# Biosorption Studies of Methylene Blue by Mediterranean Algae *Carolina* and Its Chemically Modified Forms. Linear and Nonlinear Models' Prediction Based on Statistical Error Calculation

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# Abstract

Biosorption experiments were carried out for the removal of the cationic dye Methylene Blue from its aqueous solution by the brown algae Carolina which is widely distributed in the Mediterranean Sea at Lebanese coast. Langmuir, Freundlich, Redlich-Peterson, Temkin, Elovich, and Dubinin-Radushkevich isotherm models were also investigated. The results showed that the experimental adsorption data were well represented by the Langmuir model for the linear regression analysis and both Langmuir and Redlich-Peterson isotherm models for the non-linear regression analysis. The maximum adsorption capacity  $q_{max}$  based on Langmuir is 55 mg/g at 19 °C. This confirms the monolayer coverage of Methylene Blue dye onto energetically homogenous Carolina surface. Negative values of Gibbs free energy revealed that adsorption process is spontaneous.

Carolina algae was chemically modified by treatment with NaOH,  $CaCl_2$  or formaldehyde. The biosorption of Methylene Blue was enhanced with the process of cross linking using formaldehyde with  $q_{max}$  of 64 mg/g. The results of isothermal study using modified algae also showed that the experimental adsorption data is well fitted into Langmuir model.

Keywords: Biosorption, Algae, Thermodynamics, Methylene Blue, Isotherm, Statistical error, Chemical modification

# 1. Introduction

Many dyes are used in textile, carpet, and cotton industries. There are many structural varieties of dyes that fall into either: azo, anthraquinone, xanthen, phtalocyanin group and other. These dyes cause pollution and toxicity problems due to their complex structure and synthetic origin.

Over 10,000 commercially available dyes exist and more than  $7 \times 10^5$  tones per year are produced annually (Pearce et al., 2003; Robinson et al., 2001). Due to their good solubility, synthetic dyes are common water pollutants and they are found in trace quantities in industrial wastewater. 2 % of produced dyes are discharged directly in aqueous effluent (Pearce et al., 2003; Robinson et al., 2001).

Minor releases of dyes impact the aesthetics and health of receiving bodies, causing imbalances in these ecosystems. Elimination of dyes from waste waters is one of the major environmental problems because of difficulty in treating such waste waters by conventional treatment methods, as most of the dyes are stable to light and oxidizing agents. Methylene Blue (MB), an organic cationic dye usually used to dye cotton and wool, can cause serious health problems such as vomiting, hard breathing, and mental disorder (Ghosh & Bhattacharyya, 2002). Possible treatments such as filtration, oxidation, sedimentation and adsorption for cotton textile wastes and their associated advantages and disadvantages are listed (Babu et al., 2007).

Adsorption techniques for waste water treatment have become more popular in recent years owing to their efficiency. Activated carbon is mainly used to remove dyes from aqueous solutions due to its high adsorption capacity, but it is very expensive. Many reviews appeared in literature about the low cost adsorbents used (Allen & Koumanova, 2005; Rafatullah et al., 2010). Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dye removal (Babu et al., 2007; Allen & Koumanova, 2005; Rafatullah et al., 2010; Nandi et al., 2008).

The use of algae for the removal of color from its aqueous solution is a recent method for treatment of waste water (Caparkaya & Cavas, 2008; Kumar et al., 2005). Marine algae have been also reported to have high metal binding capacities due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals (Caparkaya & Cavas, 2008; Ho, 2004). In this project the ability of marine algae (Carolina) and its chemically modified form to remove the basic dye Methylene Blue is studied.

# 2. Experimental

# 2.1 Sorption equilibrium

The case of a sorption process considered here involves a solid phase (sorbent: algae) and a liquid phase containing a dissolved species to be sorbed (sorbate: dye) (Volesky, 2003).

The uptake of dye by the sorbent Q is defined as the amount of dye in (mg) bound by 1g of solid phase:

$$q(mg/g) = \frac{(C_i - C_f) \times V}{m} \tag{1}$$

To determine the percentage of dye removal, the following equation is used:

% dye removal = 
$$\frac{C_o - C_f}{C_o} \times 100$$
 (2)

Where: m (g) is the amount of added sorbent (algae). V (L) is the volume of sorbate solution contacted (batch) with the adsorbent.  $C_i$  and  $C_f$  (mg/L) are the initial and final (equilibrium) concentrations of the sorbate in solution, respectively.

# 2.2 Sorbent Preparation

The marine algae was collected from Lebanese shore El Manara. The seaweed was washed with tap water to remove salt, epiphytes and other contaminants and then with distilled water again. The material was dried at 70  $^{\circ}$ C for 16 h, then grounded with mortar and stored in a dessicator.

# 2.3 Chemical modification of algae

Different pre-treatments of biomass by chemical modification have been tested to improve its stability as well as its adsorption capacity, making it suitable for industrial use.

