Attenuated total reflectance-Fourier transform infrared spectroscopic analysis confirmed the presence of lac dye on the *G. tenuistipitata* material. The efficiency of lac dye removal by this biomass material at 20 g l⁻¹ and with an initial dye concentration of 50 mg l⁻¹ in acidic solution was 71%, which indicated its potential usefulness as a new dye biosorbent.

Keywords: *Gracilaria tenuistipitata*; Lac dye; Laccase; Biosorption; Dye removal

Introduction

Dyes have been used in many industries, such as those involving textiles, paper and pulp, paint, solvents, cosmetics, plastics, pharmaceuticals and food. The effluent of these industries often contain toxic compounds, including discharged dyes, which increase the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of aquatic ecosystems [1]. In order to partly alleviate these effects, many studies have been undertaken to remove dyes from wastewaters by adsorption methods, including, among others, activated carbon [2], peat [3], chitin [4], and silica [5], or through other means such as ozonation, photo-oxidation, electrocoagulation, froth flotation, reverse osmosis, ion exchange, membrane filtration, and flocculation [6-8]. However, these processes have some disadvantages, including the use of expensive materials, complicated procedures, and the formation of byproducts or high energy demands [9,10].

One alternative approach is to use other biosorbents for metal or dye removal from industrial effluents. Such adsorbents can usually be inexpensively sourced and often have high biosorption efficiencies with fewer chemical or other sludge problems [11]. In this

context, dried biomass from marine algae has shown good promise as a biosorbent to remove metals [12] or dyes from wastewater. For example the disazo dye CI Acid Black 1 was removed by the brown marine algae *Sargassum glaucescens* and *Stoechospermum marginatum* [13] and by the brown macroalga *Nizamuddina zanardinii* [14]. In addition, removal of malachite green from aqueous solution by the marine alga *Caulerpa racemosa* var. *cylindracea* [15] has been demonstrated, while synthetic acid orange II dye can be effectively adsorbed from aqueous solution by untreated and chemically modified dried biomass from *S. marginatum* [16].

Lac dye, the soluble part of stick lac, is a natural red dyestuff that is widely used for dyeing cotton and silk in Thailand [17]. The dye is composed mainly of two major anthraquinone-based components: laccaic acids A and B [18]; three minor components, laccaic acids C, D, and E, have also been characterized [18-20] (Figure 1). In previous work, it has been shown that chitosan is a useful mordant to improve lac dyeing of silk and cotton [21-24] and the thermodynamics of adsorption of laccaic acid onto chitosan under acidic conditions over various concentrations has been determined, together with some ecological toxicity studies [25]. It was found that chitosan has potential to interact with laccaic acid via electrostatic forces, hydrogen bonding, and ion-dipole interactions under acidic condition, and thus could be a useful adsorbent for lac dye effluent. Although chitosan is a low-cost adsorbent, it is necessary to prepare it from chitin in the shells of crabs or shrimps by alkaline hydrolysis of the acetamide groups. This process then has the potential for environmental pollution, as well as producing chitosan with inconsistent molecular weight and degree of residual acetylation characteristics.

We thus turned our attention to other potential marine-derived biosorbents, in particular the alga *Gracilaria tenuistipitata* [26]. *G. tenuistipitata* was chosen for use as a biosorbent of this dye because it is abundant and easily collected in the Phuket area in

Thailand. In addition, the algal cell wall material has amino and hydroxyl groups [12] similar to those in the chitosan structure. Therefore, laccic acids could interact with the cell wall material of algae in an analogous way to the non-covalent interactions with chitosan. Other *Gracilaria* species have shown potential for the biosorption of dyes from aqueous solution, including the acid dye Benewol Red by *G. fisheri* [27], CI Acid Black 1 by *G. persica* biomass [28], and the removal of reactive acid dye, methylene blue, and crystal violet by *G. corticata* [29-31]. In the case of *G. corticata* biomass, it was shown that the biosorption mechanism of crystal violet from aqueous solution occurred by electrostatic interactions between the negatively charged seaweed surface and positively charged crystal violet cations [31]. As far as can be ascertained, *G. tenuistipitata* has not been investigated previously for dye biosorption capability. This alga, which is a major source of agar, also has the potential to be used as a sustainably harvested dye biosorbent with later use as a fertiliser or soil conditioner, possibly after suitable composting. The focus of our present work has been on the first phase of this study to determine bioadsorbancy characteristics with respect to lac dye as a model for a natural dye. The effect of initial pH, biomass dosage, temperature, and contact time as well as initial dye concentration on the kinetics and thermodynamics of biosorption were investigated. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopic analysis of the dye biosorption was also undertaken to confirm the functional groups in the dried biomass that affect laccic acid uptake and to inform possible ways to improve biosorption. The results are discussed in this paper.

