# Adsorption of Methylene Blue on Chemically Modified Algal Biomass: Equilibrium, Dynamic, and Surface Data

**Eugenia Rubín, Pilar Rodríguez,* Roberto Herrero, and Manuel E. Sastre de Vicente**

Departamento de Química Física e Enseñaría Química I, Universidade da Coruña, Alejandro de la Sota 1, 15008 A Coruña, Spain

*Sargassum muticum* biomass was chemically modified to test its sorption capacity toward a model organic cation: methylene blue. Two different classes of treatments, specifically the esterification of the carboxylic acids and the extraction of the lipid fraction, have been applied. Chemical modification of the biomass increases the sorption capacity, especially if the lipid fraction is removed from the algae. The maximum dye uptake was obtained for biomass obtained after the extraction of the lipid fraction by means of acetone under reflux treatment, with a $q_e$ value of 860 $mg \cdot g^{-1}$ from the Langmuir isotherm. Maximum uptakes were found in the pH range of 4 to 10. The equilibrium was achieved in (30 to 60) min, depending on the algal pretreatment. The pseudo-first-order empirical model can describe the process as a whole. Plots of the sorption capacity $q_t$ versus the square root of time, at the initial stages of the sorption process, fit the intraparticle diffusion equation, so an intraparticle diffusion coefficient of $5.46 \cdot 10^{-8}$ $cm^2 \cdot s^{-1}$ is obtained for methylene blue in chemically modified *S. muticum*. Specific surface areas of the involved biomaterials are calculated from maximum uptakes at equilibrium and critically analyzed.

## Introduction

Methylene blue (MB) has different applications in various fields. For example, investigations on the structure and therapeutic activities of methylene blue, historically the first synthetic compound ever used as an antiseptic in clinical therapy and the first antiseptic dye to be used therapeutically,[1] have played a major role in the development of phenothiazines, a large class of drugs employed as antihistamines and neuroleptics.

Recently, its potential to slow cognitive decline in Alzheimer's disease has attracted the attention of the scientific community.[2] Although a cationic dye, there is strong indication that methylene blue passes the blood−brain barrier.

Methylene blue has wider applications which include coloring paper, dyeing cottons and wool, temporarily coloring hair, and coating paper stock.[3] Also, the most popular method for assessing the photocatalytic activity of titania films and powders is based on the photobleaching of methylene blue.[4,5]

In the environmental field, methylene blue is frequently used as a model organic cation in the research area devoted to the study of the interactions between organic contaminants and different biomaterials in the search of new sorbent biomass-based materials, which can be used as an alternative for and/or to complement conventional adsorbents such as activated carbon.[6] In addition, the methylene blue adsorption method can be used to measure the specific surface area of adsorbent particles,[7] clays, activated carbon, zeolites, silica, and biomaterials[8,9] in aqueous suspensions.

An important question to be investigated is the effect of chemical modification on the sorbent properties of biomaterials, so bearing in mind the relevance of algal biomass along the oceans, with a large number of applications and uses in human activity, this work deals with the adsorption of methylene blue by chemically modified biomass of the brown alga *Sargassum muticum*. This alga is a pest fouling organism in European coasts that competes with the local fucalean species and may also interfere with the "sea industry";[10] for this reason, it would constitute an ideal material to be used as an adsorbent. Equilibrium, dynamic, and surface data are reported.

* Corresponding author. Phone: +34 981167000, ext. 2197. Fax: 34 981167065. E-mail: prbarro@udc.es.

## Experimental Section

***Preparation of the Adsorbent.*** The adsorbent used was the alga *S. muticum* collected in A Coruña (Galicia, NW Spain). The algae were washed with generous amounts of distilled water and dried in an oven at 60 °C overnight. Then they were ground in an analytical mill (IKA A 10) and sieved in the pore size range from (0.5 to 1) mm. Finally, the biomass was chemically modified by applying two different classes of treatments, specifically the esterification of the carboxylic acids and the extraction of the lipid fraction.

The modification of the carboxyl groups was performed by means of a pretreatment with an acidic methanol solution. A 3 g portion of the dried biomass was suspended in 200 mL of methanol and 1.8 mL of concentrated HCl to make the mixture 0.1 M in HCl. The mixture was shaken for 24 h at room temperature. Then the biomass was thoroughly rinsed with deionized water and subsequently filtered off. Finally, it was dried overnight at 60 °C. This treatment results in the esterification of the carboxylic acids.[11]

For the extraction of the lipid fraction three different types of treatments were used.

