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Biosorption potential of *Gracillaria corticata* in the sequestration of malachite green from aqueous solutions

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Gracillaria corticata, a red alga, has been tested for its ability to remove malachite green (MG) from aqueous phase. The surface morphology of *G. corticata* is studied using Scanning Electron Microscopy (SEM). The analytical evidence from FTIR spectra confirms the involvement of amine group in the biosorption of malachite green. The effects of biosorbent concentration, initial *p*H, temperature, adsorption time and initial dye concentration are studied for the biosorption of MG using *G. corticata*. At various initial MG concentrations (20 - 100 mg/L), batch sorption equilibrium have been attained within 1 h. However the equilibrium is slow as the time progresses. Kinetics of MG biosorption has been analyzed using pseudo second order model. The experimental data is also analyzed using Langmuir, Freundlich and Temkin isotherm models. Out of which, Langmuir model describes the isotherm data with high coefficient of determination ($R^2 = 0.996$). So, based on Langmuir model the maximum dye uptake of 76.92 mg/g is reported at *p*H 10.0 and temperature 303K. Different thermodynamic parameters such as ΔH°, ΔG°, ΔS° are evaluated and it is found that the present system is spontaneous, endothermic and increased randomness in nature. Thus, the investigation has proved *Gracillaria* biomass to be an effective low cost, eco-friendly biosorbent for the treatment of dye-bearing wastewater.

Keywords: Biosorption, Algae, Dye, Malachite Green, Biomass, Wastewater, Modeling

Dyes are synthetic organic compounds applied to various substrates to color their products. The molecular structure reveals that dyes are embodies with various functional groups hence, it make them more stable and it is quite tedious for degradations[1,2]. Dyes have an unlimited application apart from the textile industries such as paper, food, cosmetics, agricultural, leather tanning etc. Textile industries are known to cause severe water pollution due to the release of large quantities of untreated dye into natural water bodies. In spite, the color is one of the factors even its presence at mild level makes the water undesirable. Thus, these dye and dye stuffs released into the environment perhaps causes various health related disease[3]. Hence, the dyeing industries are problematic issue in the current scenario.

Therefore, various studies were undertaken by researchers for the decolorization of dye using a range of physical and chemical methods. These include coagulation, flocculation[4], ozonation and oxidation[5], membrane separation technique[6], reverse osmosis and adsorption by activated carbon[7]. Amongst all treatment methods adsorption has been found out to be a simple and cost effective method with high efficiency for the removal of dye bearing wastewater. Also, it is highly applicable method for the large scale treatment of dye in high concentration. Activated carbon is reported to be an eminent sorbent for the adsorption operation of dye removal. But due to its high cost the usage has been limited[8,9].

Thus, it is taken as a challenge by researchers for finding a suitable alternate sorbent which have the property more or less similar to activated carbon. It was concluded that biomaterials would definitely serve as alternate sorbent to commercially availiable activated carbon[10,11]. Several biomaterials have used for the bisorption studies such as wheat straw[12], durain peel[13], rice husk[14-16], orange peels[17], wheat straw[18]. In the present investigation the marine red algae collected from the coastal area of Tamil Nadu is used as biosorbent for the removal of basic cationic dye malachite green and its biosorption capacity is evaluated.

Malachite green is a common dye used in the textile and paper industries. Despite the fact that, malachite green is suspected to be mutagen and teratogen[19] because of its potent antifungal activity is used in the aquaculture to prevent the fungal infection in fishes

and other aquatic organism[19]. Malachite green and its major metabolite leucomalachite green (LMG) perhap gets accumulated in the organs of fish and other marine organisms[20]. Thus, it should be monitored and certainly controlled particularly in the nations like India. In the present study, malachite green is chosen as the model dye in order to evaluate the biosorption capacity of marine red algae *Gracillaria corticata* for the removal the malachite green dye from the simulated aqueous dye solution.

Experimental Section

Preparation of algal biosorbent

The raw marine red algae *Gracillaria corticata* was collected from Mandapam (Tamil Nadu, India). The biomass was washed thoroughly with excess quantities of distilled water subsequently dried at 60°C for 24 h in hot air oven. The biomass was chopped into pieces using the domestic grinder. The particles were sieved to get a size ranging from 0.5-1.0 mm. The biomass prepared was stored in an air tight bottle later used for the sorption experiment without any further modification.