Experimental

Materials and chemicals

The marine alga *Gracilaria tenuistipitata* (Gracilariales) was acquired from coastal waters in the intertidal zone at Ao Tang Khen (latitude: 7°48'920"N, longitude: 98°24'133"E),

Phuket, Thailand in February, 2015. From morphology observations, it was classified as *Gracilaria tenuistipitata* (herbarium specimen number PMBC27937, Phuket Marine Biological Center (PMBC), Dr. Jutarat Wiriyadamrikul). The alga was washed extensively with tap water to remove dust and other particles. The clean biomass was sun dried for 24 h, and then in the oven at 70 °C for 24 h. The dried biomass (6.00 % w/w moisture content according to ASTM D4442-15 [32]) was crushed and sieved (laboratory test sieve, ASTM E11-16 [33]; Endecotts Ltd., UK; aperture 500 µm) to select biomass particulates with an average size of 0-500 µm, and then stored in airtight polyethylene bottles at room temperature. The prepared biomass was used in all biosorption experiments in this study without any further chemical or physical treatments.

Lac dye [124-04012] was purchased from the Wako Company (Japan). The laccaic acid components were isolated and then analysed using high-performance liquid chromatography and electrospray tandem mass spectrometry by Oka *et al.* [18]. It was found that the two major components are laccaic acids A and B respectively. Analytical-grade $C_8H_5KO_4$, HCl, Na_2CO_3 , and NaOH were purchased from the Merck Co., Ltd (Germany). A stock solution (1000 mg l^{-1}) of lac dye was prepared in 1.00×10^{-3} M Na_2CO_3 solution (Merck).

Instruments

A Unicam 310 UV-vis spectrophotometer (Unicam Instruments, UK) was employed for absorbance measurements using quartz cells of 1 cm path length.

A thermostatted shaker bath (SWB 5050 shaking water bath; National Labnet Company, USA) was used to study the biosorption of lac dye onto the biomass from *G. tenuistipitata*.

A pH meter (Orion 420A; Thermo Scientific, USA) was used to measure the pH values of the solutions. A centrifuge (HERMLE Z 200 A, Germany) was used to separate fine solids from the residual dye solutions.

An FT-IR spectrometer (Bruker/Tensor 27, USA) equipped with a ZnSe crystal was used for the ATR-FTIR measurements.

Biosorption experiments

Biosorption study

Biosorption experiments were conducted in a batch mode of operation to investigate the effects of various parameters, including initial pH (2.00 – 5.67), biosorbent dosage (2 – 20 g l⁻¹ of dye solution), initial dye concentration (31 – 152 mg l⁻¹), temperature (30, 40, 50, and 60 °C), and contact time (5 – 180 min) on the biosorption of lac dye. The pH was adjusted using one of two buffer systems: potassium hydrogen phthalate/hydrochloric acid and potassium hydrogen phthalate/sodium hydroxide. Experiments were performed in 125 ml screw-capped conical flasks with 50 ml of dye solutions containing the biosorbent. The flasks were agitated on a thermostatted shaker bath operated at 150 strokes min⁻¹ and a fixed temperature for 120 min; contact time experiments revealed that at this time, the system had reached equilibrium conditions. After 120 min of contact time, solutions were filtered, centrifuged at 3000 rpm (1408.68 G-force) for 30 min, and then the residual dye in the supernatant solution was determined quantitatively by UV-Vis spectrophotometry at $\lambda_{\max}$ 490 nm using a dye standard calibration curve ($y = 0.0146x$, $R^2 = 0.9994$). Then, the percentage dye removal efficiency by algal biomass was determined using the following equation:

$$\text{Dye removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of lac dye solution (mg l^{-1}) at time $t = 0$ and at equilibrium time t , respectively.

