Scientific paper

Biosorption of Methylene Blue by a Brown Alga *Cystoseira barbatula* Kützing

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Abstract

The brown alga *Cystoseira barbatula* Kützing which is widely distributed in the Mediterranean Sea was used to prepare an alternative low cost biosorbent to remove methylene blue (MB) from aqueous solutions. To determine the equilibrium adsorption capacity, the effects of contact time, temperature, pH and adsorbent dosage were studied. The contact time was studied at six hours but after 210 minutes the adsorption reached equilibrium in all concentrations (5–100 mg L^{-1}). Pseudo-first and pseudo-second order kinetic models were applied to the adsorption data. Pseudo first order model was not fitted to data however pseudo second order model was well in line with the adsorption data. Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were also investigated. According to Langmuir isotherm, the maximum adsorption capacity was estimated as 38.61 mg g^{-1} at 35 °C. Dubinin-Radushkevich equation was used to analyze the adsorption behaviour of the algal adsorbent in aqueous MB solutions. Thermodynamic parameters ΔG^o, ΔH^o and ΔS^o were also calculated by using Van't Hoff Equation. The positive enthalpy indicated that the adsorption was in endothermic nature. The adsorption enthalpy values were found as 72.464; 36.595; 33.974; 25.102 kJ mol^{-1} at different concentrations of methylene blue (5, 20, 50, 100 mg/L, respectively). High negative values of Gibbs free energy revealed that adsorption was in a spontaneous nature.

Keywords: Biosorption, *Cystoseira barbatula* Kützing, methylene blue, waste water pollution.

1. Introduction

Since the reasons of raising population, urbanization and industrialization around the world's water sources are polluted. The main force of the water pollution mostly comes from waste water which contains industrial and environmental contaminations. Dye manufacturing can cause serious problems in waste waters such as biodegradation, toxicity, light penetration and photosynthesis. In the last decade, water resources have been decreased because of global warming and also limited water resources have been polluted. There are many water treatment methods such as filtration, oxidation, sedimentation and adsorption etc.[1–3] Among these treatment methods, adsorption of pollutants onto low cost materials are the cheapest methods. The removal of the dyes in the effluents is a crucial treatment due to their strong aromatic forms containing trace alkali, acid and carcinogenic metals. Methylene blue (MB) is an organic dye usually used to dye cotton, wool, acrylic, silk and many industrial areas to color the materials. When it is used recklessly, it can cause serious illness such as vomiting, hard breathing, mental disorder and sweating.[4] On the other hand, MB is widely used as a model dye for adsorption studies. Activated carbon is mainly used to remove dyes from aqueous solutions. However, some algae from *Caulerpacaea* family such as *Caulerpa lentillifera* was reported as a "high performance biosorbent" for some dyes contain MB. *Caulerpa lentillifera's* and activated carbon's maximum adsorption capacities were found as 417 mg g^{-1} and 238 mg g^{-1}, respectively.[5] The commercial activated carbon is more expensive compared to algae. Therefore, scientists in adsorption field search low cost, which are easily found and high applicability adsorbent from nature. Turkey is surrounded by the Mediterranean Sea, the Black Sea and the Aegean Sea. Macroalgae are of great importance in Turkish Marine Flora. However, these species have not so far been used as industrial or commercial products contribute to the economy of Turkey. Among macroalgae of Turkish Marine Flora, *Cystoseira barbatula* Kützing (hereafter *C. barbatula*) is quite abundant in the Aegean Coastline of Turkey. We have been following the invasion of marine alga called *Caulerpa racemosa* var.*cylindracea* via determining some biochemical parameters since 2003 from Seferihisar coastlines (geographical coordinates are found from material and methods section) of Turkey.[6,7] For two years, we have observed high biomass of *C. barbatula* compared to *Caulerpa racemosa* var.*cylindracea* in winter season (especially in February). The structural form of algae consists of proteins and carbohydrates.[8] Therefore; we aimed to study MB adsorption onto dried biomass of *C. barbatula* to develop an adsorbent as a possible low-cost commercial product from marine algae.