Preparation of dye solution

Malachite green (MG) is selected as the model dye for the present investigation. The stock solution is prepared by an appropriate quantity of dye in 1000 mL of distilled water. The further working solutions are prepared by diluting the stock solution. Malachite green is a basic dye commonly used for various purposes. The maximum absorbance of malachite green is 617 nm.

Characterization of biosorbent

Scanning Electron Micrograph (SEM) (JSM – 6390LV, Jeol, USA) shows the changes in the surface texture before and after biosorption of dye. The Fourier Transform Infrared (FTIR) (Nicolet Avatar 370, Thermo Scientific, India) clearly indicates the relevance of functional groups towards the sorption of dye. Hence, our biomass *Gracillaria corticata* is subjected to the FTIR analysis with spectra ranging from 4000 to 400 $cm^{-1.}$

Batch biosorption experiment

Biosorption of malachite green using *Gracillaria corticata* was examined by conducting a batch experiment in an Erlenmeyer flask of 250 mL with 100 mL of dye solution by agitating in a thermostated shaking incubator (OSI-24C; Labline, India). The various operation parameters of MG biosorption onto *Gracillaria* biomass was tested by varying *p*H from 3-10, algal biomass dosage (0.1, 0.2, 0.4, 0.6, 0.8, 1.0 g), contact time (15, 30, 45, 60, 120 and 180 min) and temperature (303, 313, 323 and 333 K). The supernatant was removed and subsequently used for the analysis of residual dye content using double beam UV-visible spectrophotometer (2201; Systronics, India) at 617 nm. The amount of dye adsorbed by the biomass at equilibrium, q_e (mg/g) was calculated using the following equation[21],

$$q_e = \frac{(C_0 - C_e)V}{M} \quad \ldots (1)$$

where V is the solution volume (L), M is the mass of the biosorbent(g/L) and C_0 and $C_e$are the initial and equilibrium dye concentrations in the solution, respectively.

The rate of biosorption was calculated by conducting a batch kinetic experiment in a Erlenmeyer flask. Biomass was added to the solution at different concentration of malachite green dye and the samples were withdrawn at periodic time intervals and subsequently analyzed for the dye concentration. The dye uptake at time t, q_t (mg/g), was estimated using the mass balance,

$$q_t = \frac{(C_0 - C_t)V}{M} \quad \ldots (2)$$

Results and Discussion

Characterization of biosorbent

SEM micrograph of the biosorbent

Scanning electron microscopy is widely used to study the morphological and surface characteristics of biosorbent[22,23]. A SEM perusal of *Gracillaria corticata*, before and after biosorption, clearly visualizes the morphological changes in the surface texture of biomass. A rough morphological surface was observed before biosorption as shown in Fig. 1a whereas a smooth morphological is observed after biosorption as shown in Fig. 1b. The coverage of surface of the biosorbent is due to the biosorption of dye presumably leading to the formation of cloud formation onto the surface of the biosorbent. Similar kind of changes was observed in the dye biosorption by different adsorbents such as diatomaceous earth, *Ricinuscommunis* and Tamarind fruit shell[24-26].

FT-IR spectroscopy of the algal biomass

The Fourier transform Infrared spectroscopy investigation was executed to acquire knowledge

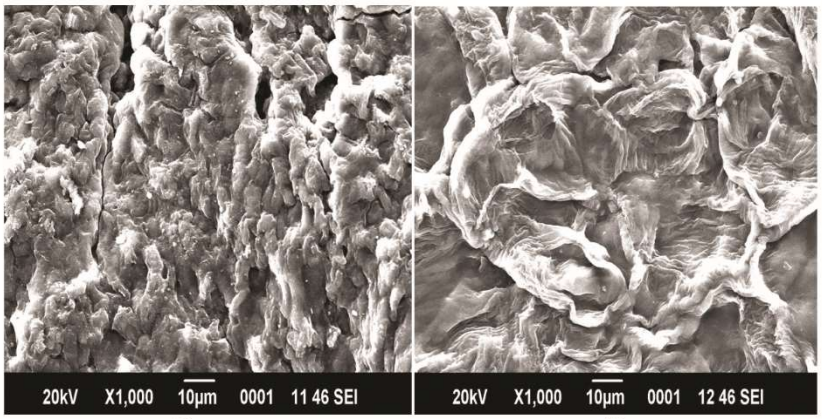

Fig. 1 — Scanning electron microscopy images of *Gracillariacorticata*

on the possible interaction between the functional groups of biomass and dyes. FTIR spectra dye-free *G. corticata* biomass and dye loaded *G. corticata* biomass were studied respectively.