Biosorption kinetic study

A stock solution of lac dye (1000 mg l^{-1}) was made up in $1.00 \times 10^{-3} \text{ M Na}_2\text{CO}_3$ solution. The different concentrations of dye solution were prepared by diluting from the stock solution (1000 mg l^{-1}) in a buffer system of potassium hydrogen phthalate/hydrochloric acid solution at $\text{pH } 2.20 \pm 0.10$. The required dye solution (50 ml) in each screw-capped conical flask (125 ml) was shaken in a thermostatted shaker bath operated at 150 strokes min^{-1} . After 30 min, the biosorbent (0.20 g), which had been prewarmed in the thermostatted bath for 30 min, was immersed in the dye solution. After different immersion times, the dye solutions were decanted, and then centrifuged at 3000 rpm for 30 min. Dye concentrations in the supernatant were determined at time zero and at subsequent times using a calibration curve based on absorbance at λ_{max} 490 nm vs dye concentrations in standard lac dye solutions. The amount of dye adsorbed per gram of biosorbent (q_t , mg g^{-1}) at any time was calculated using the mass balance equation:

$$q_t = (C_i - C_t) \frac{V}{W} \quad (2)$$

where C_i and C_t are the initial dye concentration and the dye concentration (mg l^{-1}) after dyeing time t respectively. V is the volume of the dye solution (l) and W is the mass of biosorbent (g) used.

Biosorption isotherm study

Lac dye solutions at different concentrations were freshly prepared by diluting from the stock solution (1000 mg l^{-1}) in a buffer system of potassium hydrogen phthalate/hydrochloric acid solution at $\text{pH } 2.20 \pm 0.10$. The experiments were carried out by shaking biosorbent (0.20 g) with different concentrations of dye solution (50 ml) in a conical flask with screw cap at 30, 40, 50, and 60 °C in a thermostatted shaker bath operated at 150 strokes min^{-1} for 2 h. After the equilibrium time, the dye solutions were decanted and then centrifuged at 3000 rpm for 30 min. Dye concentrations were determined at time zero and at the equilibrium time using a dye calibration curve based on absorbance at λ_{max} 490 nm vs dye concentrations in standard lac dye solutions. The amount of dye adsorbed per gram of biosorbent at the equilibrium time (q_e , mg g^{-1}) was calculated using the mass balance:

$$q_e = (C_i - C_e) \frac{V}{W} \quad (3)$$

where q_e (mg g^{-1}) is the biosorption capacity of biosorbent at equilibrium, V is the volume of the dye solution (l), and W is the mass of biosorbent (g) used.

ATR-FTIR analysis

An FT-IR spectrometer was used for the ATR-FTIR measurements for qualitative assessment of any changes in the main characteristic group absorption bands of the lac dye, dried algal biomass, and algal biomass after dye biosorption. The ATR-FTIR spectra were recorded using a single reflection horizontal ATR accessory with a ZnSe crystal. The ATR-FTIR spectra were acquired at a spectrum resolution of 4 cm^{-1} , with 16 scans, over the range of $4000\text{-}600 \text{ cm}^{-1}$. A background scan of the clean ZnSe single crystal was also recorded.

Results and discussion

The influence of initial pH

Other studies have shown that the initial pH of dye solutions is one of the important environmental factors influencing the biosorption process because it affects the adsorbate solubility and the degree of ionisation of relevant functional groups in the adsorbent [34]. The effect of different initial pH values on the removal of lac dye at constant initial dye concentration, temperature, and biomass dosage is shown in Figure 2. It was found that the highest percentage lac dye biosorption (41%) was observed at an acidic pH of 2.00 – 2.20. The variation in the uptake capacity of the *G. tenuistipitata* biomass across the pH range may be explained in terms of its effective isoelectric points. Isoelectric points around pH 3.0-4.0 have been reported for most algal species [34]. At a pH lower than the isoelectric point, cell wall functional groups are protonated. The neutralization of laccaic acid A, in water containing 4% of dimethyl sulfoxide by volume, by 0.1 M sodium hydroxide gave pK_{a2} and pK_{a3} values of about 4.4 and 6.5 [35]. Therefore, laccaic acids A and B, the major laccaic acid components, would be expected to interact with the biomass surface via electrostatic bonds, hydrogen bonding, and ion-dipole interactions under acidic conditions. A similar result was observed with Acid Orange 7 (AO7) dye removal by biomass derived from a freshwater algal *Spirogyra* sp. [36]. Therefore, the initial pH of the dye solution for the subsequent biosorption experiments on the biosorption isotherms was fixed at 2.20 ± 0.10 . The biosorption capacity of biosorbent at equilibrium (q_e) at pH 2.20 ± 0.10 was found to be 5.20 mg g^{-1} .