# 2.4 Pre-Treatment with NaOH

15 g of biomass were weighed and washed twice with 0.1 M HCl, followed by centrifugation at 2800 rpm and then washed again with deionized water. The biomass was then reacted with 150 mL of 0.1 M NaOH for 24 h.

The mixture was centrifuged and the collected biomass was washed three times with deionized water, then dried in an oven at 60  $^{\circ}$ C for 24 h (Baig et al., 1999).

# 2.5 Pre-treatment with CaCl<sub>2</sub>

5 g of dried biomass was treated with 200 mL of 0.2 M CaCl<sub>2</sub> solution at pH 5. The mixture was shaken for 24 h on a rotary shaker at 175 rpm and room temperature. The biomass was then filtered off followed by washing with deionised water to remove the excess of calcium and it was dried in an oven at 60  $^{\circ}$ C for 24 hours (Matheickal et al., 1999).

# 2.6 Pre-treatment with Formaldehyde (cross-linking)

A mixture of 17 mL of 36 % formaldehyde and 33 mL of 0.1 M HCl solutions was added to 2.5 g of dried biomass. The mixture was stirred for 1 h. The biomass was then filtered off, washed with distilled water, 0.2 M Na<sub>2</sub>CO<sub>3</sub> and finally with distilled water. It was dried overnight at 60 °C and at 110 °C for 2 h, (Leusch et al., 1995).

# 2.7 Isotherm Experimental Procedure

The experiment was done by agitating a mixture of 0.1 g of sorbent (algae) and 30 mL of sorbate MB (10 - 1000 mg/L) at 215 rpm in a shaking incubator (SHIN SAENG SKIR-601 model) for 4 h at constant temperature and pH = 7. The solutions were then separated from the sorbent by centrifugation using centrifuge (Centuriol scientific LTD) for 5 min at 3000 rpm. The temperatures used are 19, 25 and 39 °C.

In order to determine the concentration of solution, the absorbance was measured at  $\lambda max = 663$  nm using UV -Visible Spectrophotometer (Jasco-V530 double beam).

# 2.8 FTIR Analysis

FTIR spectrophotometer (Shimadzu 8300) was used for the determination of functional groups on algal surface. Pellets were prepared with 3 mg algae and 100 mg KBr.

# 2.9 Thermal analysis

Thermogravimetric–differential scanning calorimetry (TG-DSC) curves were recorded on SETARAM LABSYS Thermal analyser in the flow of  $N_2$  within the 20 - 950 °C temperature range, with a heating rate of 3 °C/min, (Hammud et al., 2006).

# 3. Results and discussions

# 3.1 Characterization of algae by FTIR

FTIR spectroscopy offers excellent information on the nature of the bonds present on the surface of Carolina algae. Several intense characteristic bands in the IR spectra can be attributed to functional groups present in seaweed and in polysaccharides. The results are shown in Table 1. The peaks obtained from grinded algae attributed to functional groups are at: 3412 (–OH, NH<sub>2</sub>), 2400 - 3000 (–COOH), 1030 (C-O) and 1633 (C=O) cm<sup>-1</sup>. The IR spectra of algae with adsorbed Methylene Blue showed a minor shift in the IR stretch of functional group such as (> C=O) shows a greater shift in IR as a result of chelation (Hammud et al., 2006).

# 3.2 Optimum condition

# 3.2.1 Effect of Adsorbent Dosage

The effect of adsorbent dosage for MB adsorption onto *Carolina* is shown in (Fig. 1). Initial dye concentration of MB was selected as 20 mg/l, the adsorbent dosage was taken between (0.01 - 0.20 g), and the solution volume was 30 mL. The results showed that when the adsorbent dosage increased, the % removal of dye increased as well. Since an increase in mass of algae provides more binding sites. The optimum algae mass was found equal to 0.1 g.

# 3.2.2 Effect of shaking

The adsorption of MB on algae was done in two ways soaking and shaking, Fig. 2. The results showed that the equilibrium adsorption with shaking is obtained in short time compared to soaking. By shaking the dye is brought faster into contact with algae sites, while by soaking the contact is achieved only by the slow diffusion process from solution.

# 3.2.3 Effect of pH

The pH of solution is an important parameter for controlling the sorption process. The interaction between sorbate (dye) and sorbent (algae) is mainly affected by ionization states of the functional groups on both dye molecule and biosorbent surface.

The adsorption of MB onto Carolina algae was studied in solution with pH range between 1.8 and 10.0 by addition of diluted NaOH and HCl solution (0.1 M). The initial dye concentration and the weight of Carolina algae was maintained at 20 mg/L and 0.1g respectively at 25  $^{\circ}$ C. The sorption capacity of biosorbent increased with increasing initial solution pH from 1.8 to 6, and then it remains constant, indicating that the optimum pH is 7, Table 2.