In the present investigation, the spectral analysis has been studied at a wavelength of (500-4000 cm^{-1}). The strong deformation around 3000-3500 cm^{-1} indicated the presence of -OH and –NH groups on the surface of *G. corticata* biomass. A shift in the peak (2943.58-3482.34 cm^{-1}) has proved, of course there is a strong binding of malachite green on to the biomass with H-C-H symmentric and asymmetric stretch and also indicates the noteworthiness of alkyl groups in biosorption. Thus, it is assumed that the shift may be to formation of chemical bond between functional groups present on algal biomass and MG[24]. Similarly, the peaks at 1636.66, 1406.13 cm^{-1} corresponds to C=O stretching due to the functional groups such as alkyl and ketones respectively. The various other peaks present in the spectra of free *G.corticata* biomass are 2621.18, 2100.58, 1583.57, 1509.39, 1393.16, 1326.82, 1509.39, 1178.35, 1026.59, 885.44, 765.25, 713.03, 659.62, 536.54, 425.65 cm^{-1}. Subsequent to the biosorption, there is a significant displacement of the peak to 1636.66, 1406.13, 626.92 cm^{-1} respectively. Such kind shift arises due to the formation of bonds between the function groups[27,28]. These observations significantly illustrates owing to the presence of functional groups on the surface of the *G. corticata* biomass which is responsible for the biosorption of malachite green dye. Even then, it is investigated that the role of hydroxyl and amine groups are far more important than the sorption of dye. Thus, it is revealed that various interactions between biomass and dye has attributed towards the removal of dye.

Effect of initial solution *p*H

*p*H is a factor which influencesthebiosortion process. According to the results, at *p*H 3 and 4, adsorption was poor, with the others (*p*H - 5, 6, 7, 8, 9 and 10) it was noteworthy. At *p*H 3 the uptake was noted as 1.0 mg/g. It was noted that as the *p*H is increased the uptake of dye also increased, hence at *p*H 10.0 the maximum uptake was recorded as 64.67 mg/g. Therefore, *p*H 10.0 is opted for further studies. The fact that uptake of malachite green was less at acidic medium was due to the presence of excess H^+ ions surrounding the biomass inducing a repulsive forces. Therefore, there is a decline in the interaction of ions of malachite green with binding sites of biosorbent. A similar result were reported in the several studies of biosorption of basic dyes on to various biosorbents such as banana stalk waste, peanut hull, polyglutamic acid-based adsorbent[29-31]. Hence, the adsorption was low due to the mobility of H^+ ions[32].

Effect of biomass dosage

The biomass dosage plays a key role in the sorption process. The uptake is decreased while increasing the dose of biomass (Fig. 2). When biomass concentration is increased from 0.1 to 1.0 g, the dye uptake value is significantly reduced 65.67 to 8.88 mg/g. However, the percentage of biosorption is elevated when the biomass is increased. Splitting effect of flux is the key factor for the decrease in the uptake of dye on to unit weight of the biomass, whereas the percentage of color removal is up regulated because at higher biomass concentration, of course there is a rapid superficial adsorption onto the cell surface than the lower biomass concentration.

Biosorption Isotherms

The biosorption results were analyzed with three isotherm models namely, Langmuir, Freundlich and Temkin. The main assumption in the Langmuir adsorption model[33] is maximum biosorption corresponds to the formation of saturated solute monolayer on the surface of the biosorbent. Langmuir model has successfully explained the biosorption of basic cationic dye in the aqueous phase[29,34]. This model, strictly assumes that adsorbed molecules has no further interaction with other adsorbate also there is no any monolayer formation over the surface of the biosorbent[35]. Langmuir model is expressed as follows:

$$q_e = \frac{K_L q_{max} C_e}{1+K_L C_e} \quad \ldots (3)$$

where, q_e (mg/g) is the uptake of dye per unit mass of the biosorbent and C_e (mg/L) is the amount of unadsorbed dye per unit mass of sorbent in solution at equilibrium. $q_{max,}$ the maximum uptake of dye per unit mass of the biosorbent in order to complete the formation of monolayer onto the surface of algal biomass at high C_e, K_L is a constant relates the affinity of the binding site towards the sorbate (L/mg). The linearised Langmuir isotherm model is given by,

