Removal of Methylene Blue from aqueous solution by marine green alga *Ulva lactuca*

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Biosorption of colours is an important technology for treatment of different types of industrial wastewaters containing dyes. The objective of this study was to convert green alga *Ulva lactuca* to dye adsorbents for wastewater treatment. The importance of commonly available green alga *Ulva lactuca* was investigated as viable biomaterials for the biological treatment of synthetic basic blue 9 (5-ch1oro-*N*,*N*,*N'*,*N'*-tetramethyl-5λ^4-phenothiazine-3,7-diamine) effluents. The results obtained from the batch experiments revealed the ability of the green algae to remove the basic blue 9, and this was dependent on the dye concentration, pH, and algal biomass. We investigated the equilibrium and kinetics of adsorption, and the Langmuir and Freundlich equations were used to fit the equilibrium isotherm. The adsorption isotherm of basic blue 9 followed both the Langmuir and Freundlich models with a correlation coefficient of ∼0.96–0.99, and the adsorption kinetics followed the pseudo-second-order model ($R^2 = 1.0$). The maximum adsorption capacity was about 40.2 mg of dye per gram of dry green algae at pH 10, $25 \, g \, l^{-1}$ dye and $2.5 \, g \, l^{-1}$ alga concentrations. This study demonstrated that the green algae could be used as an effective biosorbent for the treatment of dye-containing wastewater streams.

Keywords: Biosorption; Basic dye; Methylene Blue; Green algae; *Ulva lactuca*; Wastewater treatment; Removal of dyes

1. Introduction

Effluents from the dying and finishing process in the textile industry are known to contain colour, high amounts of surfactants, dissolved solids, and possibly heavy metals such as Cr, Ni, and Cu [1]. The effluents from the dyestuff manufacturing and other similar industries are also generally highly coloured with a large amount of suspended organic solids, and hence are important sources of water pollution [2]. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic [3], and it is difficult or impossible to remove these by conventional biological treatment processes [4].

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Biological treatment processes are reported to be efficient in the removal of suspended solids and the reduction in chemical oxygen demand but are largely ineffective at removing colour from waste water [5]. Therefore, investigations have been conducted on physico-chemical methods of removing colour from textile effluent [2]. These studies include the use of coagulants [6], oxidizing agents [7], ultra-filtration, electro-chemical, and adsorption techniques [5]. Adsorption has been found to be an efficient and economic process to remove dyes, pigments, and other colourants, and also to control the biochemical oxygen demand [8, 9].

There are relatively few studies on the use of aquatic plants as a biosorbent for dyes. Low *et al.* [10] reported the potential of *Hydrilla verticillata* as absorbent for removal of basic dye Methylene Blue under various conditions. The *Ulva lactuca* is another species of algae that is widespread along the shores. It grows well in intertidal waters and accumulates high nutrient levels in urban areas contaminated by domestic sewage [11].

In the present study, aqueous solutions of Methylene Blue dye was used as a model compound in an attempt to use *Ulva lactuca* as an adsorbent. Although not greatly hazardous, Methylene Blue can have various harmful effects [12]. The purpose of this work was to investigate the adsorption capacity of *Ulva lactuca* to remove Methylene Blue from aqueous solution and the kinetics and mechanisms of adsorption of Methylene Blue on various weights of algae [13].

2. Material and methods

Ulva lactuca was washed with sea water, tap water, and then distilled water several times. The clean algae were exposed to the sun for several days followed by oven drying at $100\,^{\circ}C$ for 24 h, and the dried algae were milled and sieved. Methylene Blue (MB) supplied by BDH was used as absorbate and was not purified prior to use. All the other chemicals used in this study were of reagent grade. Double-distilled water was used for preparing all of the solutions and reagents.

Batch adsorption experiments were carried out using appropriately diluted $1000\,mg\,l^{-1}$ stock solutions to the required initial concentrations. Adsorption experiments were carried out at room temperature $(25 \pm 2\,^{\circ}C)$ [10]. The initial concentrations (5, 10, 15, 20, and $25\,mg\,l^{-1}$) of MB were obtained by measuring the adsorption at λ_{max} 663 nm using a UV-VIS spectrophotometer (Milton Roy, Spectronic 21D). Exactly 100 ml of MB solution of known initial concentration (concentration range $5\text{–}25\,mg\,l^{-1}$) was shaken at a constant agitation speed (200 rpm) with a required dose of algae (0.125, 0.25, 0.5, 0.75, and 1.0 g) of a fixed particle size (0.315–0.8 nm) for a specific period of contact time (range 5–120 min). The algae were selected according to size using a topmost sieve shaken on a mechanical shaker 'Betriebsanleitung vibration testing sieve mechanical machine Thyr 2' for 20 min. The pH of the solutions was adjusted to the required value (range: 2–10) by adding either 1 M HCl or 1 M NaOH solution. The optimum pH was pH 10. After equilibration, the final concentrations (C_f) were measured at λ_{max} 663 nm. The percentage of dye removal and adsorbed ($mg\,g^{-1}$) were calculated using the following relationships:

$$\text{Percentage removal} = 100 \times (C_i - C_f)/C_i \tag{1}$$

$$\text{Amount adsorbed } (q_e) = (C_i - C_f)/m, \tag{2}$$

where C_i and C_f are the initial and final concentration $(mg\,l^{-1})$ of dye, respectively, and m is the mass of algae $(g\,l^{-1})$.

3. Results and discussion

The results obtained from the present investigation revealed the ability of *Ulva lactuca* in treating MB.

3.1 *Effect of contact time*

The removal of different concentrations of dye colour by *Ulva lactuca* biomass was monitored at various contact times and is shown in figure 1. The dye uptake profiles distinctly showed three phases: the rate of removal/uptake was less initially (phase 1), progressively increased, attained a rapid phase with progression of contact time (phase 2), and finally levelled and attained saturation after a contact time of 45 min, remaining more or less constant thereafter up to 120 min. The pattern of graphs was almost the same for all the dye concentrations and biomass concentrations. Our results suggest that 30 min of contact time is required for the initial contact of the algal biomass. After phase 1, the dye uptake was increased and reached saturation at *c*. 45 min. The rate of dye uptake level reached saturation more or less at the same time (45 min) for all concentrations of biomass, and removal was constant.

3.2 *Effect of algal biomass*

The variations of dye removal (saturation) values are shown in figures 1 and 2 for all the algal biomass and dye concentrations. An increase in adsorbent amount led to a decrease in dye removal for most studied concentrations of dye. This study is not in agreement with the results obtained by Namasivayam *et al.* [8] and Lee *et al.* [14], where the sorption capacity increased with increasing biomass dosage.
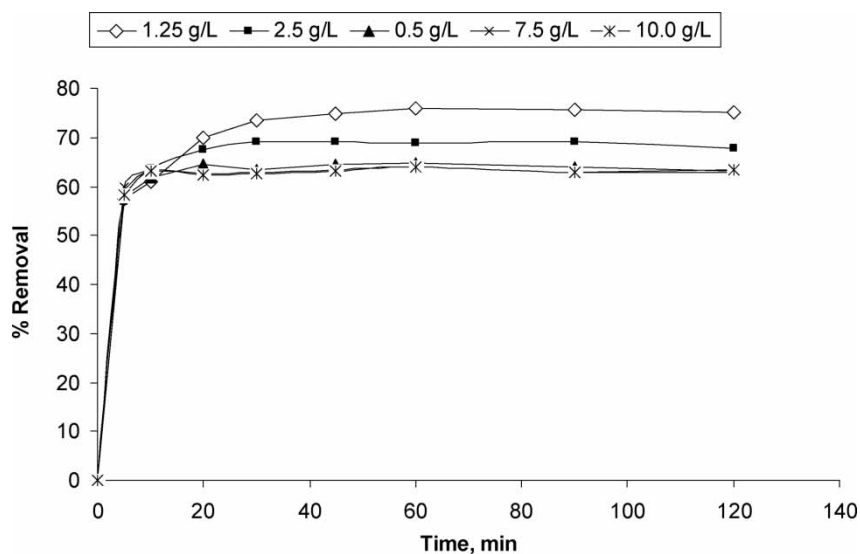