***1. Pretreatment with Acetone, Ethanol, or Methanol.*** A 1 g portion of dried biomass was added to 100 mL of acetone, ethanol, or methanol aqueous solution, 50 % (v/v). Then it was agitated for 24 h at room temperature. Afterward the biomass was thoroughly rinsed with deionized water and filtered off. Finally, it was dried in an oven at 60 °C overnight.[12]

***2. Pretreatment with Acetone under Reflux.*** A 2 g portion of dried biomass was added to 150 mL of acetone, and the mixture was heated under reflux for 6 h. The biomass was then

10.1021/je100666v 
Published on Web 11/30/2010

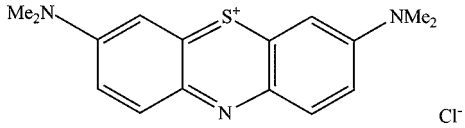


**Figure 1.** Chemical structure of the methylene blue dye.

filtered off followed by washing with deionized water, and it was dried in an oven at 60 °C overnight.[11]

***3. Pretreatment with Chloroform/Methanol.*** A 1 g portion of dried biomass was added to 100 mL of a mixture of 2:1 chloroform/methanol. Then it was agitated for 24 h at room temperature. Afterward the biomass was rinsed thoroughly with deionized water and filtered off. Finally, it was dried in an oven at 60 °C overnight.[13]

Pretreated biomass was kept in plastic containers refrigerated at 4 °C for further use. The biomass weight loss was determined after each treatment. All experiments were done at least in duplicate.

***Dye Solution Preparation.*** The dye used in this study is methylene blue (C.I. 52015, Panreac, dye content 82 %), a cationic thiazine whose chemical structure is shown in Figure 1.

Stock solutions of methylene blue, without further purification, were prepared by dissolving accurately weighed dye in deionized water at a concentration of 1000 mg·L$^{-1}$. Working solutions were prepared by dilution.

***Dye Adsorption Experiments.*** To carry out the adsorption experiments, a constant mass of alga (0.1 g) was weighed into a conical flask and 40 mL of dye solution was added to it. The mixture was shaken at 175 rpm and at room temperature for 2 h, when equilibrium was reached. Then the algae were separated by decantation, and the dye concentration was analyzed using a UV/vis spectrophotometer (Varian Cary 100 Bio) at a $\lambda_{max}$ of 665 nm. The solutions involved were diluted to the proper concentrations to give absorbances in the range of 0.1 to 1 before the measurements were taken. The concentration of methylene blue was calculated by means of its absorption coefficient, obtained from standard calibration curves.

Preliminary tests were run to determine the sorption capacity of the raw alga, but it was observed that untreated algae easily decomposed and the decomposition products interfered in the absorbance measurements and, consequently, in the determination of methylene blue in aqueous solution.

First, the effect of the pH of the solution on the adsorption capacity of the alga was examined for each treatment, adjusting the pH value between 1 and 10 by the addition of dilute HCl or NaOH. Then, varying the dye concentration within the range of (10 to 1000) mg·L$^{-1}$ and adjusting the pH to 5.5, the binding capacity of the sorbent was determined. The adsorption capacity of the alga was determined from the concentration difference of the solution at the beginning and at equilibrium:

$$q_e = \frac{V(C_i - C_e)}{1000m} \quad (1)$$

where $C_i$ and $C_e$ are the initial and equilibrium dye concentrations (mg·L$^{-1}$), $V$ is the volume of the solution (mL), and $m$ is the mass of algae used (g).

Finally, several kinetic experiments were performed as follows: a constant mass of alga (0.125 g) was weighed and transferred into a thermostated cell at (25.0 ± 0.1) °C, 50 mL of dye solution of different concentrations [(50, 100, 200, and 500) mg·L$^{-1}$] were added to it, and the mixtures were shaken.