2. Experimental

2. 1. Sorbent Preparation

C. barbatula Kützing was collected from Seferihisar coastline of Gümüldür in Turkey in January 2008. The coordinates of the area were 38° 07’55.75’’N, 26° 50’07.58’’E. Non-living seaweed was picked up from 0.3 m depth by hand. The wet alga samples were taken in to the plastic bags which were filled with seawater then sent to the laboratory immediately. In the laboratory, the wet alga was first washed with tap water to remove salt, epiphytes and other contaminants and then they were washed with distilled water again. The material was dried at 70 °C for 16 hours. After being dried, the alga was grounded with mortar and pestle and stored in a desiccator. Grinding material which has 500 μm pore size was used in the experiments. Before and after adsorption the differences in the functional groups on algal surface were determined by using Perkin Elmer FT-IR spectrophotometer (Spectrum BX-II). Pellets were prepared with 1 mg alga and 100 mg KBr for analysis. The results are shown in Table 1.

Table 1: Functional groups of dried and MB attached alga[8,9]

Functional group	Standard wavenumber[9] (cm^{-1})	Wavenumber from the pure alga (cm^{-1})
Hydroxyl; O–H	3250–3700	3412
Amine;NH_2	3300–3500	3412
Carboxyl;COOH	2400–3300	2929
C–O	1050–1300	1033
Sulfonyl; S=O	1040–1200	1033
Carbonyl;C=O	1670–1780	1633
Alkyl CH	2900–3000	2929

As it can be seen from Table 1, the peaks obtained from grinded alga at 3412 (–OH, $-NH_2$), 2929 (–COOH, alkyl CH), 1033 (S=O, C–O) and 1633 (C=O) cm^{-1} might show the possible functional groups of alga. The similar FT-IR profiles were reported by some researchers who are interested in algae species.[10–12]

2. 2. Preparation of Dye Solution

The methylene blue (MB, from Fluka) was used without purification. Stock solution of MB was prepared with distilled water and concentration was adjusted to 100 mg L^{-1}. Four types of dye concentration (5 mg L^{-1}, 20 mg L^{-1}, 50 mg L^{-1}, 100 mg L^{-1}) were prepared from stock solution by using distilled water for diluting.

2. 3. Adsorption Experiments

Sorption studies were carried out to find equilibrium data. The experiments were performed at different temperatures (25, 35 and 45 °C). Adsorbent dosage was selected as 0.1 g for initial experiments. Polyethylene vessels were filled with 30 mL various concentration dye solutions and 0.1 g dried *C. barbatula* was added. The solutions were agitated at 215 rpm, in a temperature controlling shaker (Barnstead Max400) for six hours. The samples were centrifuged at 10000 rpm for 10 minutes. Dye concentrations in supernatants were measured by using Shimadzu UV-Visible 1601 model spectrophotometer at 665 nm. The amount of dye adsorbed onto *C. barbatula* at equilibrium was calculated by using the equation as shown below:

$$q_e = \frac{C_o - C_e}{M} V \tag{1}$$

where C_o and C_e are the initial and equilibrium concentrations of MB (mg L^{-1}), respectively. q_e is the amount of dye adsorbed onto *C. barbatula* at equilibrium (mg g^{-1}), V is the volume of the dye solution (L) and M is the amount of the adsorbent used (g).To determine the percentage of dye removal following equation is used:

$$\%\ \text{dye removal} = \frac{(C_o - C_e)}{C_o} 100 \tag{2}$$

3. Results and Discussion

3. 1. Effect of pH on the Adsorption of MB

In order to obtain the optimum pH for the adsorption of MB onto *C. barbatula,* the effects of pH were studied in range of pH 3.0 between 11.0. For adjusting pH, 0.1 N NaOH and 0.1 N HCl were used. In this analysis, initial dye concentration was determined as 100 mg L^{-1} and experiment was carried out at 35 °C.