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}}\left(\frac{1}{C_e}\right)\frac{1}{q_{max}} \quad \ldots (4)$$

A plot of specific adsorption ($1/q_e$) against the equilibrium concentration ($1/C_e$) would serve to calculate the maximum biosorption capacity of the biomass. The Langmuir constants q_{max} and K_L were determined from the slope and the intercept of the plot and tabulated in Table 1

The dimensionless separation factor R_L describes the essential features of Langmuir isotherm[36] is represented as follows:

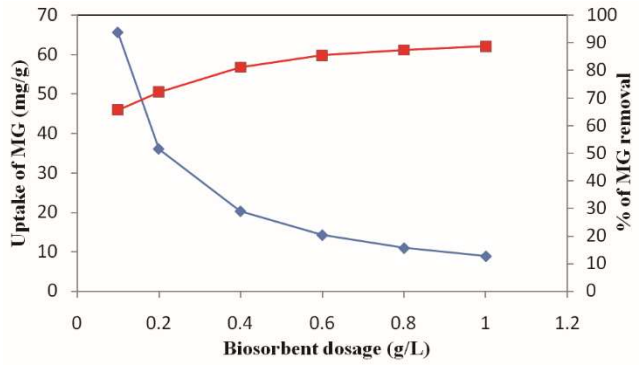

Fig. 2 — Effect of biomass loading (V: 100 mL; C_0: 100 mg/L; Temp:30°C; *p*H: 10)

$$R_L = \frac{1}{(1+K_L C_0)} \quad \ldots (5)$$

whereC_0 is the initial concentration of dye in the solution (mg/L), and K_L(L/mg) is Langmuir constant.

The separation factor $R_L$is of four different forms such as unfavorable (R_L> 1), linear (R_L = 1), favourable (0 <R_L< 1), or irreversible (R_L = 0) based on the shape of isotherm. If R_L values are between 0 and 1, then it clearly indicates the isotherm is favourable. In the present study R_L value was noted as 0.1370 in the biosorption of malachite green onto *Gracillaria* biomass (Table 2). Therefore, the adsorption is favourable.

Freundlich isotherm is an empirical relation generally employed for the determination of biosorption in a heterogeneous system[37]. The Freundlich constant values are elevated at *p*H 10. This clearly indicates adsorption capacity also reached to the peak value which is summarized in the Table 1. Therefore, it is ensured that there is better affinity between the biomass and the dye solution[38]

$$q_e = K_F C_e^{1/n} \quad \ldots (6)$$

In Eq.6 K_F (mg/g) is the adsorption capacity of the sorbent and *n* corresponds to the favorability of the adsorption process. Freundlich isotherm is perhaps

Table 1 — Langmuir, Freundlich and Temkin isotherm model constants and correlation coefficients for adsorption of MG onto *Gracillaria corticata* biomass

Isotherm	Parameters
Langmuir	
q_{max}	76.92
K_L	0.1625
R^2	0.996
Freundlich	
K_F	14.67
n	2.189
R^2	0.964
Temkin	
A	1.476
B	17.11
R^2	0.987

Table 2 — Langmuir separation factor for *Gracillaria corticata* biomass

Initial MG dye concentration (mg/L)	R_L
20	0.235
40	0.133
60	0.093
80	0.071
100	0.057

applied to simplify the integration of the presumable constants. The scrupulous perception of adsorption favourability is well elucidated by means of the degree of exponent 1/n. If $n > 1$ then it naturally reflects that adsorption is favourable[39-41]. The linearisedFreundlich equation is given by:

$$\ln q_e = \ln K_F + \frac{1}{\mathrm{n}} \ln C_e \quad \ldots (7)$$

The values of K_F and $1/n$ are obtained from the intercepts and slopes, respectively, of the plot of $\ln(q_e)$ against $\ln(C_e)$ and the corresponding values are presented in Table 1.