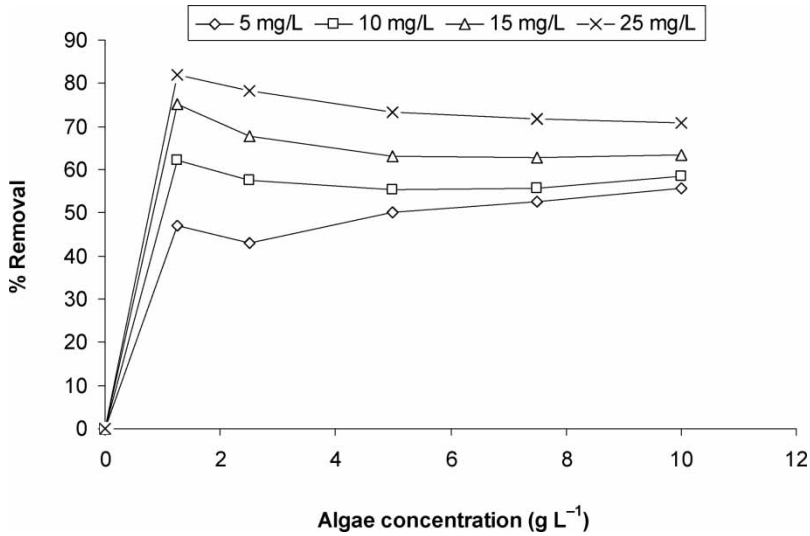Figure 1. Effect of different weights of algae on the adsorption of dye initial concentration of MB $= 25\,\mathrm{mg\,l^{-1}}$.

Figure 2.   Effect of weight of algae on the removal efficiency at different dye concentrations.

3.3   *Effect of pH*

The pH value of the solution was an important parameter in controlling the adsorption process. Basic dye upon dissolution released coloured dye cation in solution, and the adsorption of these charged dye groups onto the adsorbent surface was primarily influenced by the surface charge on the adsorbent, which in turn was influenced by the pH solution (figure 3). The maximum affinity for this dye cation could be expected at alkaline pH values. At a low pH value, a fewer anionic adsorption sites on the dried *Ulva lactuca* were generated, and sorption was unfavourable, probably because of excess H^+ competing with dye molecule for sorption sites on the dried *Ulva lactuca*. The observed values also agree well with the results reported in the literature [10, 15–18]. Another possible interference to biosorption mechanisms was
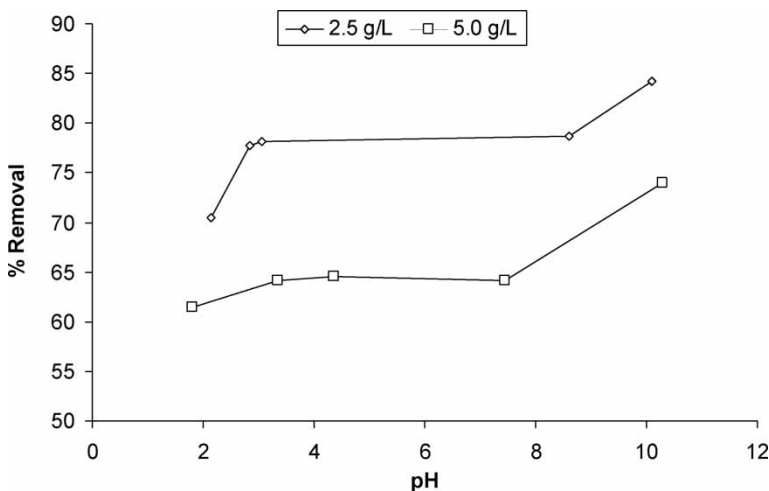

Figure 3.   Amount of MB removed for two weights of algae at different pHs for the dye concentration $15\,mg\,l^{-1}$.

Table 1. Comparison of the first- and second-order adsorption rate constants for calculated and experimental q_e values at 25 mg l^{-1} initial MB concentration and different *Ulva lactuca* concentrations.

Parameter	First-order kinetic model				Second-order kinetic model		
Algae conc. (g l^{-1})	q_e (exp.)	K_{ad}	q_e (calc.)	R^2	K_2	q_e (calc.)	R^2
1.25	16.603	0.032	2.203	0.846	0.040	16.75	1.000
2.50	7.835	−0.302	0.815	0.657	0.116	7.15	1.000
5.00	3.660	−0.025	0.102	0.565	0.883	3.66	1.000
7.50	2.394	−0.058	0.060	0.841	2.503	2.40	1.000
10.00	1.782	−0.063	0.014	0.637	7.173	1.78	1.000

Note: Conc.: concentration; exp.: experimental; calc.: calculated; the units of q_e are mg g^{-1}, K_{ad} min^{-1}, and K_2 g mg^{-1} min^{-1}.

high ionic strength–high ionic strength, which significantly reduced the binding of cation to biomass [19].