The influence of contact time

The influence of contact time on the biosorption process were studied in the time range 5–180 min at initial dye concentrations of 50, 80, 100, and 120 mg l⁻¹, pH 2.20 ± 0.10, and a temperature of 30.0 ± 0.5 °C with a fixed biosorbent dose (4.00 g l⁻¹). As shown in Figure 3, the biosorption rapidly increased during the first 40 min of contact time; thereafter, the biosorption decreased gradually and equilibrium was attained in about 120 min. The higher uptake of dye during the initial stage of biosorption might be due to the availability of a larger number of vacant surface sites, with the remaining vacant surface sites being more difficult to occupy owing to the repulsive forces between dye adsorbed on the algal biomass and in the solution phase [16]. Similar results have also been reported in the literature, where the rate of dye removal was rapid initially and then gradually slowed until equilibrium was achieved [16,36]. The optimum contact time for the biosorption of lac dye onto *G. tenuistipitata* biomass was fixed at 120 min.

The influence of initial dye concentration

The influence of initial dye concentration in the range 31 – 152 mg l⁻¹ on the algal biosorption capacity was studied with a 4.00 g l⁻¹ biosorbent dose, at pH 2.20 ± 0.10, and a temperature of 30.0 ± 0.5 °C. As shown in Figure 4, the biosorption capacity of the biosorbent at equilibrium was increased from 3.11 to 17.43 mg g⁻¹ by increasing the initial dye concentration from 31 to 152 mg l⁻¹, consistent with the increased concentration gradient or driving force in the higher initial dye concentration. However, a saturation phenomenon should be expected at concentrations higher than those tested in this work, which usually leads to constancy or even a decrease in biosorption capacity and, at the same time, a decrease in biosorption efficiency [37]. An increase in biosorption capacity for Acid Black 1 (AB1) from 7.23 to 23.37 mg g⁻¹ onto the brown macroalga, *N. zanarinii* was seen by increasing the initial dye concentration from 10 to 50 mg l⁻¹ [14].

The influence of biosorbent dosage

The influence of varying biosorbent dosage ($2 - 20 \text{ g l}^{-1}$) on the biosorption process was studied with 50 ml of dye solution under the optimal pH and contact time conditions. As can be seen from Figure 5, while the dye removal efficiency increased along with the increase in biosorbent dosage, the biosorption capacity of biosorbent at equilibrium (q_e) decreased as its dosage increased. The change in q_e observed may be due to complex interactions of several factors such as availability of solute, electrostatic interactions and interference between binding sites. The last is an important factor because, at high biosorbent dosages, the available dye molecules are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting in low dye uptake. A similar observation was previously reported for the biosorption of acid dye by marine brown macroalgae [13], and in the removal of basic yellow dye from aqueous solutions by the green alga *C. scalpelliformis* [38].

The influence of temperature

The effect of temperature on the *G. tenuistipitata* biosorption capacity was investigated at 30, 40, 50, and 60 °C and the results are shown in Figure 6. Biosorption capacity of biosorbent at equilibrium (q_e) at different initial dye concentrations decreased with increasing temperature from 30 to 60 °C. The equilibrium uptake of the lac dye decreased with increasing temperature, suggesting that biosorption between *G. tenuistipitata* biomass and the dye molecules was an exothermic process and the mechanism was mainly physical biosorption, dominant at lower temperature. Similar results were found in the removal of basic yellow dye from aqueous solution by biosorption on the green alga *C. scalpelliformis* [38].