Temkin isotherm is based on the assumption indirect interaction of sorbate/adsorbate on the adsorption isotherms. Thus, the heat of adsorption increases linearly over the surface of biosorbent[42] and further the adsorbate molecules possess a maximum binding energy upto certain limit[43]. The general Temkin isotherm model is as follows:

$$q_e = \left(\frac{RT}{b}\right) (\ln C_e) \quad \ldots (8)$$

and can be linearized as

$$q_e = B \ln A + B \ln C_e \quad \ldots (9)$$

where $B = RT/b$, b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (K). The constant values A and B are obtained by plotting q_e versus $\ln C_e$.

Table 1 summarizes the results of three isotherm models such as Langmuir, Freudlich and Temkin. Out of these Langmuir isotherm observed to have a highest coefficient of determination (R^2= 0.996) which fits well with the experimental data. However, the Freundlich and Temkin isotherms are found to have a less agreement with experimental data with a coefficient of determination R^2= 0.964 and R^2= 0.987 respectively. Therefore, according to the Langmuir model the adsorption capacity is found to be 76.92 mg/g at 303K. This is because of the homogeneous distribution of active binding sites on the surface of the red algae *Gracillaria coricata.* In addition, the Langmuir model assumes the adsorbent surface is homogenous.

A similar result was observed in the sorption of MG on different sorbents. Some of the dye biosorption results which coincide with the present investigations are biosorption of methylene blue onto oil palm fibre activated carbon[44], palm kernel fibre[45] and algal biomass[46]. However, the present study results shown to have higher q_{max} value compared to that of the previous work. In Langmuir isotherm, q_{max} is the most important parameter which is the measure of adsorption capacity of the biosorbent. The various q_{max} value for different adsorbents are listed in Table 3. This clearly reveals *Gracillaria corticata* could serve as a good sorbent for the sorption of malachite green.

Table 3 — Comparison of adsorption capacities of various biosorbents for Malachite Green

Adsorbents	q_{max}(mg/g)	Conditions		Reference
		*p*H	Temp. (K)	
Gracillaria corticata	76.92	10.0	303	This study
Turbinaria conoides	66.67	8	303	47
Wood Apple Shell	34.56	7.5	299	48
Chlorella-based biomass	18.40	7.0	298	49
Annona squamosa seed	25.91	6.0	300	50
Potato peel	32.39	4	298	51
Dried cashew nut bark carbon	20.09	6.6	-	52
Tamarind fruit shell	1.95	5	303	53
Neem sawdust	4.35	7.2	303	54
Saccharomyces cerevisiae	17.00	5.0	308	55
Lemon peel	51.73	-	305	56
Cellulose powder	2.422	7.2	298	57
Caulerpa racemosa	25.67	6.0	318	58

Biosorption kinetics

The batch full scale operation depends on the biosorption kinetics of malachite green onto *Gracillaria corticata* biomass. The kinetic parameters facilitate to design and modeling of the biosorption process[49].In the present study three familiar kinetic models were used to fit the obtained experimental data such as Pseudo-first-order model, Pseudo-second-order model and Elovich model. Lagergren described the linear form of pseudo-first-order model[58] which is presented as follows:

$$(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \quad \ldots (10)$$

A linear plot of log (q_e−q_t) against time as shown in Fig. 3 gives the rate constant of the reaction. If the plot is straight and linear, then it indicates that biosorptionof malachite green onto the *Gracillaria* biomass is appropriate for the Lagergren's equation. Hence, the biosorption process obviously follows the pseudo-first-order rate kinetics[59,60]. The constant values of the first order kinetics (k_1) and q_e are evaluated from the Lagergren's model and presented along with their corresponding coefficient of determination in Table 4. The obtained data deviate with the calculated q_e values. Therefore, sorption of malachite green does not follow the first order kinetics.

The linearised form of pseudo-second-order kinetics can be expressed as[61]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots (11)$$

where, (q_e) equilibrium adsorption capacity and k_2 (g/mg h) the second order constant can be determined from the plot of t/q_t versus t as shown in Fig. 4. The corresponding coefficient of determination along with the k_2 and q_e are presented in Table 4. It is noted that there is a good relation between the experimental and the calculated q_e. Thus, pseudo-second-order model very well suits with adsorption kinetics of malachite green. The previous study results of methylene blue biosorption by hazelnut shells and wood sawdust[63], activated carbon rattan sawdust based activated carbon[44] and activated carbon prepared from bamboo[64] shown to have a well resemblance pertaining to the biosorption of malachite green onto *Gracillaria corticata* biomass.