**Table 1. Adsorption Parameters Obtained Using the Langmuir Isotherm Equation and Percentage of Weight Loss of Algal Biomass Due to the Treatments (pH 5.5)**

| | $q_{max}$ | $b$ | | weight loss |
|---|---|---|---|---|
| treatment | mg·g$^{-1}$ | L·mg$^{-1}$ | $R^2$ | % |
| $HNO_3$ | 279 ± 4[a] | 0.025 ± 0.01 | 0.999 | 37[b] |
| $H_2CO$ | | | | 39[b] |
| $CHCl_3$/MeOH | 841 ± 81 | 0.045 ± 0.007 | 0.995 | 30 |
| $Me_2CO$ reflux | 860 ± 100 | 0.05 ± 0.01 | 0.994 | 29 |
| $Me_2CO$ | 402 ± 8 | 0.13 ± 0.01 | 0.996 | 31 |
| MeOH | 416 ± 10 | 0.13 ± 0.01 | 0.995 | 30 |
| EtOH | 436 ± 10 | 0.12 ± 0.01 | 0.996 | 28 |
| MeOH/$H^+$ | 358 ± 8 | 0.11 ± 0.01 | 0.993 | 38 |

[a] Reference 9. [b] Reference 14.

Aliquots were withdrawn at various time intervals for 2 h, and the concentration of dye was determined as indicated above. The amount of adsorption at time $t$, $q_t$ (mg·g$^{-1}$), was calculated according to

$$q_t = \frac{V(C_i - C_t)}{1000m} \quad (2)$$

where $C_t$ (mg·L$^{-1}$) is the dye concentration at time $t$.

## Results and Discussion

***Equilibrium Data.*** Chemical modification of seaweed stabilizes the raw biomass and improves its sorption capacity; however, it also implies a weight loss in the treated material. As shown in Table 1, analogous biomass weight losses (about 30 %) were found after the extraction of the lipid fraction by the different methods used in this work. A higher loss (about 38 %) was observed in the case of esterification of carboxylic acids. This fact can be explained as a consequence of the acid treatment used; similar decreases in the amount of biomass were found after a simple acid wash and formaldehyde cross-linking by Lodeiro et al.[14] These authors stated that, as a result of the acid treatment, the Na, K, Ca, and Mg ions bound to active sites in the biomass are replaced with protons, thus accounting for the greatest weight losses.

The sorption equilibrium binding has been described in terms of the Langmuir isotherms, given by eq 3.[15] The Langmuir theory assumes that sorption takes place at specific sites within the adsorbent, which means that, once a dye molecule occupies a site, no further adsorption can take place at that site. Therefore, at equilibrium, the saturation point is reached beyond which no further adsorption can occur, and the saturation monolayer can then be represented by the following expression:

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

where $q_{max}$ is the maximum amount of adsorption, $b$ is the affinity constant, and $C_e$ is the solution concentration at equilibrium.

The nonlinear fits of eq 3 to the experimental data for the different pretreated algal biomass are shown in Figure 2, and the corresponding $q_{max}$ and $b$ values are given in Table 1 in which the data for $q_{max}$ refer to 1 g of treated biomass. From the $q_{max}$ values it is observed that, in general, when lipids are removed from the alga, especially by means of chloroform/methanol and acetone reflux pretreatments, the adsorption capacity is higher than for the other treatments. A similar

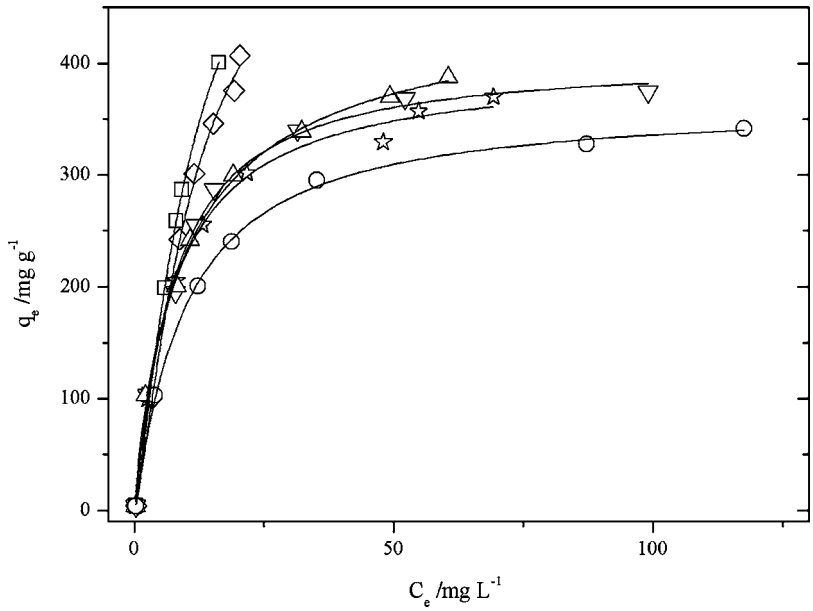


**Figure 2.** Nonlinearized isotherms for methylene blue adsorption by *S. muticum* at pH 5.5: ◇, $CHCl_3$/MeOH; □, $Me_2CO$ reflux; ☆, $Me_2CO$; ▽, MeOH; △, EtOH; ○, MeOH/$H^+$. The lines correspond to Langmuir isotherm fits.

