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Isotherm, kinetics and mechanistic studies of methylene blue biosorption onto red seaweed *Gracilaria corticata*

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ABSTRACT

The present research was undertaken in order to examine the feasibility of a novel biosorbent *Gracilaria corticata* (red seaweed) for the removal of methylene blue (MB) from aqueous solutions. Biosorption studies were conducted as a function of equilibrium pH, initial dye concentration, and biosorbent dosage. It was identified that the biosorption capacity of *G. corticata* strongly depends on solution equilibrium pH and highest biosorption capacity of 28.9 mg/g was observed at pH 8. The Fourier transform infrared analysis confirmed interaction of dye molecules with binding sites on the surface of *G. corticata*. Also, the scanning electron microscopy images revealed morphological cell surface changes after biosorption of MB onto *G. corticata*. The removal efficiency of MB from solution with an initial concentration of 150 mg/L varied from 50.8 to 94.9% for an increase of the seaweed dose from 2 to 5 g/L. Kinetic study was performed using pseudo-first- and pseudo-second-order models, but higher degree of correlation coefficient and low % error values were obtained for the pseudo-second-order kinetic model. Experimental isotherms were favorable and the data were analyzed using the Langmuir, Freundlich, Redlich–Peterson, and Toth models, with the latter successfully described MB isotherm with high correlation coefficient and low % error values. The biosorption capacity of *G. corticata* toward MB was determined as 95.41 mg/g, according to the Langmuir model.

Keywords: Biosorption; Isotherm; Methylene blue; Seaweed; Water treatment

1. Introduction

Population explosion and industrial advancements have resulted in a sharp deterioration of several ecosystems, posing serious threats to human health and environment. Several civic bodies have promulgated regulations monitoring the emission of contaminants from industrial waste streams. Correspondingly, research is focusing toward the wide range of technologies for wastewater treatments. Among different pollutants range, synthetic dyes pose serious environmental concern, as the effluents from the dyeing and finishing processes in the textile industry are known to contain color, high amounts of surfactants, dissolved solids, and possibly heavy metals such as Cr, Ni, and Cu [1]. Dyes are generally believed to be toxic and carcinogenic, or derived from other known carcinogens [2]. Hence, removal of dyes is of utmost importance prior to discharge of wastewaters into the

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environment. Various physical, chemical, and biological methods have been used for the treatment of dye-containing wastewater. Biological processes such as biosorption [3], bioaccumulation [4], and biodegradation [5,6] have been proposed as potential techniques for the removal of dyes from textile effluents. Considering that most synthetic dyes resist degradation, removal using dead biomasses (biosorption) is gaining momentum in recent years.

Seaweed biomass is a renewable natural resource and it is considered to be a cost-effective and efficient biosorbent due to its physicochemical characteristics [7]. Currently, seaweed biomass is cultivated and harvested to manufacture hydrocolloids (agar, alginate, and carrageenan) for use in the food and chemical industries. Several research reports [7,8] highlighted the potential of seaweeds to sorb heavy metal ions. 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 [8]. Marine algae, apart from in very few cases [9,10], have not been utilized for the removal of dyes.

Thus, the present study was undertaken to examine the biosorption potential of *Gracilaria corticata* toward the removal of methylene blue (MB) from aqueous solution. *G. corticata* is a predominant red marine algal species found in the coastal regions of Indian subcontinent, belonging to the family *Gracilariacea* [11]. It finds application in agar production as well as in animal feed. Few studies pointed out that *Gracilaria* species possess good metal binding capacity [12,13]. However, to date, no study has been conducted to explore the biosorption capacity of *G. corticata* toward dye molecules. The biosorption property of *G. corticata* as a function of pH, initial dye concentrations, and biosorbent dosage was investigated. Different equilibrium and kinetic models were used to describe MB-seaweed experimental data.

2. Materials and methods

2.1. Preparation of biosorbent and chemicals

The red seaweed, *G. corticata*, was collected from the beaches of Mandapam region, Tamilnadu, India. After collection, the seaweed sample was extensively washed with deionized water to remove wastes and salt debris attached to it. The wet biomass was sun-dried initially, followed by drying in hot air oven at 70°C for 5 h. The dried biomass was then grounded in a blender to obtain particles with average size of 0.75 mm for sorption experiments.