At low pH the functional groups present on algae such as hydroxylic and carboxylic groups are neutral and the amino groups are in cationic form providing weak attraction with cationic dye MB. While at neutral and high pH the amino groups are neutral and the hydroxylic and carboxylic groups are in anionic forms providing strong electrostatic attraction with dye (Negative adsorption).

# 3.2.4 Effect of contact time on the adsorption of MB

We studied here the effect of contact time of adsorbed dye onto Carolina at temperature 25  $^{\circ}$ C and at different dye concentrations (10, 20 and 50 mg/L). Fig. 3 shows the plots of the capacity q (mg/g) versus contact time t (min.). It was found that q increased with increase in initial dye concentration. q also increased with increase in contact time until an optimum time is reached at t = 20 min.

#### 3.3 Adsorption isotherm

#### 3.3.1 Adsorption isotherm model

The biosorption equilibrium describes the distribution of a solute phase between the liquid phases and solid phases after the sorption reaction reached equilibrium condition. In the present work, equilibrium studies were carried out at three temperatures (19, 25, and 39  $^{\circ}$ C). The equilibrium data were analyzed using most commonly used isotherms equations: Langmuir, Freundlich, Redlich-Peterson, Temkin, and Elovich models. The nonlinear and the linearized isotherm models expressions are given by the equations described below:

i Model (1): *Langmuir model* (Langmuir 1918). The Langmuir isotherm considers sorption as a chemical phenomenon. Langmuir's isotherm is known as monolayer adsorption onto a surface with a finite number of similar active sites. The well known nonlinear expression of the Langmuir model is given by Eq. (3) and the derived linear forms in Eq. (4) respectively:

$$Q_e = \frac{Q^0 K_L C_e}{1 + K_L C_e} \tag{3}$$

$$\frac{1}{Q_e} = \frac{1}{Q^0 K_L} \frac{1}{C_e} + \frac{1}{Q^0}$$
(4)

where  $Q^0$  (mg/g) is the maximum sorbate uptake under the given condition.  $K_L$  is a coefficient related to the affinity between the sorbent and sorbate.

Langmuir isotherm determines whether the adsorption is favorable or unfavorable. To determine the

characteristic behavior of the adsorption, dimensionless equilibrium parameter is used:  $R_L = \frac{1}{1 + K_L C_o}$ . Where

C<sub>o</sub> is the highest initial dye concentration. For a favorable adsorption R<sub>L</sub> value must be between 0 and 1.

ii Model (2): *Freundlich model* is based on sorption onto a heterogenous surface (Freundlich, 1906). The Freundlich relationship is exponential, Eq. (5):

$$Q_e = K_F (C_e)^{1/n} \tag{5}$$

The linear form of Freundlich equation, Eq. (6) is:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{6}$$

where:  $K_{\rm F}$  and *n* are Freundlich constants.

The Freundlich isotherm constant  $n_F = (1/n)$ , indicates the heterogeneity factor. In the literature,  $n_F$  values lower than 1 indicate the existence of strong adsorption between adsorbent and sorbate (Freundlich, 1906).

iii Model (3): *Redlich-Peterson* model is a general equation that includes both Freundlich and Langmuir features (Redlich & Peterson, 1959).

$$Q_e = \frac{A_{RP}C_e}{1 + K_{RP}(Ce)^{\beta}} \tag{7}$$

where  $A_{RP}$ ,  $K_{RP}$ , and  $\beta$  are parameters to be estimated.  $\beta$  lies between 0 and 1, it has two limiting behaviors: Langmuir form for  $\beta = 1$  and Henry's law form for  $\beta = 0$ .

iv Model (4): *Temkin* model: Explain sorbent/sorbate interactions in relation to heat of adsorption (Temkin, 1941). Non linear and linear Temkin equations 8 and 9 are:

$$Q_e = \frac{RT}{b} \ln(K_T C_e) \tag{8}$$

$$Q_{\rho} = B_T \ln(K_T) + B_T \ln(C_{\rho}) \tag{9}$$

where  $B_T = (\text{RT}/b)$  is a factor related to the heat of adsorption and  $K_T$  is Temkin equilibrium constant (L/mg).

v Model (5): *Elovich* model: deals with multilayer adsorption, based on a kinetic principle that adsorption site increase exponentially with adsorption.  $K_E$  is Elovich equilibrium constant and  $Q_E$  is Elovich maximum adsorption capacity (Elovich & Larinov, 1962). Non linear and linear Elovich forms are described in equations 10 and 11.

$$\frac{Q_e}{Q_E} = K_E C_e \exp(-\frac{Q_e}{Q_E}) \tag{10}$$

$$\ln(\frac{Q_e}{C_e}) = \ln(K_E Q_E) - \frac{Q_e}{Q_E}$$
(11)

#### 3.3.2 Computational method and error calculation (unmodified algae)

In the following, the computational part of the obtained experimental measurements is introduced. To obtain the curve which best fits the data in least-squares sense, the following minimization problem is solved by calculating:

Half the sum of squares of errors (F):

$$F(x) = (1/2)\sum \left(f(x, xdata_i) - ydata_i\right)^2$$
(12)

where  $xdata_i$  and  $ydata_i$  are the experimental measurements, and  $f(x, xdata_i)$  is a function of the linear or nonlinear curve proposed to fit the given data. The  $xdata_i$  is the equilibrium concentration  $C_e$ . The value of the objective function F(x) measures the discrepancy between the considered model  $f(x, xdata_i)$  (the calculated adsorption capacity  $Q_{e,calc}$ ) and the observed data  $ydata_i$  (the experimental adsorption capacity  $Q_{e,exp}$ ). The computational package of MATLAB is considered for solving the data fitting problem. In particular we have used the function lsqcurvefit from the optimization toolbox of MATLAB to do this job. The solution of this problem yields the best values of the parameters in the used model. Five models have been tried in our computations using linear and nonlinear equations. The least value of F(x) indicates that the corresponding curve is the best one among the five isotherm model. This should be also supported with the highest value of commonly used regression correlation coefficient  $R^2$ . The obtained final parameters values of the optimization solver lsqcurvefit are given in Table 3. Moreover, we have calculated closely related error functions described below in order to support the conclusion about the best-fitting equation for each models. Table 4 lists the results for nonlinear expression, and Table 5 for linear expression.

Average relative error deviation (ARED)

$$ARED = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{f(x, xdata_i) - ydata_i}{ydata_i} \right| x100$$
(13)

Where N is the number of data point

The Marquardt's percent standard deviation (MPSED)

$$MPSED = \sqrt{\frac{\sum_{i=1}^{N} \left(\frac{f(x, xdata_i) - ydata_i}{ydata_i}\right)^2}{N - P}} x100$$
(14)

Where P is the number of parameters in each isotherm model. *The hybrid fractional error function (HYBRID):* 

$$HYBRID = \frac{1}{N-P} \sum_{i=1}^{N} \left| \frac{f(x, xdata_i) - ydata_i}{ydata_i} \right| x100$$
(15)

*Chi-square test*  $(\chi^2)$ 

$$\chi^{2} = \sum_{i=1}^{N} \frac{\left(f(x, xdata_{i}) - ydata_{i}\right)^{2}}{f(x, xdata_{i})}$$
(16)

Correlation coefficient of Pearson (r)

$$r = \frac{N(\Sigma XY) - (\Sigma X)(\Sigma Y)}{\sqrt{\left[N \Sigma X^2 - (\Sigma X)^2\right] \left[N \Sigma Y^2 - (\Sigma Y)^2\right]}}$$
(17)

Where  $X = ydata_i$  and  $Y = f(x, xdata_i)$ Coefficient of determination  $(r^2)$ 

$$r^2 = \frac{S_{XY}}{S_{(XX)}S_{(YY)}} \tag{18}$$

Where S(XY) is the sum of squares of X and Y, S(XX) is the sum of squares of X and S(YY) is the sum of squares of Y.

#### Squared correlation coefficient $(R^2)$

Where *R* is the correlation between the experimental data and the used model. This error function is defined as:

$$R = \frac{\sum (X - \overline{X})(Y - \overline{Y})}{\sqrt{\sum (X - \overline{X})^2 (y - \overline{y})^2}}$$
(19)

Determination of the best fitting isotherm model is based on the use of the eight error functions described above, by calculating the error deviation between experimental and predicted equilibrium adsorption data, for both linear and nonlinear analysis.

From the values of  $F_{final}$  (smallest one) and  $R^2$  (highest one) in the overall results of the considered four models one sees that Langmuir and Redlich-Peterson model represents the best fitting curve using nonlinear expression, Table 4. Langmuir model is also the best fit for linear expression, Table 5. Fig. 4 and Fig. 5 show the four best fitting curves together with the experimental data at T = 25 °C and 39 °C respectively using nonlinear models.

According to the results of Langmuir model described in Table 3, the adsorption capacity  $Q^0$  decreases with increasing temperature. The R<sub>L</sub> values obtained ranging from 0.02 - 0.2, which lies between 0 and 1, confirmed that Langmuir isotherm was favorable for the adsorption of MB onto *Carolina*. Linearized form of Langmuir equation Eq. (4) was plotted as  $1/Q_e$  vs  $1/C_e$ , Fig. 6. Parameters are listed in Table 3.

The slope value  $K_F$  and the intercept value  $n_F$  were estimated from the Freundlich linear isotherm equation Eq. (6), are shown in Table 3, Ln  $K_F$  is roughly a measure of the adsorption capacity. The results revealed that

regression coefficient values ( $R^2$ ) were found smaller than those obtained with Langmuir isotherm using linear and non linear model respectively. The  $n_F$  values obtained (Table 3) are lower than 1 indicating strong adsorption between the adsorbent and adsorbate (Basha et al., 2008). The calculated error is greater in the case of Freundlich compared to Langmuir which rules out the application of this model to this adsorption study.