behavior, that is, an increase of sorption capacity when the lipid fraction was extracted, was found[12] for the adsorption of Cr(VI) by a chemically modified biomass of *Rhizopus nigricans*, for the sorption of hydrophobic organic compounds on geosorbents,[16] and for the adsorption of polycyclic aromatic hydrocarbons on soil organic matter.[17] Besides, the extraction of lipids from geosorbents and soil organic matter increased the nonlinearity of the isotherms; this indicates that the lipids strongly compete for hydrophobic sorption sites.[16,17] Lipid extraction treatments appear to expose more binding sites and improve the adsorptive properties of the adsorbent. Therefore, the removal of lipids from the algal biomass could provide additional sorption sites that could be occupied by methylene blue, increasing the surface area for the sorption of methylene blue and, consequently, the adsorption capacity of *S. muticum*.

The esterification of the carboxylic groups of algae was done to estimate the role of these functional groups in the dye adsorption process, that is, to check the contribution of electrostatic interactions in binding equilibrium. The evaluation of the interactions responsible for sorption has been carried out in various studies in the literature: For heavy metal cations the carboxyl functional groups of alginate play a predominant role in the overall metal binding properties of the algal biomass to cadmium and lead.[18] Similar results are found for methylene blue adsorption by *Aspergillus niger*.[11] In this case, not only carboxyl but also amino groups could be the main binding sites for fungal biomass, while phosphate groups are less likely to be major binding sites. For the binding of ionic dyes to the biomass of peanut hull, the electrostatic interactions between the cationic dye and the carboxylate anion may be the primary mechanism,[19] and the hydroxyl group is an important functional group in the adsorption of both anionic and cationic dyes. On the other hand, adsorption of Cr(VI) and As(V) onto methylated yeast biomass[20] results in a marked increase of the adsorbed amount with increasing methylation degree, indicating that the negatively charged carboxylic groups within the cell walls of methylated yeast inhibit the adsorption/access of Cr(VI) and As(V) anions onto/to the cell wall. In our case, for the biomass treated with acidic methanol, the adsorption capacity of the alga is slightly higher than that for *S. muticum* treated with $HNO_3$, suggesting that the carboxylate interaction with methylene blue molecules does not contribute highly in the adsorption process and that hydrophobic interactions can be the key drivers, as methylation enhances the hydrophobic character of the alga surface.

As shown in Figure 3, the uptake was unaffected in the pH range of 4 to 10 and for pH values below 4 there is a decrease in methylene blue adsorption as the solution becomes more acidic. However, at low pH the dye uptake is still not negligible.

For the adsorption of $Cd^{2+}$ on *S. muticum*,[14] the algal affinity for the metal is explained by an exchange between the metal ions in solution and protons initially present in the biomass; the relevance of the negative charge in the algal system has been carefully discussed by Rey-Castro et al.[21] in a detailed study on the acid−base behavior of *S. muticum* biomass directly and also in connection with the protonation of the most important component of the alga: the alginic acid.[22] In the case of methylene blue, a purely electrostatic interaction between the negative charge of the alga and the positive charge of the dye cannot be considered to be the unique adsorption mechanism. Different types of interactions should account for the adsorption process as an important amount of dye is adsorbed at low pH values, for which the alga is completely protonated; moreover, the increase in the adsorption capacity occurs 2 pH units below the carboxylic group p$K_a$, which is 3.85 for a degree of dissociation of 0.5.[14] These facts suggest that hydrophobic interactions can account for dye sorption, which has been reported by different authors to contribute to the description of the binding of methylene blue with different kinds of surfaces.[9,23−25] As the pH increases, the alga surface becomes negatively charged, thus promoting the access of the dye cation into the adsorption sites.