Figure 1 pointed out that in the range of 3.0–7.0 the dye removal increased sharply and after pH 7.0 the amount of dye removal changes were little. Pavan et al (2008) have also found the best pH range between 7.0–10.0 for the MB removal due to the electrostatic interactions between adsorbent and MB.[13]

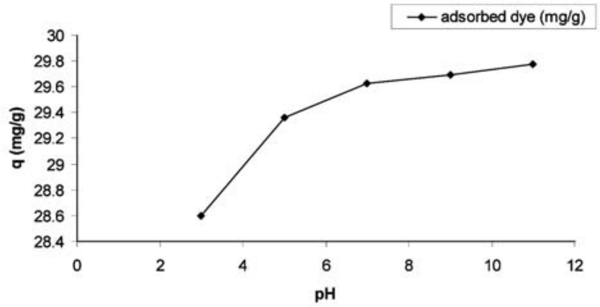

Figure 1. Effect of pH on MB adsorption onto *C. barbatula* (initial dye concentration: 100 mg L^{-1}, temperature: 35 °C).

3. 2. Effect of Adsorbent Dosage on the Adsorption of MB

The effect of adsorbent dosage for MB adsorption onto *C. barbatula* was shown in Figure 2. Initial dye concentration of MB was selected as 100 mg L^{-1}

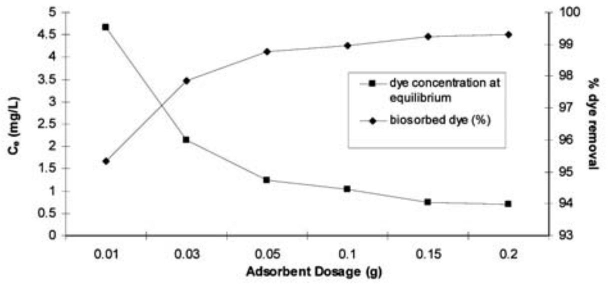

Figure 2. Effect of adsorbent dosage on MB adsorption onto *C. barbatula* (initial dye concentration: 100 mg L^{-1}, temperature: 35 °C).

The adsorbent dosages were taken between 0.01–0.25 g and initial dye concentration was determined as 100 mg L^{-1}. The results showed that when the adsorbent dosage increased, the removal of the dye increased as well. As Pavan et al (2008) reported, the more adsorption surface causes the more adsorption of MB yellow passion fruit waste.[13] In the present study, adsorption increased up to the value of 0.1 g adsorbent dosage then remained constant. Therefore, the adsorbent dosage in following experiments was selected as 0.1 g.

3. 3. Effect of the Contact Time and Temperature on the Adsorption of MB

In our study, we studied the effect of contact time to the adsorbed dye onto *C. barbatula* at various temperatures (25, 35 and 45 °C). It was very interesting to note that there were no remarkable differences among adsorption values at different temperatures studied. Therefore, the values at only 25 °C were presented in the present study.

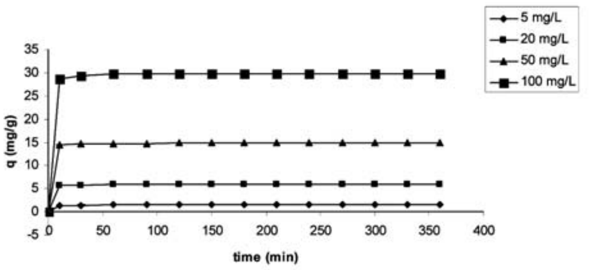

Figure 3. The adsorption of MB by *C. barbatula* at 5, 20, 50, 100 mg L^{-1} concentrations. The values are the mean of three separate experiments (T = 25 °C).

Figure 3 shows the plots of the amount of adsorbed dye (q_e) versus contact time t (min) at different dye concentrations. From the Figure 3 it can be observed that, both contact time and the quantity of adsorbed dye on *C. barbatula* increased at the same time. The results indicated that after 210 minutes the adsorption reached equilibrium in all concentrations.

3. 4. Adsorption Kinetics

Adsorption is a widely used process for interpreting the equilibrium amount between sorbent and sorbate. In our study, adsorption data are applied to the pseudo-first order and pseudo-second order kinetic models to find the rate constants of adsorption. Lagergren first order kinetic expression was used mostly in the literature to show adsorption capacity on different adsorbents.[14,15] Pseudo-first order equation is:

$$\log(q_e - q) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{3}$$

where q_e is the amount of dye adsorbed at equilibrium (mg g^{-1}), q is the amount of dye adsorbed (mg g^{-1}) at time t (min) and k_1 is the pseudo first order rate constant (min^{-1}).