Elovich kinetic model is based on the adsorption capacity and is expressed as:

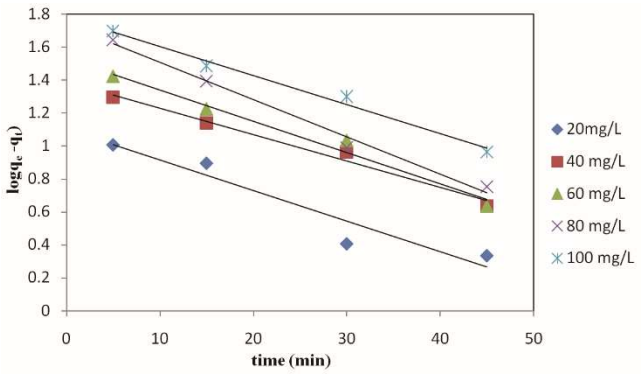

Fig. 3 — Pseudo-first-order sorption kinetics of MG on *Gracillaria* biomass

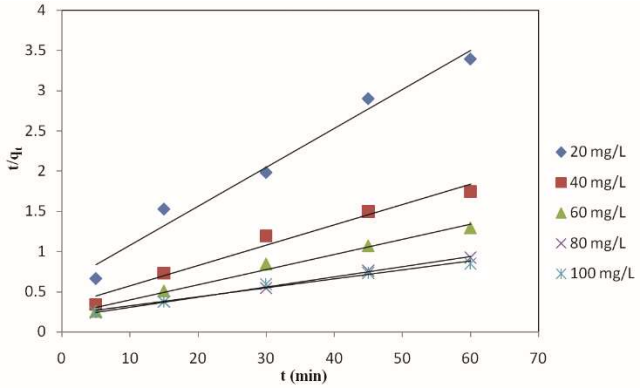

Fig. 4 — Pseudo-second-order sorption kinetics of MG on *Gracillaria* biomass

Table 4 — Kinetic parameters for the MG biosorption onto *G.corticata* at different initial dye concentrations

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo first order			Pseudo second order			Elovich		
		K_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	K_2 (g/mgmin)	$q_{e,cal}$ (mg/g)	R^2	α (g/mg min)	B (g/mg)	R^2
20	17.67	0.046	14.75	0.935	0.0038	20.83	0.977	0.986	0.239	0.083
40	34.33	0.041	28.70	0.966	0.0019	40	0.973	0.940	0.130	0.955
60	46.33	0.046	39.17	0.971	0.0015	55.56	0.985	0.921	0.095	0.981
80	64.6	0.052	58.74	0.987	0.0007	83.33	0.998	1.168	0.056	0.995
100	70.5	0.041	64.86	0.987	0.0005	90.90	0.983	1.227	0.051	0.983

$$\frac{dq}{dt} = \alpha exp(-\beta q_t) \quad \ldots (12)$$

The linearised Elovich equation is as follows:

$$q = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \quad \ldots (13)$$

The constant values such as β and α are determined from the slope and intercept of the plot by plotting ln t against q. The obtained values are summarized in the Table 4. It is found that Elovich model does not fit well. Thus, pseudo second order model is precise for the sorption of malachite green onto *Gracillaria corticata* biomass.

Intraparticle diffusion model

Weber's intraparticle diffusion gives a clear picture about the rate controlling steps which causes the adsorption kinetics[65]. The experimental data were fitted with the Weber's intraparticle diffusion model to elucidate the mechanism behind the adsorption kinetics. It is an empirical relationship similar to the adsorption processes, where the uptake is proportional with $t^{1/2}$ rather than with contact time*t*[66] which is expressed as follows:

$$q_t = K_{id}t^{1/2} + C \quad \ldots(14)$$

where *C* is the intercept and$k_{id}$is the intraparticle diffusion rate constant (mg/g $h^{1/2}$) which are evaluated from the plot q_t versus $t_{1/2}$[67] and respective values are summarized in Table 5. In spite, boundary layer effect perhaps facilitates to predict the rate controlling steps. Suppose, *C* is larger, the contribution of sorption surface has a high impact on the rate controlling step. The plot q_t versus $t_{1/2}$ is linear and the regression of the line passes through the origin, hence one can say that rate-limiting step is governed by intraparticle diffusion. A linear plot was not attained at various concentrations also the plot was not passing through the origin which clearly indicates that the intraparticle diffusion model is not only the sole rate limiting step in addition some other mechanism also governs the process of biosorption[67,68].