Kinetics of biosorption process

The kinetic data were analysed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. The linear form of the pseudo-first-order rate equation [39] can be expressed as:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where k_1 (min^{-1}) is the rate constant of pseudo-first-order biosorption, and q_e and q_t are the amount of dye adsorbed per gram of biosorbent (mg g^{-1}) at equilibrium and time t respectively. A plot of $\log (q_e - q_t)$ vs t then provides access to the first-order rate constant (k_1) and the calculated dye uptake values ($q_{e,\text{cal}}$) from the slope and intercept of this line.

Biosorption kinetics was studied at initial dye concentrations of 50, 80, 100, and 120 mg l^{-1} as used previously (Figure 3) and the data were examined in terms of the three kinetic models noted above. The model constants and the coefficient of determination values (R^2) obtained for these models are shown in Table 1. The best-fit model was based on these coefficient values. In the case of pseudo-first-order kinetic model, the values of R^2 were found to be low compared with those for the pseudo-second-order kinetic model. Furthermore, there were significant differences between the calculated ($q_{e,\text{cal}}$) and experimental dye uptake values ($q_{e,\text{exp}}$) with the first-order model, suggesting that the biosorption kinetics of lac dye onto *G. tenuistipitata* biomass did not follow pseudo-first-order kinetics.

The experimental data were further examined by the pseudo-second-order kinetic model, which is given by the following equation [40]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \quad (5)$$

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the rate constant of pseudo-second-order kinetics. The slope and intercept of (t/q_t) vs t were used to calculate the experimental dye uptake values ($q_{e,\text{exp}}$) and the pseudo-second-order rate constant (k_2).

The experimental data (Table 1 and Figure 7) fitted well to the pseudo-second-order kinetic model with the highest coefficient of determination values ($R^2 = 1.00$) (Table 1). It was found that the calculated dye uptake values ($q_{e,\text{cal}}$) were close to the experimental dye uptake values ($q_{e,\text{exp}}$) in the case of this kinetic model. This is consistent with the initial rapid phase involving physical biosorption at the cell surface and then the subsequent slower phase including other mechanisms such as complexation, microprecipitation or biosorption, or saturation of binding sites. Biosorption should be the rate-controlling step [41].

The intraparticle diffusion model was also tested in order to verify the influence of mass transfer resistance on the binding of lac dye onto *G. tenuistipitata* biosorbent. The intraparticle diffusion model is expressed:

$$q_t = k_{\text{id}} t^{0.5} + C \quad (6)$$

where k_{id} ($\text{mg g}^{-1} \text{ min}^{-0.5}$) and C represent the intraparticle diffusion rate constant and intercept respectively. The intraparticle diffusion rate constant (k_{id}) can be obtained from the slope of the plot of q_t vs the square root of the contact time ($t^{0.5}$).

According to the intraparticle diffusion model, the plot of q_t vs the square root of contact time should be a straight line passing through the origin if the biosorption process follows this model. Therefore, biosorption kinetic data were processed to determine whether intraparticle diffusion was the rate-determining step. It has been reported previously that the plot of q_t vs $t^{0.5}$ may have multilinearity features, indicative of two or more steps being involved in the biosorption process [42]. Different phases were observed in this plot from our data (Figure 8), representing different stages in biosorption. An initial phase followed by a linear portion and then a plateau. The initial phase might be due to surface biosorption and rapid external diffusion (boundary layer diffusion). The second linear portion was the gradual biosorption stage where the intraparticle diffusion was rate controlled. The plateau (third portion) was the final equilibrium stage, where the intraparticle diffusion declines owing to the very low solute concentration in solution. The slope of the second portion of the plot has been defined as the intraparticle diffusion rate constant (k_{id}), and the values obtained are shown in Table 1. The linear plot of the intraparticle diffusion model does not pass through the origin as shown in Figure 8. The deviation from the origin may be due to differences in the rate of mass transfer in the initial and final stages of biosorption. This is indicative of some degree of boundary layer control and thus intraparticle diffusion was not the rate-determining step in the biosorption of lac dye onto *G. tenuistipitata* biomass at all initial dye concentrations.