***Dynamic Data: Rate Constants and Diffusion Coefficients.*** Figure 4 shows the plots of methylene blue adsorption by chloroform/methanol-pretreated *S. muticum* against time for different initial dye concentrations. From these plots it is clear that the contact time significantly affects the dye uptake,

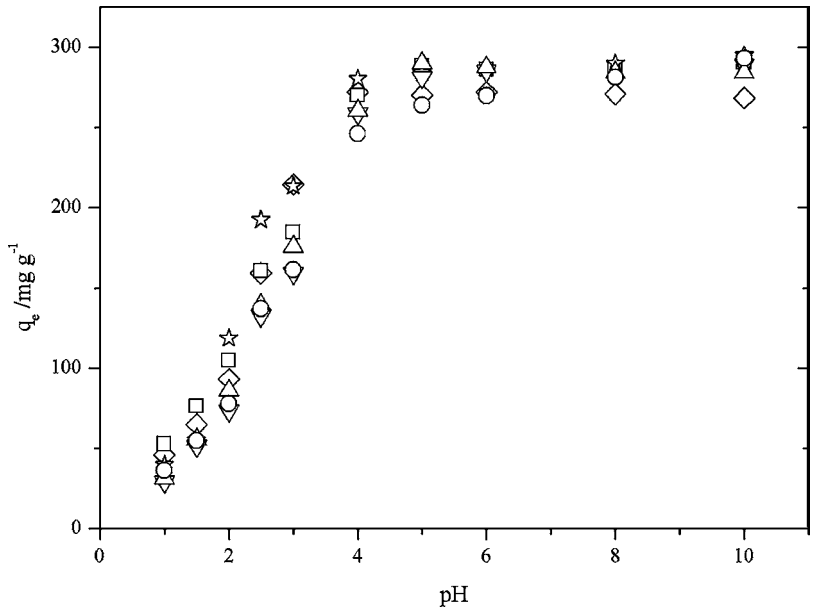


**Figure 3.** Effect of pH on the sorption of methylene blue by *S. muticum* with different pretreatments (initial dye concentration 750 mg·L$^{-1}$): ◇, $CHCl_3$/MeOH; □, $Me_2CO$ reflux; ☆, $Me_2CO$; ▽, MeOH; △, EtOH; ○, MeOH/$H^+$.

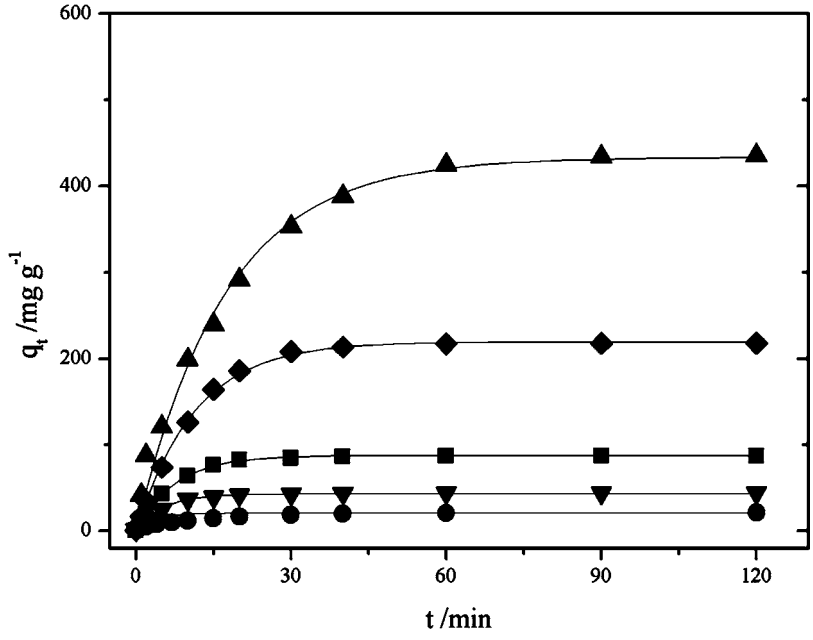


**Figure 4.** Adsorption of methylene blue onto chloroform/methanol-pretreated *S. muticum* against time for different initial dye concentrations: ▲, $[MB]_o$ = 1000 mg·L$^{-1}$; ◆, $[MB]_o$ = 500 mg·L$^{-1}$; ■, $[MB]_o$ = 200 mg·L$^{-1}$ ▼, $[MB]_o$ = 100 mg·L$^{-1}$; ●, $[MB]_o$ = 50 mg·L$^{-1}$. The lines correspond to the pseudo-first-order model.