All chemicals used in this study were of analytical grade and purchased from Ranbaxy Fine Chemicals Ltd. India; whereas MB was purchased from Sigma-Aldrich Corporation, Bangalore, India.

2.2. Biosorption experimental procedure

The pH of the MB solution was initially adjusted and maintained throughout experiments using 0.1 M HCl or 0.1 M NaOH. In all the experiments, 0.5 g of *G. corticata* biomass was contacted with 100 mL of dye solution in 250 mL Erlenmeyer flasks. The contents were then agitated in an incubated rotary shaker at 150 rpm for 2 h at 30°C. Once equilibrium was reached, the mixture was centrifuged (REMI R-8C, India) at 3,500 rpm for 5 min and the supernatant liquid was analyzed in a spectrophotometer (UV-1800, Shimadzu, Japan) at 665 nm. Calibration was performed using 1, 5, and 10 mg/L of MB solutions and the samples were diluted appropriately in the above ranges before analysis. The amount of dye biosorbed was calculated from the difference between the dye quantity initially added to the seaweed biomass and the dye content of the supernatant using the following equation:

$$Q_e = V \times (C_0 - C_f)/M \quad (1)$$

where Q_e is the equilibrium dye uptake (mg/g); C_0 and C_f are the initial and final dye concentrations in the solution (mg/L), respectively; V is the volume of dye solution (L); and M is the mass of biosorbent (g). For pH edge experiments, initial MB concentration was fixed at 150 mg/L and pH was varied from 4 to 9. In the case of isotherm experiments, initial MB concentrations were varied from 50 to 300 mg/L.

To evaluate the possibility of desorption, 0.5 g of air-dried MB-loaded *G. corticata* was exposed to 50 mL of desorbent solution in 250 mL flasks. The reaction mixture was kept in a rotary shaker at 150 rpm for 60 min. After centrifugation, the concentration of MB in the supernatant was examined using a spectrophotometer.

2.3. FTIR and SEM analysis

Fourier transform infrared analysis of seaweed samples before and adsorption was performed in Bruker RFS 27. Scanning electron microscopy images of samples were captured using Hitachi S4800 EDX.

2.4. Isotherm and kinetic modeling

Four equilibrium isotherm models were used to describe the MB biosorption data as follows:

$$\text{Langmuir model}: \ Q_e = \frac{Q_{max} b C_f}{1 + b C_f} \tag{2}$$

$$\text{Freundlich model}: \ Q_e = K_F C_f^{1/n_F} \tag{3}$$

$$\text{Redlich-Peterson model}: \ Q_e = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{\beta_{RP}}} \tag{4}$$

$$\text{Toth model}: \ Q_e = \frac{Q_{max} b_T C_f}{[1 + (b_T C_f)^{1/n_T}]^{n_T}} \tag{5}$$

where Q_{max} is the maximum MB uptake (mg/g), b is the Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant (mg/g) $(L/mg)^{1/n_F}$, n_F is the Freundlich exponent, K_{RP} is the Redlich–Peterson isotherm constant (L/g), a_{RP} is the Redlich–Peterson isotherm constant $(L/mg)^{\beta_{RP}}$, β_{RP} is the Redlich–Peterson model exponent, b_T is the Toth model constant (L/mg), and n_T is the Toth model exponent.

Different rate equations have been used to correlate the experimental kinetics data of the biosorption processes as follows:

$$\text{Pseudo first order model}: \ Q_t = Q_e(1 - \exp(-k_1 t)) \tag{6}$$

$$\text{Pseudo second order model}: \ Q_t = \frac{Q_e^2 k_2 t}{1 + Q_e k_2 t} \tag{7}$$

where Q_e and Q_t represent the amount of MB molecules biosorbed at equilibrium and at any time (t), respectively (mg/g), k_1 is the first-order equilibrium rate constant (min^{-1}), and k_2 is the second-order equilibrium rate constant (g/mg min).