3.4 *Adsorption dynamics*

The adsorption rate constant is determined from the first-order rate expression given by Lagergren rate equation [14, 20] as follows:

$$\log(q_e - q_t) = \log q_e - k_{ad} \times t/2.303, \tag{3}$$

where q_e and q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_{ad} the rate constant of adsorption (min^{-1}). Values of k_{ad} were calculated from the plots of $\log(q_e - q_t)$ vs. t for different concentrations of Methylene Blue (table 1). The experimental q_e values do not agree with the calculated values obtained from the linear plots. This shows that the adsorption of MB on *Ulva lactuca* is not a first-order reaction.

The second-order kinetic model [21] is expressed as follows:

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e, \tag{4}$$

where k_2 is the rate constant of second-order adsorption (g mg^{-1} min^{-1}). If the second-order kinetics is applicable, then the plot of t/q_t vs. t should show a linear relationship (figure 4).
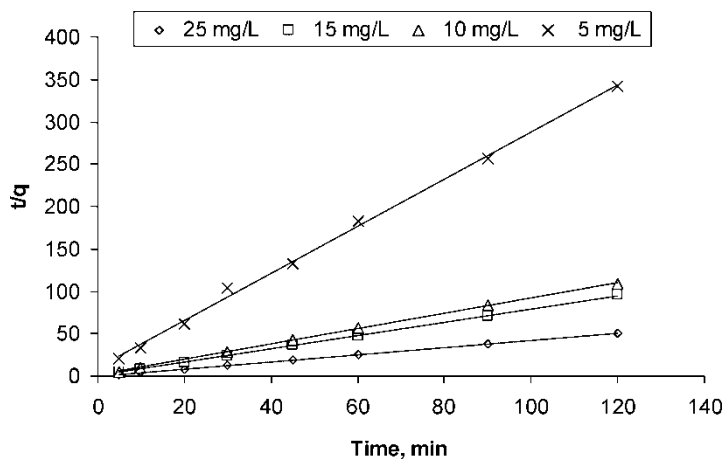

Figure 4. Pseudo-second-order model at different initial dye concentrations and 7.5 g l^{-1} of algae.

There is no need to know any parameter beforehand, and the adsorption capacity at equilibrium q_e can be calculated from equation (4). Also, it is more likely to predict the behaviour over the whole range of adsorption [21]. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q_t vs. t. This shows a good agreement between experimental and calculated q_e values (table 1). The correlation coefficients for the second-order kinetic model are 1.0. These indicate that the adsorption system belongs to the second-order kinetic model. Similar phenomena have been observed in the biosorption of dye removal black B on biomass [22, 23] and adsorption of Congo Red on coir pith carbon [24].

3.5 *Adsorption isotherms*

The adsorption data were analysed with the help of the following linear forms of Freundlich and Langmuir isotherm [25], as follows:

$$\log q_e = \log k_f + (1/n) \log C_e, \tag{5}$$

where, $\log k_f$ is roughly a measure of the adsorption capacity, and $1/n$ is an indicator of adsorption effectiveness.

The Langmuir isotherm is:

$$C_e/q_e = (1/ab) + (C_e/b), \tag{6}$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent ($mg\,g^{-1}$), and a and b are the Langmuir constants, which are the measure of Langmuir sorption affinity ($l\,g^{-1}$) and monolayer adsorption capacity in ($mg\,g^{-1}$), respectively. The values of the Freundlich and Langmuir parameters were obtained from linear correlations between the values of (*i*) $\log q_e$ and $\log C_e$ and (ii) C_e/q_e and C_e, respectively (table 2). The adsorption isotherms along with the correlation coefficient are presented in figures 5 and 6. The observed linear relationships as evidenced by the *r*-values (close to unity) indicate the applicability of these two adsorption isotherms and the monolayer coverage on the adsorbent surface. The monolayer adsorption capacities of the adsorbents possess a high adsorption capacity and hence could be employed as low-cost adsorbents for the removal of MB. Further, the essential characteristics

Table 2. Freundlich and Langmuir constants for the adsorption of MB dye on alga using different weight.

Parameter	Concentration of alga *U. lactuca* ($g\,l^{-1}$)				
	1.25	2.5	5.0	7.5	10.0
Freundlich					
$\log K_f$	1.432	1.604	1.101	1.134	1.453
$1/n$	3.978	3.283	1.908	1.095	1.955
r	0.954	0.959	0.948	0.957	0.996
Langmuir					
a	0.625	1.038	0.742	0.824	0.936
b	3.012	6.268	7.001	9.013	10.994
r	0.958	0.999	0.962	0.954	0.999
R_L	0.660	0.660	0.540	0.460	0.520