Biosorption isotherm studies

The isotherm equations used in this study for analyzing biosorption equilibrium data were the Langmuir and Freundlich isotherms. The obtained coefficient of determination (R^2) values from these models (Table 2) were used as the criteria for comparing the applicability of the isotherms.

The most widely used Langmuir equation, which is valid for monolayer biosorption onto a surface with a finite number of identical sites [43], is expressed as:

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (7)$$

where Q (mg g^{-1}) is the maximum biosorption capacity of biosorbent to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e (mg l^{-1}), q_e (mg g^{-1}) is the amount of dye adsorbed per gram of biosorbent at equilibrium, and b (l mg^{-1}) is the Langmuir constant related to the energy of biosorption. The value of Q represents a practical limiting biosorption capacity when the surface is fully covered with dye molecules.

The linear form of the Langmuir isotherm equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{Qb} + \left(\frac{1}{Q}\right)C_e \quad (8)$$

The values of Q and b are calculated from the slopes and intercepts of the straight lines of plot of (C_e/q_e) vs C_e (figure not shown). Table 2 lists the calculated values of the parameters Q and b . The fact that the experimental Langmuir biosorption parameters have negative slopes suggests that the biosorption behavior data are not consistent with the assumption of the Langmuir approach.

The Freundlich isotherm is an empirical equation based on biosorption on a heterogeneous surface and is given by the equation [36]:

$$q_e = K_F C_e^{1/n} \quad (9)$$

where K_F (mg g^{-1}) is generally indicative of the biosorption capacity and $1/n$ is the biosorption intensity. The following linear form of the Freundlich expression yields the constants K_F and $1/n$:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (10)$$

Therefore, K_F and $1/n$ can be determined from the linear plot of $\log q_e$ vs $\log C_e$ (Figure 9). The magnitude of the exponent $1/n$ gives an indication of the favourability of biosorption. Values of $n > 1$ obtained represent favourable biosorption conditions. However, the values of n were lower than 1 at 323 and 333 K (Table 2) indicating less favourable biosorption.

Based on the correlation coefficient shown in Table 2, the biosorption of lac dye onto *G. tenuistipitata* biomass can be described well by the Freundlich equation. Also, the Freundlich equation gave a better fit of the experimental data than the Langmuir equation (Figure 9). The value of K_F has been used as a relative measure of biosorption capacity, and it was found that K_F increased with decreasing temperature in line with an exothermic biosorption process of the lac dye.

Another model that considers the effects of indirect adsorbate-adsorbate interactions on the biosorption isotherm has been proposed by Temkin and Pyzhev [44]. They noted that the heat of biosorption of all the molecules on the adsorbent surface layer would decrease linearly with coverage because of adsorbate-adsorbate interactions. The Temkin isotherm can be expressed in its linear form as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (11)$$

where $B_1 = RT/b$, K_T is the equilibrium binding constant (l mg^{-1}) corresponding to the maximum binding energy, and B_1 is related to the heat of biosorption. The values of the parameters are listed in Table 2. However, the correlation coefficients (R^2) are significantly lower than those for the Freundlich isotherm. The Freundlich isotherm fits the experimental data for biosorption of lac dye by *G. tenuistipitata* biomass significantly better than the other isotherms.

Biosorption thermodynamic parameters

In order to obtain further quantitative information on the biosorption process, values for the free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were determined from the experiments carried out at different temperatures using the following two equations [45]:

$$\log(q_e / C_e) = \Delta S^\circ / (2.303 R) - \Delta H^\circ / (2.303 RT) \quad (12)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (13)$$

The values of ΔH° and ΔS° were assessed from the slopes and the intercepts of the linear plot of $\log(q_e/C_e)$ vs $1/T$ ($R^2 = 0.9900$). These values were then used together with Eqn (13) to calculate ΔG° . These thermodynamic parameters for the dye biosorption process in this study are listed in Table 3. The negative enthalpy change (ΔH°) observed suggests that the interaction of lac dye adsorbed by *G. tenuistipitata* biomass is an exothermic process, which

is supported by the increasing biosorption of dye with the decrease in temperature. The negative value of ΔS° reflects the decreased randomness at the solid/solution interface during the biosorption of dye on the algal material, consistent with progressive opening of the algal structure, which would enhance dye mobility and extent of penetration. The positive values of ΔG° pointed to a non-spontaneous biosorption process at 30, 40, 50, and 60 °C respectively. The decrease in ΔG° with decreasing temperatures indicated that a better biosorption is actually obtained at lower temperature.