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

$$\%\ \text{Error} = \frac{\sum_{i=1}^{N} \left(Q_{exp,i} - Q_{cal,i}/Q_{exp,i}\right)}{N} \times 100 \tag{8}$$

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

3. Results and discussion

3.1. Effect of equilibrium pH

The interaction between dye molecule and biosorbent is basically a combined result of charges on dye molecules and the surface of the biosorbent [14]. The solution pH is an important environmental parameter influencing the sorption behavior of solute onto the surface of biosorbent. The impact of pH on both the active biosorbent surface binding sites and the dye solution chemistry is of great significance [3]. In the present study, the effect of equilibrium pH on biosorption of MB by *G. corticata* was studied over a pH range of 4–9 (Fig. 1). Results indicated that the solution pH strongly influenced the biosorption of MB by *G. corticata*. The amount of dye removed at equilibrium increased with increasing pH, significantly up to pH 8. The pH of the aqueous solution affects both the surface charge of the biosorbent material as well as the degree of ionization of the dye molecule. At acidic pH values, due to the presence of excess H^+ ions in solution, surface of *G. corticata* will be protonated by H^+ ions and thus, the overall charge of the biomass will be positive. On the other hand, basic dyes release colored positively charged dye ions in solution which will exhibit electrostatic attraction toward the negatively charged cell surface [15,16]. Considering that the overall charge of the biomass at strong acidic conditions is positive, the electrostatic attraction of cationic dyes is less and hence relatively lower uptake was observed (Fig. 1). As the pH increases, the concentration of H^+ ions decreases and

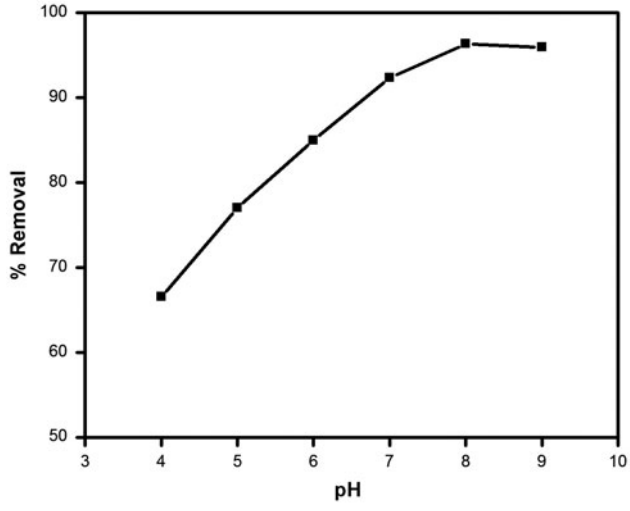

Fig. 1. Effect of pH on the biosorption of MB (temperature = 30°C; initial MB concentration = 150 mg/L).

thus more MB molecules occupy the binding sites of *G. corticata* through electrostatic attraction. The reason for decreasing dye uptake with further increase in pH after 8 was unclear, but it might be the alteration of activity of binding sites in the *G. corticata* biosorbent [3].

3.2. FTIR and SEM analysis

The FTIR analysis of raw and MB-biosorbed *G. corticata* were carried out to understand the role of binding sites during biosorption of MB onto *G. corticata*. Fig. 2(a) illustrates that raw *G. corticata* displayed a number of absorption peaks, indicating the complex nature of the red seaweed. Some of the important peaks observed in raw *G. corticata* sample appeared at 3,269 cm^{-1} (–OH, –NH stretching), 2,923 cm^{-1} (asymmetric CH_2 stretch), 2,355 cm^{-1} (–P–H– group), 1,633 cm^{-1} (asymmetric C=O stretch of COOH), 1,412 cm^{-1} (symmetric C=O), 1,235 cm^{-1} (C–O (COOH) stretch), and 1,020 cm^{-1} (C–O (alcohol) band) [17,18]. Significant changes in functionality of red seaweed were visible after exposure to MB molecules (Fig. 2(b)). In MB-loaded *G. corticata*, peaks were shifted to 3,277 (–OH, –NH stretching), 2,925 (asymmetric CH_2 stretch), 2,357 (–P–H– group), 1,637 (asymmetric C=O stretch of COOH), 1,405 (symmetric C=O), and 1,030 cm^{-1} (C–O (alcohol) band). This result is possibly due to interaction of dye molecules with binding sites on the surface of *G. corticata*, which in turn caused the observed wavenumber changes.

The morphological structure of *G. corticata* and MB-sorbed *G. corticata* was studied using scanning electron microscopy (Fig. 3(a) and (b)). Surface protuberance and microstructures can be observed, which may be due to Ca and other salt crystalloid deposition [19]. After MB biosorption, the surface of *G. corticata* appears flattened in comparison to the raw seaweed sample.