Note: Data used: pH 10, speed 200 rpm, contact time 5–120 min, particle size 0.315–0.80 nm, room temperature ($25 \pm 2\,°C$), concentration of dye 25 mg l^{-1}. The units of K_f and b are mg g^{-1}, and a l g^{-1}.
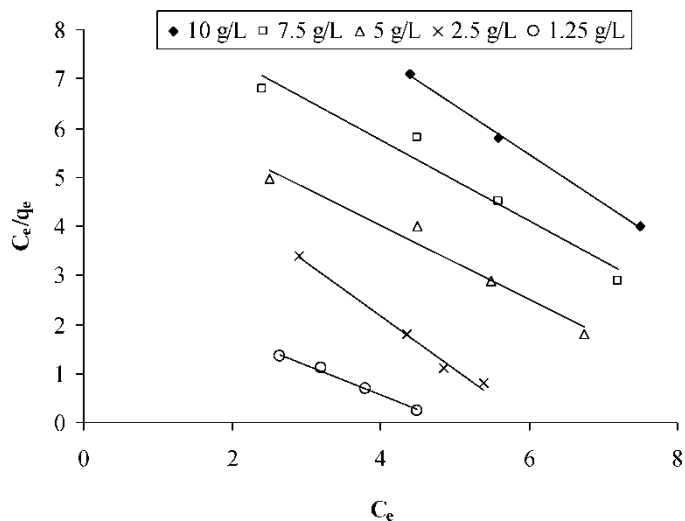
Figure 5.   Fitting adsorption data with Langmuir.

of the Langmuir isotherm can be described by adsorption factor R_L, which is defined by the following equation

$$R_L = 1/(1 + aC), \tag{7}$$

where C is any adsorbate concentration of dye at which the adsorption is carried out $(mg\,l^{-1})$, and a is the Langmuir sorption affinity $(l\,g^{-1})$. The value of adsorption factor R_L indicates the nature of the adsorption process as given below (table 3). In the present study, the values of R_L computed are in the range of 0–1, indicating that the adsorption process is favourable for all weights which may indicate low-cost adsorption. Moreover, the adsorption capacity of *Ulva lactuca* for Methylene Blue was equivalent to rice-husk carbon $(37.7\,mg\,g^{-1})$ and straw
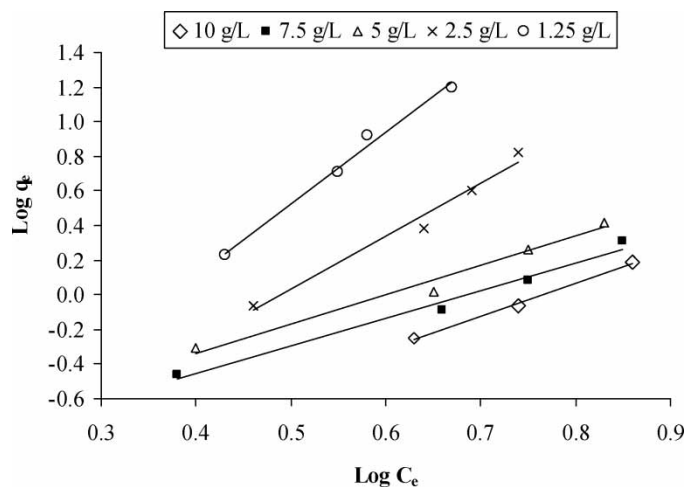

Figure 6.   Fitting adsorption data with Freundlich.

Table 3. Adsorption factor values and corresponding nature of adsorption process.

R_L value	Nature of adsorption process
>1	Unfavourable
1	Linear
0–1	Favourable
0	Irreversible

carbon ($42.6\,\mathrm{mg\,g^{-1}}$) but higher than the bamboo-dust carbon ($7.2\,\mathrm{mg\,g^{-1}}$), coconut-shell carbon ($8.16\,\mathrm{mg\,g^{-1}}$), and groundnut-shell carbon ($7.5\,\mathrm{mg\,g^{-1}}$).

4. Conclusions

The results of the present study showed a broader pH sorption, and the kinetics data showed that sorption was quite rapid. Since *Ulva lactuca* is readily available in the environment, it is more economical and can yield a sorbent of a higher sorption capacity than others. Furthermore, regeneration is not necessary because it is available biological material. Since this study was performed using synthetic waste water and at a laboratory scale, the results obtained may have some variation if they are applied to real waste water. Parameters such as equilibrating time, pH, dosage, and concentrations may stand as important factors in the adsorption process. Further studies focusing on real waste water from different sources are needed.

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