Pseudo-second order can also describe the kinetic of the adsorption.[16] The equation is:

$$\frac{t}{q} = \frac{1}{k_2 . q_e^{\,2}} + \left(\frac{1}{q_e}\right)t \tag{4}$$

where k_2 is the pseudo second order rate constant (g mg^{-1} min^{-1}).

From log (q_e–q) versus time (min) graphs, the rate constants and correlation coefficient values of first order model were found at 298 K. As can be seen from Figure 4, the adsorption did not comply well with the first-order model for the adsorption of MB onto *C. barbatula* because of the absence of linearity at the plot between log (q_e–q) and t.

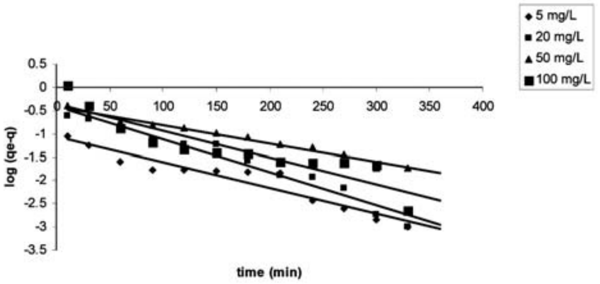

Figure 4. First-order sorption kinetics of MB by *C. barbatula* at different dye concentrations (Adsorbent dose = 0.1 g, T = 25 °C).

Pseudo-second order kinetic model is used as a presentation of chemisorption behaviour of the reaction.[8,16,17] In present study, pseudo second order model were fitted better when compared with the first order kinetic model (Table 2). Therefore, the adsorption data in the present study supported the chemisorption.

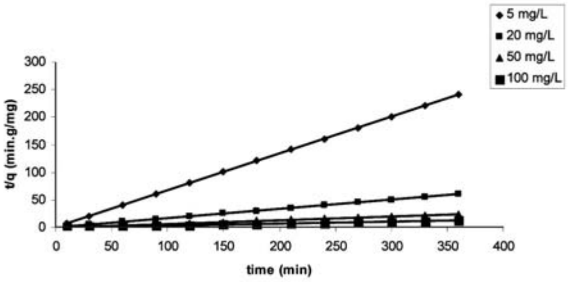

Figure 5. Pseudo-second order sorption kinetics of MB by *C. barbatula* at different dye concentrations (Adsorbent dose = 0.1 g, T = 25 °C).

The linearity of the plots also showed the appropriation of the model at 298 K (Figure 5). Table 2 showed the rate constants of the kinetic models at 298 K. As can be seen from the Table 2, the correlation coefficients (R^2) of the pseudo-second order model were higher than those of the correlation coefficients of the pseudo first order model.

3. 5. Adsorption Isotherms

The experimental data was estimated by using Langmuir, Freundlich and Dubinin-Radushkevich equations. In the present investigation, linearized form of the Langmuir and Freundlich equations were used to find the adsorption isotherms as shown below:

Langmuir[18]:

$$\frac{1}{q}=\frac{1}{q_m}+\frac{1}{bq_m}.\frac{1}{C_e} \tag{5}$$

Freundlich[19]:

$$\log q=\log K_F+\frac{1}{n}\log C_e \tag{6}$$

where q_m is the maximum adsorption capacity, C_e is the equilibrium concentration of dye at the equilibrium time, b is Langmuir constant; n and K_f are Freundlich constants.

Langmuir's isotherm is known as monolayer adsorption. In this process, adsorbate covers the specific area of the adsorbent.[18] In our study, we plotted $1/C_e$ versus 1/q to obtain the Langmuir constants. The results are given in Table 3.

As can be seen from Figure 6, Langmuir isotherm data gave a good linearity in the graph. Linear regression

Table 2: Pseudo first and second order adsorption kinetics at different initial dye concentrations for the adsorption of MB onto *C. barbatula* at 298 K.