which is fast during the initial stages of the contact period and thereafter becomes slower as equilibrium is approached; besides, the necessary contact time to reach equilibrium depends on the initial dye concentration. Similar results were found for methylene blue adsorption by all the chemically modified algae utilized in this work. The only difference between the various biomasses was the speed of the adsorption process. In particular, the adsorption on algae treated with chloroform/methanol was the fastest process, while that with methanol-pretreated material was the slowest.

***Kinetic Models.*** Various models have been tested to analyze the kinetics of the adsorption process. To examine the controlling mechanism, the pseudo-first-order and the pseudo-second-order kinetic equations were used to fit the experimental data of the dye adsorption by differently treated biomasses.

The pseudo-first-order Lagergren equation[26] in the integrated form can be expressed as follows:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{4}$$

where $q_e$ and $q_t$ are the sorption capacity at equilibrium and at time $t$, respectively (mg·g$^{-1}$), and $k_1$ is the rate constant of pseudo-first-order sorption (min$^{-1}$).

The integrated rate law for the pseudo-second-order reaction can be written as[27]

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{5}$$

**Table 2. Kinetic Parameters Obtained Using the Pseudo-First-Order and Pseudo-Second-Order Models for the Various Chemical Treatments and Different Methylene Blue Initial Concentrations**

| $[MB]_o$ / mg·L$^{-1}$ | $q_{e,exptl}$ / mg·g$^{-1}$ | $k_1$ / min$^{-1}$ | $q_e$ / mg·g$^{-1}$ | $R^2$ | $10^2\ k_2$ / g·mg$^{-1}$·min$^{-1}$ | $q_e$ / mg·g$^{-1}$ | $R^2$ |
|---|---|---|---|---|---|---|---|
| | | | $CHCl_3$/MeOH | | | | |
| 50 | 22 | 0.27 ± 0.02 | 21.3 ± 0.4 | 0.982 | 1.7 ± 0.2 | 23.1 ± 0.4 | 0.987 |
| 100 | 44.1 | 0.19 ± 0.01 | 43.3 ± 0.7 | 0.989 | 0.58 ± 0.08 | 47.1 ± 0.9 | 0.988 |
| 200 | 86.9 | 0.135 ± 0.002 | 86.9 ± 0.3 | 1.000 | 0.19 ± 0.04 | 96.4 ± 3 | 0.983 |
| 500 | 218 | 0.087 ± 0.002 | 219 ± 1 | 0.999 | 0.044 ± 0.009 | 250 ± 9 | 0.983 |
| 1000 | 436 | 0.059 ± 0.004 | 433 ± 9 | 0.991 | 0.014 ± 0.003 | 508 ± 14 | 0.992 |
| | | | $Me_2CO$ Reflux | | | | |
| 50 | 21.2 | 0.18 ± 0.01 | 20.6 ± 0.3 | 0.991 | 1.1 ± 0.1 | 22.8 ± 0.5 | 0.991 |
| 100 | 42.4 | 0.126 ± 0.007 | 41.2 ± 0.5 | 0.995 | 0.37 ± 0.05 | 45.8 ± 0.9 | 0.993 |
| 200 | 84.6 | 0.084 ± 0.002 | 84.3 ± 0.7 | 0.998 | 0.11 ± 0.02 | 96 ± 2 | 0.991 |
| 500 | 208 | 0.066 ± 0.004 | 207 ± 3 | 0.994 | 0.032 ± 0.005 | 241 ± 7 | 0.990 |
| | | | $Me_2CO$ | | | | |
| 50 | 21.7 | 0.23 ± 0.02 | 21.1 ± 0.3 | 0.988 | 1.4 ± 0.2 | 23.1 ± 0.5 | 0.983 |
| 100 | 44 | 0.17 ± 0.01 | 43.9 ± 0.7 | 0.989 | 0.49 ± 0.08 | 48 ± 1 | 0.980 |
| 200 | 89 | 0.158 ± 0.007 | 88.6 ± 0.8 | 0.997 | 0.23 ± 0.03 | 97 ± 2 | 0.989 |
| 500 | 217 | 0.101 ± 0.004 | 216 ± 2 | 0.997 | 0.054 ± 0.008 | 244 ± 7 | 0.988 |
| 1000 | 430 | 0.096 ± 0.011 | 430 ± 12 | 0.960 | 0.032 ± 0.006 | 462 ± 16 | 0.957 |
| | | | MeOH | | | | |
| 50 | 21.4 | 0.107 ± 0.003 | 20.9 ± 0.2 | 0.998 | 0.54 ± 0.06 | 24.0 ± 0.6 | 0.992 |
| 100 | 43 | 0.084 ± 0.002 | 42.4 ± 0.3 | 0.999 | 0.22 ± 0.03 | 49 ± 1 | 0.988 |
| 200 | 84.3 | 0.083 ± 0.004 | 83 ± 1 | 0.996 | 0.11 ± 0.01 | 95 ± 2 | 0.992 |
| 500 | 212 | 0.057 ± 0.002 | 213 ± 2 | 0.999 | 0.025 ± 0.003 | 253 ± 8 | 0.991 |
| | | | MeOH/$H^+$ | | | | |
| 50 | 21.4 | 0.16 ± 0.02 | 19.8 ± 0.6 | 0.964 | 0.98 ± 0.11 | 22.0 ± 0.4 | 0.991 |
| 100 | 42 | 0.095 ± 0.011 | 40 ± 1 | 0.971 | 0.29 ± 0.05 | 44 ± 1 | 0.987 |
| 200 | 82 | 0.066 ± 0.004 | 80 ± 1 | 0.994 | 0.083 ± 0.010 | 94 ± 2 | 0.993 |
| 500 | 201 | 0.047 ± 0.003 | 198 ± 4 | 0.993 | 0.020 ± 0.003 | 242 ± 7 | 0.993 |