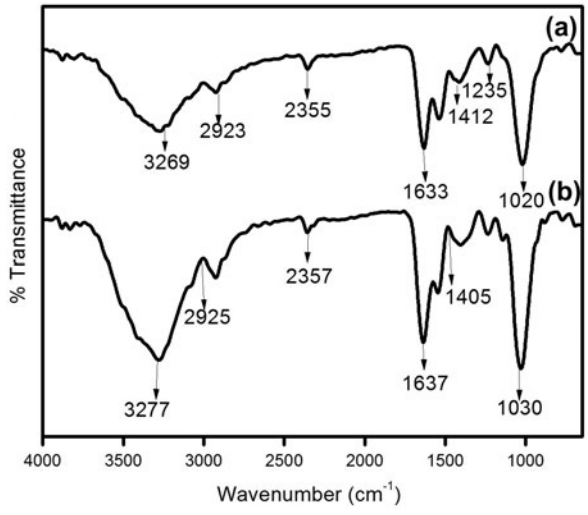

Fig. 2. Fourier transform infrared adsorption spectra of the *G. corticata* (a) and MB-loaded *G. corticata* (b).

3.3. Sorption kinetics of MB biosorption

The biosorption of MB molecules onto *G. corticata* was strongly influenced by initial MB concentration. Fig. 4 shows the effect of MB concentration during the uptake of MB onto *G. corticata*. In general, biosorption of MB increased with the increment of the initial MB concentration from 100 to 300 mg/L and attained maximum biosorption at 300 mg/L. This result confirms the fact that higher initial dye concentration provides an important driving force to overcome mass transfer resistances between the biosorbent and the biosorption medium. Similar observation was also reported in other investigations [15,20]. For any sorption process, an analysis of the kinetic data is important because kinetics describe the uptake rate of adsorbate, which in turn controls the resident time in sorbent–solute interface [21]. From Fig. 4, it was obvious that the biosorption of MB increased with the increase in contact time. Precisely, removal of MB by *G. corticata* was rapid for the first 60 min followed by slow attainment of equilibrium in 240 min. This may be due to the availability of number of vacant biosorption sites at the initial stage. After the surface binding sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the biosorbent particles. Around 90% of MB was sorbed within 60, 90, and 240 min for 100, 200, and 300 mg/L, respectively. The very fast kinetics observed with *G. corticata* represents a significant benefit during continuous dye effluent treatment systems.

In order to investigate the mechanism associated with dye biosorption onto red algal biomass, the pseudo-first-order and pseudo-second-order kinetics models were examined to describe the experimental kinetics data. The parameters of the pseudo-first-order and pseudo-second-order kinetics models along with corresponding R^2 and % error values are summarized in Table 1. From the results, it was clear that both models were able to describe MB kinetics at different MB concentrations examined. However, based on error analysis, the application of pseudo-second-order model to MB kinetics data resulted in high R^2 and lowest % error values. The pseudo-second-order kinetic model is based on the assumption that the rate-controlling step in the biosorption process is the chemical interactions