		Pseudo first order rate constants			**Pseudo second order rate constants**		
C_i (mg/L)	**q_e, exp (mg/g)**	**k_1 (1/min)**	**q_e, cal (mg/g)**	**R^2**	**k_2 (g/mg.min)**	**q_e, cal (mg/g)**	**R^2**
5	1.495	0.0126	0.0844	0.9170	0.4603	1.4992	1
20	5.973	0.0163	0.3828	0.9590	0.1323	5.9916	1
50	14.920	0.0089	0.3714	0.9790	0.0794	14.925	1
100	29.817	0.0133	0.4439	0.8247	0.0943	29.850	1

Table 3: Langmuir, Freundlich and Dubinin-Radushkevich (DR) isotherm constants for the adsorption of MB by *C. barbatula.*

Langmuir constants				**Freundlich constants**				**Dubinin-Radushkevich constants**			
Tempe. (K)	**q_m (mg g^{-1})**	**b (L mg^{-1})**	**R^2**	**K_f**	**n**	**n_f**	**R^2**	**q_m (mg g^{-1})**	**Bx10^{-8} (mol^2 kj^{-2})**	**E (kj mol^{-1})**	**R^2**
298	21.929	2.5910	0.9935	39.884	1.2094	0.8268	0.9875	19.344	3.0	4.0824	0.8979
308	38.610	2.2920	0.9997	81.771	1.1057	0.9044	0.9631	24.727	3.0	4.0824	0.9693
318	–12.077	–1.710	0.9699	138.26	0.8343	1.1985	0.9623	51.893	10	2.2360	0.6928

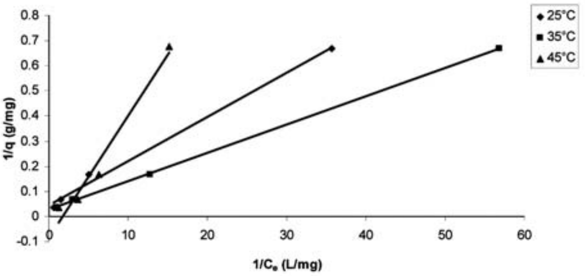

Figure 6. Langmuir isotherm plots for the adsorption of MB, by *C. barbatula* at different temperatures.

coefficient values were found as 0.9935, 0.9997 and 0.9699 at 298, 308, and 318 K, respectively.

Maximum adsorption capacity was observed 38.610 mg g^{-1} at 308 K. Langmuir isotherm determines the adsorption favorable or unfavorable. To determine the characteristic behavior of the adsorption, dimensionless equilibrium parameter is used.[20] The equation is given as:

$$R_L = \frac{1}{1+bC_o} \tag{7}$$

where b is the Langmuir constant and C$_o$ is the highest dye concentration (100 mg L^{-1}). The R$_L$ values were found 0.0038, 0.0043 at 298 and 308 K, respectively. For the favorable adsorption R$_L$ value must take place $0 < R_L < 1$. In our investigation, R$_L$ values confirmed that Langmuir isotherm was favorable for the adsorption of MB onto *C. barbatula*.

The plot of log q versus log C$_e$ describes Freundlich isotherm for the adsorption of MB by *C. barbatula* at different temperatures. Freundlich constants are shown in Table 3.

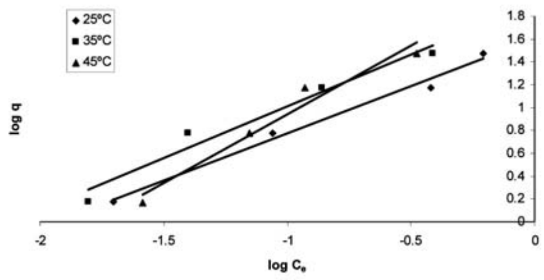

Figure 7. Freundlich isotherm plots for the adsorption of MB, by *C. barbatula* at different temperatures.