Table 5 — Intraparticle diffusion coefficients and intercept values for Biosorption of MG on *Gracillariacorticata* Biomasss

Initial dye concentration (mg/L)	K_{id} *(mg/g $h^{1/2}$)*	Intercept value (C)	R^2
20	2.232	1.242	0.967
40	4.202	2.499	0.977
60	5.768	3.818	0.972
80	8.577	2.540	0.977
100	9.069	1.086	0.995

Thermodynamic studies

Biosorption is a temperature dependent process. Thermodynamic analysis of equilibrium sorption data assist to determine the spontaneity and heat exchange of malachite green biosorption onto the *Gracillaria corticata* biomass as well gives a brief knowledge on the thermodynamic parameters such as change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) The Gibbs free energy change for biosorption of MG onto Gracillaria biomass is estimated using the following expression:

$$\Delta G^{\circ} = -RT\ln K_c \quad \ldots(15)$$

Vant Hoff's equation gives a general relation between the standard enthalpy change and standard entropy change which is expressed as follows:

$$\ln K_c = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \quad \ldots(16)$$

where K_c is equilibrium constant for sorption, R gas constant, T temperature (K). The value of ΔH° was calculated from the slope of the linear regression of $\ln K_c$ versus 1/T.TheK_c value was determined by the relation given below:

$$K_c = \frac{q_e}{C_e} \quad \ldots(17)$$

where q_e denotes the quantity of MG adsorbed on *Gracillaria* biomass at equilibrium (mg/L), C_e is the malachite green in solution at equilibrium concentration (mg/L). Table 6 illustrates the thermodynamic parameters that were calculated by above equations. ΔG°gives a hint about the type of adsorption.

In the present investigation, negative ΔG° value indicates the feasibility and spontaneous nature for the biosorption of malachite green. Hence, it confirms the affinity of *Gracillaria* biomass for MG sorption. ΔH° another thermodynamic parameter which was found to be positive, therefore it indicates the endothermic nature of the biosorption processes. In addition the positive standard entropy reveals that there is increase in randomness at the solid-liquid interface during the sorption of MG onto the surface of *Gracillaria corticata*. Analogous results were obtained in the sorption experiment using carbon prepared from *Arundodonax* root[69] and de-oiled soy[70], bentonite[71] and hen feathers[72].

Table 6 — Thermodynamic parameters of *G. corticata* biomass at different temperature

Initial dye concentration (mg/L)	Temperature (K)	K_c	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
20	303	5.66	-4368.19	53758.34	190.55
	313	8.09	-5438.76		
	323	15.66	-7387.59		
	333	39.00	-10142.62		
40	303	6.01	-4519.34	52029.01	185.06
	313	7.89	-5373.71		
	323	15.00	-7272.12		
	333	39.00	-10141.24		
60	303	5.12	-4796.00	29814.00	111.32
	313	6.31	-5999.23		
	323	9.34	-7455.73		
	333	14.78	-3204.34		
80	303	3.57	-3204.34	20336.04	77.45
	313	4.33	-3814.94		
	323	5.50	-4578.64		
	333	7.42	-5548.19		
100	303	1.88	-1592.09	21524.94	76.01
	313	2.33	-2204.13		
	323	2.90	-2862.65		
	333	4.12	-3923.05		

Conclusion

Marine red algae, *Gracillaria corticata* was successfully utilized as low cost biosorbent for the removal of toxic dye malachite green. Species of *Gracillaria* is abundantly found in many parts of world oceans, thus it would serve as cheap source for the production of biosorbent. The batch experimental results showed the importance of solution *p*H and temperature in biosorption of MG. The comparative results on biosorption capacity of various biosorbents revealed that *Gracillaria* biomass can be effectively used as prominent biosorbent for the sequestration of MG containing wastewater. The equilibrium isothermal results were well described with Langmuir model. The biosorption kinetics was profound to be explained by pseudo-second-order rather than the pseudo-first-order and Elovich model. The current thermodynamic parameter information depicts that the biosorption reaction is spontaneous, endothermic with increased randomness. However, further column studies have to be carried out to invigilate the feasibility of scale up of the biosorption process.

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