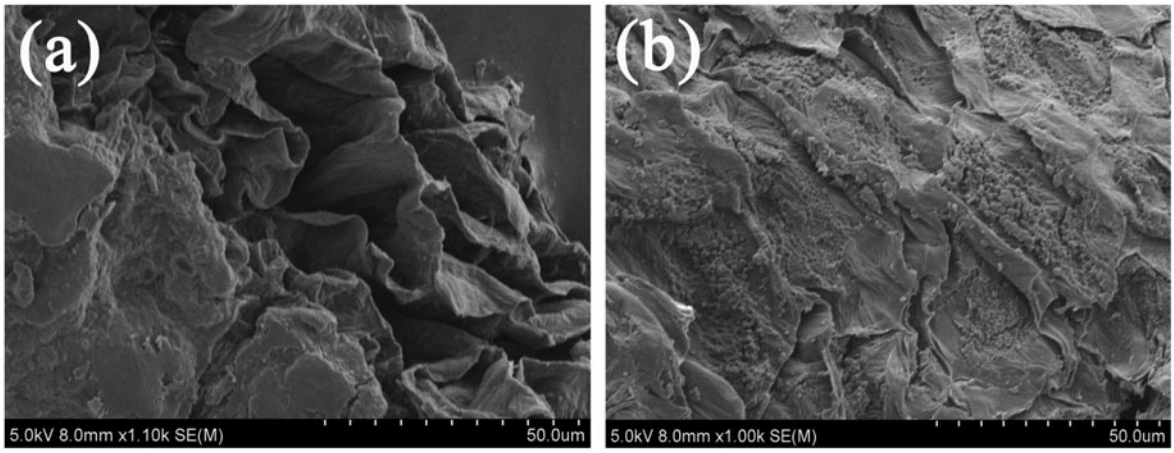

Fig. 3. Scanning electron microscopy pictures of the *G. corticata* (a) and MB-loaded *G. corticata* (b).

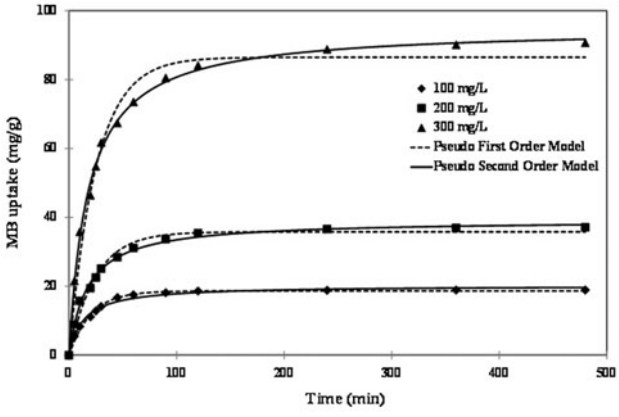

Fig. 4. Kinetics of MB biosorption onto *G. corticata* (temperature = 30˚C).

between superficial functional groups of biosorbent and dye molecules. Several investigators reported that pseudo-second-order model better described sorbate–solute kinetics effectively [22,23]. On the other hand, the pseudo-first-order equation was found to not fit well over the entire contact time range, but was generally applicable over the initial periods of the sorption process [3]. For both models, the calculated rate constants decreased with increased concentration (Table 1). Fig. 4 presents kinetics curves as predicted by the pseudo-first- and pseudo-second-order models.

3.4. Effect of seaweed dosage on MB biosorption

The effect of seaweed dosage on removal of MB was examined by varying adsorbent dosage from 2 to 8 g/L (Fig. 5). From the analysis of experimental data, it was observed that the MB removal efficiency increased with increase in seaweed dosage. The percentage biosorption increased from 50.8% at lower biosorbent dosage (2 g/L) to 95.0% at higher biosorbent dosage (5 g/L). Further increase in seaweed dosage had no influence on percent removal. On the other hand, the MB uptake capacity of the *G. corticata* was found to have reduced from 38.1 mg/g at low

Table 1
Kinetic model constants for the biosorption of MB by *G. corticata*

Model		100 mg/L	200 mg/L	300 mg/L
Pseudo-first-order	Q_e (mg/g)	18.62	35.79	86.49
	k_1 (min^{-1})	0.0498	0.0409	0.0401
	R^2	0.989	0.982	0.980
	Error (%)	2.16	3.10	3.14
Pseudo-second-order	Q_e (mg/g)	20.21	39.22	95.15
	k_2 (g/(mg min))	0.0037	0.0015	0.0006
	R^2	0.991	0.995	0.997
	Error (%)	0.720	0.202	0.407

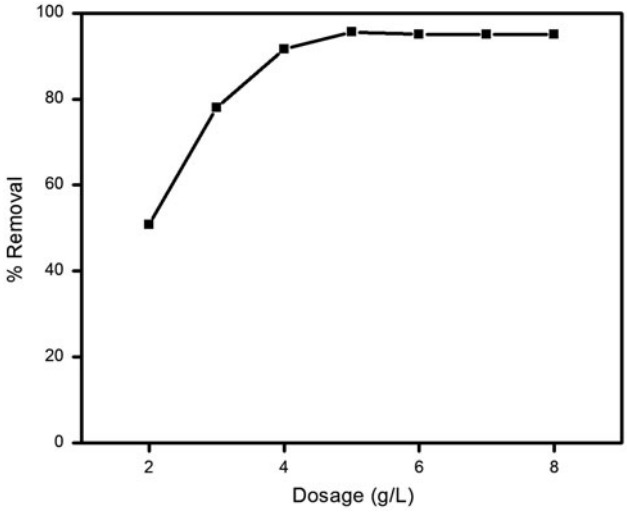

Fig. 5. Effect of dosage on the biosorption of MB (temperature = 30°C; initial MB concentration = 150 mg/L).