The slope value K$_f$ and the intercept value n$_f$ were estimated from the Freundlich isotherm equation. The results revealed that R^2, regression coefficient values were found 0.9875, 0.9631, and 0.9623 at 298, 308, and 318 K, respectively. In Table 3, K$_f$ values were increased by raising temperatures. Freundlich isotherm constant of n$_f$ indicates the heterogeneity factor. In the literature, n$_f$ values which are lower than 1 interpret the strong adsorption between adsorbent and adsorbate.[21]

To explain the adsorption form, physical, ion-exchange or chemical, Dubinin-Radushkevich equation[22–25] was used.

$$\ln q_e = \ln q_m - B\left[RT\ln(1+\frac{1}{C_e})\right]^2 \tag{8}$$

where q$_m$ is the amount of the ions sorbed onto *C. barbatula* (mg g^{-1}), B is a constant related to the sorption energy (mol^2 kj^{-2}), C$_e$ equilibrium concentration of dye (mg L^{-1}) and R is ideal gas constant (8.314 J mol^{-1} K^{-1}) and temperature (Kelvin).

ε is Polanyi potential is as follows:

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \tag{9}$$

The plots of ln q$_e$ versus ε^2 enable to calculate q$_m$ and B values at different temperatures from the slopes and intercepts. Energy related to adsorption can be found from the equation below[24]:

$$E = \frac{B^{-1/2}}{\sqrt{2}} \tag{10}$$

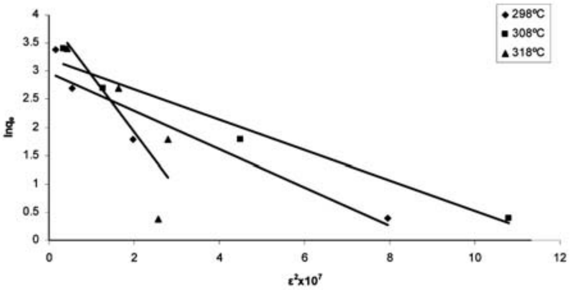

Figure 8. Dubinin-Radushkevich isotherm for the adsorption of MB at different dye concentrations (298, 308, 318 K).

Dubinin-Radushkevich expression determines the maximum adsorption capacity of the experiment[25]. The maximum adsorption capacities q$_m$ were found 19.344, 24.727, and 51.893 mg g^{-1} at 298, 308, and 318 K, respectively. It can be seen from the Table 3, q$_m$ values increased by raising temperatures. The magnitudes of E for the *C. barbatula* adsorption were found 4.082, 4.082 and 2.236 kj mol^{-1} at 298, 308, and 318 K, respectively. Smith (1981) determined that the range of energy of sorption at 2–20 kj mol^{-1} is physisorption.[26,27] According to these values adsorption in the present study, is in the physical nature.

Table 4. Comparison of maximum adsorption capacities of various materials for MB

Adsorbent	Temperature	pH	Equilibrium contact time	q_m (mg/g)	References
C. lentillifera	25	7±0.5	30 min	417	[5]
Oil Palm Fibre Activated carbon	30	6.5	24 h	277.78	[28]
Activated carbon	25	7±0.5	30 min	238	[5]
Giant duckweed	32	8	48 h	145	[29]
Yellow passion fruit waste	25	8	48 h	44.7	[13]
Rice husk	32	8	48 h	40.6	[30]
C. barbatula	35	6.4	210 min	38.61	This study
Posidonia oceanica fibres	30	6	3 h	5.56	[17]
C. racemosa var. *cylindracea*	18	7	90 min	5.23	[10]

Table 4 shows the maximum adsorption capacities of the various adsorbents related to Langmuir isotherm model. In the literature, when compared to the other algae adsorbents *C. barbatula* can be used as an alternative adsorbent due to its high adsorption capacity.

3. 6. Thermodynamic Parameters

To determine the Gibbs free energy (ΔG°), the enthalpy (ΔH°) and entropy (ΔS°) changes for the adsorption process of MB thermodynamic parameters are estimated from the equations below:

$$\ln K_d = \frac{-\Delta H^o}{R}\frac{1}{T} + \frac{\Delta S^o}{R} \quad \text{(Van't Hoff Equation)} \qquad (11)$$

$$K_d = \frac{C_s}{C_e} \qquad (12)$$

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

where C_e equilibrium concentration of dye (mg L^{-1}), C_s the amount of the dye at equilibrium (mg L^{-1}), R is ideal gas constant (8.314 J mol^{-1} K^{-1}), temperature (Kelvin).