The sorption process can also be represented by the Redlich-Peterson model, based on the low values of error functions and high "r"-functions. Also, the obtained value of  $\beta$  is equal to 1.0, Table 3. This means that the Redlich-Peterson equation is transformed into the Langmuir expression which is the best observed model in our study.

It is clear that *F* with appreciable numerical value help better to make the conclusion about the best model compared to  $R^2$  with decimal values. Taking nonlinear model at T = 25 °C as an example, and comparing Langmuir versus Freundlich model the "F" value greatly increase from 4.6635 to 148.1372 in comparison with a slight decrease in  $R^2$  value from 0.996 to 0.855, Table 4. Also, *F* value greatly changes from 4.664 (Langmuir model) to 56.957 (Temkin model) compared to negligible decrease in  $R^2$  from 0.996 to 0.942 respectively, Table 4.

While an increase in initial  $C_o$  leads to higher increase in  $Q_e$ , this also leads to higher values in non "r" error function and lower values in "r" error function:

A decrease in C<sub>o</sub> from 1000 mg/L (at T = 19 °C) to 217 mg/L (at T = 39 °C) and using Freundlich non linear model as an example, causes a large decrease in non "*r*" error function (*F*, *ARED*, *MPSED*, *HBRID*, and  $\chi^2$ ) from 143.297, 27.195, 67.594, 33.994 and 10.52 to 6.716, 11.707, 17.324, 16.389 and 1.099 respectively. In parallel with a slight increase in "*r*" error function ( $R^2$ , *r*, and  $r^2$ ) from 0.884, 0.942, and 0.887 to 0.973, 0.987, and 0.974 respectively.

Transforming the data from non linear to linear isotherm form can lead to the alteration of the isotherm constants and error distribution:

The Langmuir and Freundlich models are affected by whether the analysis is carried out linearly or nonlinearly. The calculated constants and error slightly differ by whether the analysis is carried linearly or nonlinearly for Langmuir model (except for F value). This difference is more profound in the case of Freunlich model which shows relatively greater difference in the parameter values. Taking Freundlich model at T=19  $^{\circ}$ C, the non "r" error values range from 10.5 to 143.3 for non linear model, whereas for linear model the range is from 0.2 to 11.2, Table 4 and 5.

The values of the isotherm constants greatly differ in the case of Linearization of Elovich model. The values of the error functions are also high and they greatly differ between linear and nonlinear model. This implies that the Elovich model is not applicable to our study, and the sorption mechanism does not involve a multilayer adsorption and that the adsorption sites do not increase exponentially, Table 3-5.

In the case of Temkim model, the deduced constants and the calculated error deviation are similar for Linear and nonlinear model, which is expected because of the mathematical expression are closely related, Table 4 and 5.

#### Dubinin-Radushkevich isotherm

In order to explain whether the adsorption process is physical, ion-exchange or chemical, Dubinin-Radushkevich equation is used (Dubinin and Radushkevich 1947):

$$Q_e = Q_m \exp^{\beta [RT \ln(1 + \frac{1}{Ce})]^2}$$
(20)

Where  $Q_m$  is the maximum amount of ions sorbed onto Carolina (mg/g),  $\beta$  is a constant related to the sorption energy (mol<sup>2</sup>/kj<sup>2</sup>),  $C_e$  equilibrium concentration of dye (mg/L) and *R* is ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and *T* is temperature in (Kelvin).

The plots of  $Q_e$  versus  $\varepsilon$  enable to calculate  $Q_m$  and  $\beta$  values at different temperatures, where  $\varepsilon = \text{RTln}(1 + 1/\text{Ce})$ .

Energy related to adsorption *E* can be found from the equation below:  $E = \frac{1}{\sqrt{-2\beta}}$ .

The maximum adsorption capacity  $Q_m$  of the experiment calculated from Dubinin-radushkevich (nonlinear model Eq. (20) are 49.2, 41.9 and 26.5 mg/g at 19, 25, and 39 °C respectively. These values are slightly different from those calculated from Langmuir model. The  $R^2$  values (0.875, 0.93, and 0.869) are also lower than those reported for Langmuir model in Table 5.

The magnitudes of *E* for the Carolina adsorption were found 70.72, 111.80 and 111.80 J/mol respectively. These values of E are smaller than 8 kJ/mol, indicating that the adsorption process is physical in nature (Islam & Patel, 2007).

3.3.3 Isothermal study of adsorption of MB by modified algae

This experiment was done by weighing 0.1 g of NaOH-modified algae in a set of conical flasks containing different concentrations of MB ranging from 20 to  $10^3$  mg/L then the conical flasks were shaken for 4 hours at 220 rpm, at T = 19 °C and pH 6.6.