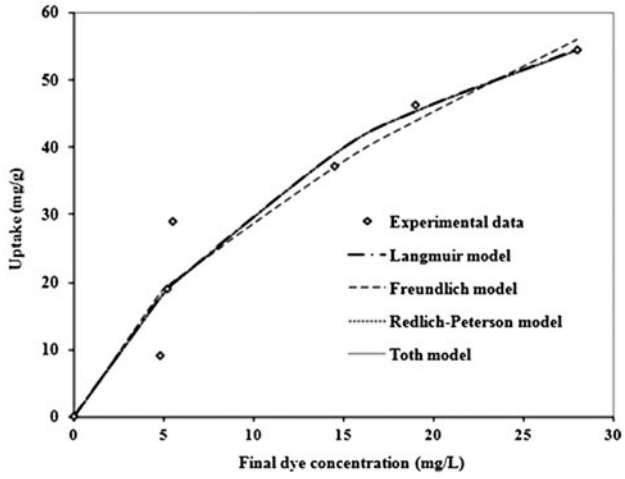

Fig. 6. Isotherms of MB biosorption onto *G. corticata* (temperature = 30°C).

biosorbent dosage (2 g/L) to 17.8 mg/g at high biosorbent dosage (8 g/L). An increase in sorbent concentration generally increases the bounded dye molecules because of an increase in surface area of the sorbent, which in turn increases the binding sites. This finding was in accordance with other research reports [24,25]. On the contrary, the dye uptake decreases by increasing the seaweed dosage and this may be due to complex interactions of several factors. The important factor is that at high sorbent dosages the available dye molecules are insufficient to cover all the exchangeable sites on the seaweed biomass, usually resulting in low dye uptake [26]. Thus, for the present study, 5 g/L was selected as optimum seaweed dosage.

3.5. MB biosorption isotherms

Biosorption isotherm is important to evaluate sorbent as it represents the relationship between dye concentration in solution and amount of dye sorbed per unit seaweed biomass at a constant temperature. Experimental MB isotherm obtained for *G. corticata* at pH 8 is presented in Fig. 6. In general, the MB uptake increases with an increase in MB concentration, which results in a L-shaped curve without a strict plateau. To evaluate isotherm data, various equilibrium models were employed in the present study, which includes the Langmuir, Freundlich, Redlich–Peterson, and Toth models. Table 2 shows the model constants along with R^2 and % error values. The Langmuir isotherm is one of the commonly used models to describe the sorption of dye molecules onto biosorbents. The model also serves to calculate the maximum uptake values, which could not be determined experimentally [3]. For the present data, the Langmuir model predicted maximum MB uptake of 95.4 mg/g. The MB biosorption capacity observed in this study was superior to the results published in the literature. *Thuja orientalis* biosorbed 91.0 mg MB/g [27], *Ulva lactuca* biosorbed 40.2 mg MB/g [28], *Posidonia oceanica* (L.) fibers biosorbed 5.56 mg MB/g [29], and *Caulerpa racemosa* var. cylindracea biosorbed 5.23 mg MB/g [30] compared to 95.41 mg MB/g by *G. corticata* in this study. Furthermore, the essential characteristics of the Langmuir model can be described in terms of dimensionless equilibrium parameter, "R_L", expressed as in the following equation [31],

$$R_L = \frac{1}{1 + bC_0} \tag{9}$$

where b is the Langmuir affinity constant (L/mg) and C_0 is the initial MB concentration. The condition based on R_L values are suggested as $0 < R_L < 1$ for favorable, $R_L > 1$ for unfavorable, $R_L = 1$ for linear, and $R_L = 0$ for irreversible to biosorption, respectively. For the present MB data, R_L was found to be 0.0019 and it reflects favorable condition for adsorption.