Using the Van't Hoff Equation ln K_d versus 1/T was plotted (Figure 9). The enthalpy and entropy values were calculated from the slope and intercept, respectively. The results are shown in Table 5.

In the present study, ΔH° was found positive in all concentrations of dye. It indicates that the interactions between dye and alga are endothermic. At all temperatures the negative values of ΔG° showed that the adsorption was spontaneous.

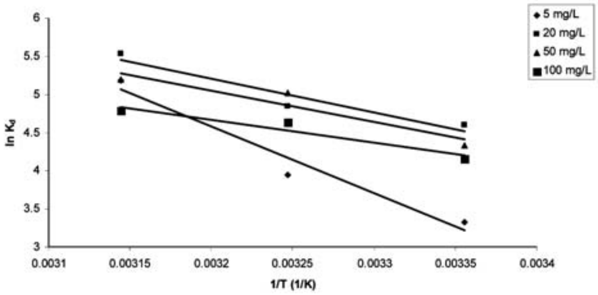

Figure 9. Plots of ln K_d versus 1/T for the adsorption of MB at different dye concentrations.

4. Conclusion

The experiment results showed that the brown alga *C. barbatula* could be used as an alternative low cost adsorbent in the removal of MB. The adsorption kinetics and isotherms parameters were found from pseudo first order, pseudo second order, Langmuir, Freundlich and Dubinin-Radushkevich equations. The contact time, adsorbent dosage and pH affected the adsorption of MB. The increased adsorbent dosage was affected positively the adsorption however, similar values were obtained after 0.1 g. In the present study, according to the experimental data pseudo second order model was fitted better when compared the linear regression correlation coefficient values. Langmuir

Table 5: Thermodynamic parameters of MB onto *C. barbatula* (T = 298, 308, 318 K).

			–ΔG (kj/mol)		
Concentration of dye (mg/L)	ΔH (kj/mol)	ΔS(j/mol K)	298 K	308 K	318 K
5	72.464	269.95	7.9811	10.680	13.380
20	36.595	160.40	11.204	12.808	14.412
50	33.974	150.69	10.931	12.438	13.945
100	25.102	119.15	10.404	11.596	12.787

model provided information about the uptake capabilities of *C. barbatula* and adsorption behaviors at different temperatures. Freundlich isotherm model indicated that the adsorption was heterogeneous. Dubinin-Radushkevich equation was used to understand the behavior of adsorption. The energy values were found 4.0824, 4.0824 and 2.2360 kj mol^{-1} respectively. These values demonstrated that adsorption process is in physical nature. According to Langmuir model, the maximum adsorption capacity was obtained 38.610 mg g^{-1} at 308 K. Thermodynamic parameters such as entropy ΔS^o, enthalpy ΔH^o and Gibbs free energy ΔG^o values showed that the adsorption process was endothermic and spontaneous. The present study revealed that *C. barbatula* can be used as an alternative low cost biosorbent for the removal of MB.

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Povzetek

Iz rjave alge Cystoseira barbatula Kützingm, ki je pogosta v Sredozemskem morju, smo pripravili nizkocenovni biosorbent za odstranjevanje barvila metilen modro (methylene blue, MB)iz vodnih raztopin. Z meritvami vpliva kontaktnega časa, temperature, pH in pa količine adsorbenta smo določili ravnotežno kapaciteto adsorpcije. Eksperimentalne podatke smo opisali z kinetičnim modelom psevdo-prvega in psevdo- drugega reda. Izkazalo se je, da kinetika pseudo- drugega reda bolje opiše proces adsorpcije. Uporabili smo tudi Langmuirjevo, Freundlichovo ter Dubinin-Radushkevich adsorpcijske izoterme. Z uporabo Langmuirjeve izoterme smo ocenili maksimalno kapaciteto adsorpcije, ki pri 35 °C znaša 38.61 mg g^{-1}. Z uporabo van´t Hoffove enačbe smo določili termodinamske parametre adsorpcije, ΔG^o , ΔH^o in ΔS^o. Ugotovili smo, da je obravnavan proces sicer spontan ($\Delta G^o < 0$), a endotermen proces. Vrednost entalpije je odvisna od koncentracije prisotnega MB.