The experiment was repeated for two other algae which are modified by  $CaCl_2$  and Formaldehyde. Langmuir, Feundlich, and Temkin isotherms were studied for the three kinds modified of algae. The results and constants parameters were shown in Table 6. Langmuir model is the most suitable isotherm that fit the obtained data and describes well the adsorption behavior of Methylene Blue onto modified Carolina algae, according to the value of  $R^2 = 0.97$ -1.00, Table 6. Linear Langmuir isotherm is plotted in Fig. 7.

The maximum uptake ( $q_{max} = 64 \text{ mg/g}$ ) was found by the adsorption of the algae modified with Formaldehyde, the  $R_L$  values confirmed that Langmuir isotherm was favorable for the adsorption of MB onto modified *Carolina sp*. We found that the uptake increased about 18 % by using the Formaldehyde modified algae compared to unmodified algae. This can be explained by the fact that binding sites are increased in the surface of biomass. The cross linking treatment is reported to diffuse into an existing cellulosic framework and reinforce it internally with short brides R-(OCH<sub>2</sub>-), (Volesky, 2003).

The carboxylate ions are also responsible for cationic dye binding by the biomass. This means that dye binding can be enhanced by increasing these ions in the biomass (Baig et al., 1999). Cellulose, and lignin, which are major constituents of most plant tissues, contains methyl esters which do not bind the cationic dye. However, these esters can be modified to caboxylate by treating the biomass with base such as NaOH.

Table 7 shows the maximum adsorption capacities of various adsorbents related to Langmuir isotherm model (Caparkaya & Cavas, 2008; Marungrueng & Pavasant 2007; Ncibi et al., 2007). The high adsorption capacity of Carolina algae let it competitive with other adsorbent.

# 3.3.4 Thermodynamic Study

To determine the Gibbs free energy ( $\Delta G^{\circ}$ ), the enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) changes for the thermodynamic parameters of adsorption process of MB by unmodified algae are estimated from the equations below:

$$\ln K_d = \frac{-\Delta H^o}{R} \times \frac{1}{T} + \frac{\Delta S^o}{R}$$
(21)

$$K_d = \frac{C_s}{C_a} \tag{22}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{23}$$

Where  $K_d$  is the adsorption equilibrium constant,  $C_e$  is the equilibrium concentration of dye (mg/L) in aqueous solution,  $C_s$  is the amount of the dye at equilibrium (mg/L) adsorbed in the solid algae, R is ideal gas constant (8.314 J/mol K), and T is the temperature in Kelvin.

By plotting Ln  $K_d$  vs. 1/T (K), the enthalpy and entropy values were calculated from the slope and intercept respectively. The results are shown in Table 8. In the range of temperature studied (292 - 312 K), the adsorption is exothermic ( $\Delta H < 0$ ), increasing order ( $\Delta S < 0$ ) and spontaneous ( $\Delta G < 0$ ).

# 3.4 Thermal analysis

The algae materials were heated up to 950  $^{\circ}$ C, where all relevant weight loss was complete. The % mass loss and (enthalpy change J/g at each peak temperature  $^{\circ}$ C) respectively for Carolina algae are:

3.8 % (50.0 J/g, 59 °C), 10.4 % (-112.5 J/g, 335 °C), 7.3 % (70.1 J/g 471 °C), 45.2 % (853 J/g, 787 °C. The % weight of the obtained white residue mainly CaO is 33.3%.

The results of thermogravimetric analysis of algae with biosorbed Methylene Blue is shown in Fig. 8. The % mass loss and temperature for algae with adsorbed Methylene Blue are: 2.5 % (38.8 J/g, 62 °C), 9.9 % (-30.5 J/g, 312 °C), 7.0 % (380 - 580 °C), 46.0 % (954.7 J/g, 786 °C). The % weight of gray residue obtained from MB treated

algae is 34.6 % which consist of mixture of mainly white CaO and black carbonaceous materials. The 1.3 % difference in the weight between the residues obtained from MB treated algae and free algae can be attributed to the carbon materials formed from Methylene Blue upon heating.

The sharp decrease at 786  $^{\circ}$ C for both cases associated with major weight loss and high endothermic heat energy is due to the conversion of CaCO<sub>3</sub> (s) to CaO (s) and CO<sub>2</sub> (g). The theoretical % weight loss due to loss of CO<sub>2</sub> gas in this step is 44 %. The experimental % loss for free algae is 45 %, while for MB treated algae it is 46 %. The weight loss occurring before this step (from 50 - 600  $^{\circ}$ C) is due to organic materials decomposition and volatilization.