ATR-FTIR spectroscopic analysis

Separate confirmation of lac dye biosorption directly on the *G. tenuistipitata* material was obtained through ATR-FTIR spectroscopic analysis. The ATR-FTIR spectra of lac dye and *G. tenuistipitata* dried biomass (algae) before and after dye biosorption are shown in Figure 10. The spectrum of algae (a) showed broad absorptions at around 3000-3700 cm^{-1} , consistent with O–H and N–H stretching vibrations, while the absorption band at 2924 cm^{-1} was assigned to symmetric C–H stretching vibrations of aliphatic groups in the cell wall material. The absorption bands at 1641 cm^{-1} and 1030 cm^{-1} may be assigned to stretching vibrations for C=O of the carboxyl group and S=O of the sulfate group in the algal biomass. *Gracilaria* species are known to produce agar with relatively high sulfate content [26,46,47]. After dye biosorption onto the algae (b), the typical O–H in plane and C=C aromatic ring stretching peak at 1283 cm^{-1} of lac dye [48] were observed. In addition, the characteristic C=C aromatic ring stretching peak at 1372 cm^{-1} of lac dye was also apparent, thus confirming the presence of adsorbed lac dye on the biomass material.

Conclusions

In this study it has been demonstrated that dried, ground biomass of the important red marine alga *Gracilaria tenuistipitata* can act as an efficient biosorbent for lac dye in aqueous solution. The biosorption capacity for lac dye was influenced by the pH of the dye solution, contact time, initial dye concentration, and temperature. The kinetics of lac dye biosorption by *G. tenuistipitata* biomass can be described by the pseudo-second-order model. In addition, the biosorption equilibrium was apparently much better fitted by the Freundlich isotherm model rather than by the two other isotherm models tested (the Langmuir and Temkin models). Thermodynamic parameters indicated an exothermic and non-spontaneous biosorption of the lac dye in the temperature range 303–333 K. Separate confirmation of dye biosorption by the algal material was obtained through ATR-FTIR spectroscopic analysis. Further studies are now being considered to improve biosorption efficiency further, to assess the biosorption characteristics with respect to other natural dyes, and also the possibility of recycling the dye-containing biomass material through composting processes to produce a potential soil conditioner or fertiliser.

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Figure 1. Chemical structures of laccase acids

Figure 2. Influence of initial pH of lac dye solution on dye removal efficiency of *Gracilaria tenuistipitata* biomass (biosorbent dosage 4.00 g l^{-1} , initial dye concentration 50 mg l^{-1} , contact time 120 min, temperature $30.0 \pm 0.5 \text{ }^{\circ}\text{C}$)

Figure 3. Influence of contact time on dye removal (q_t , amount of dye adsorbed per gram of biosorbent after time t) of *Gracilaria tenuistipitata* biomass (biosorbent dosage 4.00 g l^{-1} , pH 2.20 ± 0.10 , temperature $30.0 \pm 0.5 \text{ }^{\circ}\text{C}$)

Figure 4. Influence of initial dye concentration on dye biosorption at equilibrium (q_e) of *Gracilaria tenuistipitata* biomass (biosorbent dosage 4.00 g l^{-1} , contact time 120 min, pH 2.20 ± 0.10 , temperature $30.0 \pm 0.5 \text{ }^{\circ}\text{C}$)

Figure 5. Influence of biosorbent dosage on q_e and dye removal efficiency by *Gracilaria tenuistipitata* biomass (initial dye concentration 50 mg l^{-1} , contact time 120 min, pH 2.20 ± 0.10 , temperature $30.0 \pm 0.5 \text{ }^{\circ}\text{C}$)

Figure 6. Influence of temperature on q_e with *Gracilaria tenuistipitata* biomass (contact time 120 min, pH 2.20 ± 0.10 , biosorbent dosage 4.00 g l^{-1}) with different initial dye concentrations ($31\text{-}152 \text{ mg l}^{-1}$)