The Freundlich model is applied for adsorption onto heterogeneous surfaces with the interaction between adsorbed dye molecules. An important characteristic of the Freundlich isotherm is its potential to present an appropriate description of equilibrium data over a restricted range of concentration. Application of the Freundlich model to the experimental MB

Table 2
Isotherm model constants for the biosorption of MB by *G. corticata*

Langmuir	Q_{max} (mg/g)	b (L/mg)		R^2	Error (%)
	95.41	0.0474		0.9627	9.52
Freundlich	K_F (L/g)	n_F		R^2	Error (%)
	6.91	1.59		0.9589	10.76
Redlich–Peterson	K_{RP} (L/g)	a_{RP} (L/mg)	β_{RP}	R^2	Error (%)
	4.48	0.044	0.98	0.9628	9.47
Toth	Q_{max} (mg/g)	b_T (L/mg)	n_T	R^2	Error (%)
	90.99	0.0486	0.95	0.9629	9.43

data resulted in reasonable description (Table 2). In order to improve fitness, several three-parameter models were used. The Redlich–Person model incorporates both the Langmuir and Freundlich equations. At low concentrations, the Redlich–Peterson isotherm approaches to Henry's law and at high concentration, its behavior approaches that of the Freundlich Isotherm. Results indicated that the value of β_{RP} was less than unity (Table 2), which indicates that MB was favorably biosorbed. The Toth model derived from potential theory has proven useful in describing sorption in heterogeneous systems. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e. most sites have sorption energy less than the mean value [32]. Application of the Toth model resulted in highest R^2 and lowest % error values (Table 2).

3.6. Desorption

Attempts were also made to desorb MB from MB-loaded *G. corticata*. From Fig. 1, it was clear that acidic conditions were not favorable for MB biosorption onto *G. corticata*. Thus, it would be logical that the sorbed dye molecules can be recovered only under acidic conditions. Hence, 0.01 M HCl was employed as a desorption agent and the performance of which was very satisfactory with elution efficiency of 98.7%. Under strong acidic (low pH) conditions, the number of positively charged sites increases. These positively charged sites on the sorbent surface favor desorption of the dye cations due to electrostatic repulsion [33]. In addition, 0.01 M HCl was also least damaging to *G. corticata* with only 4.8% sorbent weight loss was observed during the sorption–desorption cycle.

4. Conclusions

The results of the present investigation demonstrate that red seaweed, *G. corticata* exhibited high biosorption capacity toward MB. The following conclusions can be made.

(1) Biosorption of MB onto *G. corticata* strongly depends on equilibrium pH, initial MB concentration, and seaweed dosage.
(2) Of different pH conditions examined, *G. corticata* performed well at pH 8 with highest experimental uptake of 28.9 mg/g.
(3) The FTIR analysis and SEM images before and after biosorption of MB molecules onto *G. corticata* confirmed the involvement of several functional groups during dye biosorption.
(4) At 5 g/L of seaweed dosage, *G. corticata* exhibited highest MB uptake and maximum removal efficiency.
(5) The MB-biosorption kinetics data were best described by the pseudo-second-order model, and equilibrium was achieved within 240 min.
(6) The Toth model is in good agreement with all the experimental isotherm data as compared to the Langmuir, Freundlich, and Redlich–Peterson models. The seaweed biomass exhibited MB uptake of 95.41 mg/g, based on the Langmuir model.
(7) According to these results, *G. corticata* can be used as an effective and alternative biomass for the removal of MB from wastewaters.

List of symbols

a_{RP} — Redlich–Peterson isotherm constant $(L/mg)^{\beta}{}_{RP}$
b — Langmuir equilibrium constant (L/mg)
b_T — Toth model constant (L/mg)
C_0 — initial dye concentrations (mg/L)
C_f — final dye concentrations (mg/L)
k_1 — first-order equilibrium rate constant (min^{-1})
k_2 — second-order equilibrium rate constant (g/mg min)
K_F — Freundlich constant $(mg/g\ (L/mg)^{1/n}{}_F)$

K_{RP} — Redlich–Peterson isotherm constant (L/g)
M — mass of biosorbents (g)
N — number of measurements
n_F — Freundlich exponent
n_T — Toth model exponent
Q_e — dye uptake at equilibrium (mg/g)
Q_{cal} — calculated dye uptake (mg/g)
Q_t — amount of dye biosorbed at anytime t (mg/g)
Q_{exp} — experimental dye uptake (mg/g)
Q_{max} — maximum dye uptake (mg/g)
R_L — dimensionless equilibrium parameter
V — volume of dye solution (L)
β_{RP} — Redlich–Peterson model exponent

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