# 4. Conclusion

The adsorption equilibrium occurred in less than 2 hours with agitation, and about 24 hours by soaking. Adsorption increased with increasing MB concentration. Fitting the data to nonlinear equation clearly distinguish the best model more than the fitting to linear equation. The *F* value is a good indicator for the best fitting model and is also competitive with  $R^2$  values. The experimental data is best fitted using Langmuir and Redlich-Peterson isotherms. The adsorption capacity  $q_{max}$  decreases with an increase in temperature. The high uptake value of Carolina algae (~ 55 mg/g) let us suggest it as promoting adsorbent for wastewater treatment. The negative values of  $\Delta G$  indicate that adsorption of MB onto Carolina is a favorable process.

The biosorption of Methylene Blue onto modified *Carolina sp.* was enhanced with the process of cross linking with formaldehyde. The results of isothermal study using modified algae showed also that the experimental adsorption data is well fitted with Langmuir model.

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Table 1. Functional groups of dried pure algae and algae with adsorbed Methylene Blue and their corresponding wave number in cm<sup>-1</sup>

Functional group	Standard wavenumber*	Wavenumber (pure algae)	Wavenumber (algae + MB)
-OH	3250-3700	3412	3410
-NH <sub>2</sub>	3300-3500	3412	3410
-COOH	2400-3000	2929	2933
C=O	1550-1750	1650	1650
С-О	1050–1300	1033	1030
Alkyl: CH 2900-3000		2929	2933
Aromatic ring	1350–1450	1417	1420

\*(Volesky 2003)

pH <sub>initial</sub>	$\mathrm{pH}_{\mathrm{final}}$	% removed	q <sub>max</sub>
1.8	1.68	40.0	2.40
2.8	7.85	65.0	3.90
3	8.12	66.3	4.00
3.7	8.23	72.8	4.37
5.8	8.28	78.0	4.68
6.8	8.39	79.5	4.80
9.8	8.35	78.3	4.70

Table 2. Variation of q and % of dye removed as a function of pH

Table 3.	Optimal	values	of the	non I	Linear	and	linear	models	parameters	for	the c	ases	of T =	- 19	°C,	T =	25	Ĉ,
and $T = 3$	9°℃																	

	T = 1	19 ℃	T = 2	25 ℃	T = 3	39 ℃
Model and parameters	Non Linear	Linear	Non Linear	Linear	Non Linear	Linear
Langmuir						
$Q^{ m 0}$	55.0877	54.1	46.4007	51.89	40.6969	37.4
$K_L$	0.0242	0.0268	0.0350	0.0236	0.0225	0.0253
$R_L$	0.0397	0.036	0.0292	0.0416	0.170	0.154
Freundlich						
$K_F$	10.0601	4.3842	9.8949	4.8800	2.5632	1.872
n	3.8685	2.4938	4.1983	2.743	1.9145	1.653
$n_F$	0.2585	0.4010	0.2382	0.3646	0.5223	0.604
Redlich-Peterson						
$A_{RP}$	1.60619		1.4202		0.88409	
$K_{RP}$	0.03965		0.0229		0.01752	
В	0.95315		1.0460		1.04321	
Temkin						
$B_T$	9.1422	9.1422	7.8403	7.8403	8.6505	8.6505
$K_T$	0.5097	0.5097	0.5705	0.5705	0.2412	0.2412
Elovich						
Q	21.9884	16.6667	21.8233	13.8889	24.3462	22.2222
$K_E$	0.0793	0.1408	0.0722	0.1851	0.0415	0.04793

Error function	$R^2$	F(x)	ARED	MPSED	HYBRID	$\chi^2$	r	$r^2$
Langmuir								
(T = 19)	0.9518	59.5525	6.6744	8.4060	8.3431	2.4798	0.9756	0.9518
(T = 25)	0.9962	4.6635	5.8444	11.6992	7.3055	0.6893	0.9981	0.9962
(T = 39)	0.9961	0.9953	4.0823	5.4566	5.7152	0.1518	0.9980	0.9961
Freundlich								
(T = 19)	0.8835	143.2965	27.1949	67.5938	33.9936	10.5192	0.9420	0.8873
(T = 25)	0.8503	148.1372	30.3598	62.9726	37.9498	12.9959	0.9248	0.8552
(T = 39)	0.9733	6.7157	11.7067	17.3241	16.3894	1.0990	0.9871	0.9743
Redlich-Peterson								
(T = 19)	0.9427	57.5739	6.2933	7.9521	7.8666	2.3300	0.9763	0.9532
(T = 25)	0.9982	1.9853	3.5003	7.9628	5.0004	0.3233	0.9991	0.9982
(T = 39)	0.9813	0.99626	4.08995	5.4300	5.7260	0.1517	0.9981	0.9961
Temkin								
(T = 19)	0.9445	68.2471	8.1721	10.7170	10.2151	2.9400	0.9719	0.9445
(T = 25)	0.9424	56.9573	14.6017	23.5051	18.2522	4.3516	0.9708	0.9424
(T = 39)	0.9849	3.7835	10.2461	18.5464	14.3445	1.4131	0.9924	0.9849
Elovich								
(T = 19)	0.9218	0.06435	63.6364	96.6415	79.5455	0.3828	0.9622	0.9259
(T = 25)	0.8428	0.1288	80.998	158.63	101.25	0.6824	0.8495	0.9217
(T = 39)	0.9359	0.00814	9.2417	12.2603	12.9385	0.03220	0.9676	0.9362