Figure 7. Pseudo-second-order biosorption of lac dye by *Gracilaria tenuistipitata* biomass (pH 2.20 ± 0.10 , temperature $30.0 \pm 0.5 \text{ }^{\circ}\text{C}$, biosorbent dosage 4.00 g l^{-1})

Figure 8. Plot of q_t vs $t^{0.5}$ in the intraparticle diffusion kinetic model for biosorption of lac dye by *Gracilaria tenuistipitata* biomass (pH 2.20 ± 0.10 , temperature $30.0 \pm 0.5 \text{ }^{\circ}\text{C}$, biosorbent dosage 4.00 g l^{-1})

Figure 9. Plot of $\log q_e$ against $\log C_e$ in the Freundlich isotherm for the biosorption of lac dye by *Gracilaria tenuistipitata* biomass (pH 2.20 ± 0.10 , contact time 120 min, biosorbent dosage 4.00 g l^{-1})

Figure 10. ATR-FTIR spectra of (a) algae before biosorption, (b) algae after dye biosorption, and (c) lac dye

Laccaic acid A $\text{CH}_2\text{CH}_2\text{NHCOCH}_3$

Laccaic acid B $\text{CH}_2\text{CH}_2\text{OH}$

Laccaic acid C $\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$

Laccaic acid E $\text{CH}_2\text{CH}_2\text{NH}_2$

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

Table 1 Comparison of the pseudo-first-order, pseudo-second-order, and intraparticle rate constants and the calculated ($q_{e,cal}$) and experimental dye uptake ($q_{e,exp}$) values for the different initial dye concentrations. Temperature 30.0 ± 0.5 °C, pH 2.20 ± 0.10 , biosorbent dosage 4.00 g l^{-1}

Kinetic models	Initial dye concentration (mg l^{-1})			
	50	80	100	120
$q_{e,exp}$ (mg g^{-1})	5.31	8.60	10.00	11.78
Pseudo-first-order kinetic model				
$k_1 \times 10^{-2}$ (min^{-1})	3.11	3.89	4.88	1.75
$q_{e,cal}$ (mg g^{-1})	1.95	3.93	6.58	14.99
R^2	0.96	0.98	0.91	0.91
Pseudo-second-order kinetic model				
$k_2 \times 10^{-2}$ ($\text{g mg}^{-1} \text{ min}^{-1}$)	3.05	2.14	1.62	1.30
$q_{e,cal}$ (mg g^{-1})	5.52	8.90	10.42	12.38
R^2	1.00	1.00	1.00	1.00
Intraparticle diffusion kinetic model				
$k_{id} \times 10^{-1}$ ($\text{mg g}^{-1} \text{ min}^{-0.5}$)	0.76	2.61	1.55	2.59
C (mg g^{-1})	4.41	6.16	8.29	9.27
R^2	0.70	0.96	0.90	0.88

Table 2 Thermodynamic isotherm parameters of lac dye by *Gracilaria tenuistipitata* biomass at different temperatures

Isotherm model	Parameters	303 K	313 K	323 K	333 K
Langmuir	Q (mg g ⁻¹)	144.9	238	-83.3	-16.72
	b (l mg ⁻¹)	1.23×10^{-3}	5.19×10^{-4}	-9.99×10^{-4}	-2.55×10^{-3}
	R^2	0.5922	0.2971	0.5415	0.6768
Freundlich	K_F (mg g ⁻¹)	1.93×10^{-1}	1.25×10^{-1}	6.93×10^{-2}	1.95×10^{-2}
	n	1.04	1.01	0.94	0.79
	R^2	0.9944	0.9964	0.9983	0.9979
Temkin	B_1	7.99	6.92	5.99	5.16
	K_T (l mg ⁻¹)	8.64×10^{-2}	7.31×10^{-2}	6.41×10^{-2}	5.16×10^{-2}
	R^2	0.9230	0.9094	0.8614	0.8216

Table 3 Thermodynamic parameters for biosorption of lac dye by *Gracilaria tenuistipitata* biomass

Concentration of dye	ΔH°	ΔS°	ΔG°			
(mg g ⁻¹)	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	(kJ mol ⁻¹)			
			303 K	313 K	323 K	333 K
51	-30.64	-115.38	4.32	5.47	6.63	7.78