Table 4. Isotherm error values with the considered	nonlinear models, at different temperatures T (°C)	)
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Table 5. Isotherm error values with the considered linear models, at different temperatures T ( $^{\circ}$ C)

Error function	$R^2$	F(x)	ARED	MPSED	HYBRID	$\chi^2$	r	$r^2$
Langmuir								
(T = 19)	0.999	1.15x10 <sup>-5</sup>	5.6519	8.0222	7.0649	0.0010	0.9996	0.9992
(T = 25)	0.993	7.29x10 <sup>-5</sup>	7.4180	9.9843	9.2726	0.0028	0.9969	0.9938
(T = 39)	0.990	$1 \times 10^{-4}$	5.0397	6.3920	7.0555	0.0018	0.9952	0.9903
Freundlich								
(T = 19)	0.886	0.2868	7.3175	11.2397	9.1469	0.2064	0.9414	0.8863
(T = 25)	0.851	0.3514	7.8426	12.0647	9.8032	0.2496	0.9228	0.8516
(T = 39)	0.973	0.0336	3.3372	4.5642	4.6721	0.0260	0.9865	0.9731
Temkin								
(T = 19)	0.944	68.247	8.1726	10.718	10.2157	2.9401	0.9719	0.9445
(T = 25)	0.942	56.957	14.6011	23.503	18.2514	4.3517	0.9708	0.9424
(T = 39)	0.984	3.7835	10.2446	18.547	14.3425	1.4133	0.9924	0.9850
Elovich								
(T = 19)	0.844	0.8217	44.8576	137.98	56.072	-0.8727	0.9189	0.8443
(T = 25)	0.802	0.8217	71.3198	392.46	89.150	0.1404	0.8957	0.8023
(T = 39)	0.944	0.5775	84.8646	114.81	118.81	-2.3343	0.9716	0.9440

Kin		Lang		]	Freundlie	Temkin				
		q <sub>max</sub> (mg/g)	b (L/mg)	R <sup>2</sup>	$R_{\rm L}$	$\mathbf{k}_{\mathrm{F}}$	n	R <sup>2</sup>	В	R <sup>2</sup>
Raw algae		55	0.0127	0.999	0.073	4.38	2.5	0.886	9.38	0.980
Algae	Formaldehyde	64	0.0336	0.970	0.0358	5.59	2.725	0.858	8.425	0.941
modified	NaOH	58	0.03	0.969	0.04	5.77	3.02	0.740	5.868	0.831
with	CaCl <sub>2</sub>	43	0.048	0.993	0.0253	5.9	3.2	0.839	5.8625	0.945

Table 6.	The result	of the isothern	n study in line	ear form for the	e three modified	algae at 19°	С
						2, 2	

Table 7. Comparison of maximum adsorption capacities of various materials for MB dye

Adsorbent	Temperature (K)	q <sub>max</sub> (mg/g)	Reference		
Activated carbon	298	238	(Marungrueng, Pavasant 2007)		
C. Barbutula	308	38.6	(Caparkaya, Cavas 2008)		
Posidonia oceanica fibres	303	5.56	(Ncibi et al., 2007)		
Carolina algae	292	55	This study		
Carolina algae modified with formaldehyde	292	64	This study		

[MB] <sub>initial</sub> (mg/L)	ΔH (KJ/mol)	ΔS (J/mol.K)	$\Delta G$ (KJ/mol) at (T in K)					
			(292 K)	(302 K)	(312 K)			
20	-24.2	-70.2	-3.65	-2.95	-2.247			
100	-22	-65.6	-2.8	-2.15	-1.49			



Table 8. Thermodynamic parameters for adsorption of MB dye onto Carolina (T = 292, 302 and 312 K)



Figure 1. Variation of q and % of MB removed as a function of mass of algae for [MB]<sub>initial</sub> = 20 ppm



Figure 2. Comparison of adsorption of MB done by soaking and by shaking at (215 rpm) 0.1g of algae, 30 ml of MB (50 mg/L) at 26  $^{\circ}$ C



Figure 3. The adsorption of MB by Carolina at 10, 20, 50 mg/L at 25 °C (Mass of algae: 0.11g)



Figure 4. The curves of the four nonlinear models with the experimental data at T = 25  $^{\circ}C$ 



Figure 5. The curves of the four nonlinear models with the experimental data at T = 39  $^{\circ}$ C



Figure 6. Linear plot of Langmuir isotherm at several temperatures for the adsorption of MB Onto Carolina



Figure 7. Linear plot of Langmuir isotherm for the three modified algae at 19 °C



Figure 8. Thermal analysis of Carolina algae with Methylene Blue