where $q_e$ and $q_t$ are the sorption capacity at equilibrium and at time $t$, respectively (mg·g$^{-1}$), and $k_2$ is the rate constant of pseudo-second-order sorption (g·mg$^{-1}$·min$^{-1}$).

From the nonlinear fit of experimental data to eqs 4 and 5, the values for the rate constants were determined ($k_1$ and $k_2$ for the pseudo-first-order and for the pseudo-second-order models, respectively) and are presented in Table 2. This table includes the equilibrium uptakes resulting from these fits ($q_e$) together with the corresponding coefficients of determination ($R^2$). Regarding the latter, they are all higher than 0.96, thus suggesting that both models can describe the kinetics of the process. However, the predicted equilibrium uptake values are in good agreement with those found experimentally in the case of the pseudo-first-order model and diverge if the pseudo-second-order equation is used, especially for the higher concentrations. The results lead to the conclusion that the pseudo-first-order model is more adequate to describe the kinetics of the process as a whole.

On the other hand, the first steps of an adsorption process can be compatible with control by diffusion, especially for large organic molecules with long contact times. In that case, it is also possible to calculate the diffusion coefficient of the adsorbate.[28]

It is common to assume, in adsorption in a batch system under rapid stirring, that the overall rate of binding depends primarily on the diffusivity of the adsorbate: diffusion through the boundary layer of the fluid immediately adjacent to the external surface of the adsorbent particle (film diffusion) and diffusion through the sorbent particles (intraparticle diffusion).

The intraparticle diffusion process can be described by the so-called Weber−Morris model.[29] According to this model, uptake varies almost proportionately with the square root of time, and the intraparticle diffusion constant can be obtained from the slope of the plot of $q_t$ versus the square root of time by using the following equation:

$$q_t = k_i t^{0.5} \tag{6}$$

where $q_t$ is the sorption capacity at time $t$ and $k_i$ is the intraparticle diffusion constant. If this plot passes through the origin, then intraparticle diffusion is the rate-controlling step. In the case where the lines have a nonzero intercept, external film and intraparticle diffusion contribute to the actual adsorption process. On the other hand, such plots may present multilinearity, which indicates that two or more steps occur in the sorption process.

In an attempt to assess the contribution of intraparticle diffusion to the sorption of methylene blue to the algal biomass, plots of the sorption capacity at specific times against the square root of time were made for different initial dye concentrations (Figure 5). Similar dependencies were obtained for all the chemically modified algae used in this study. $q_t$ versus $t^{1/2}$ plots are linear and pass through or very close to the origin. This indicates that there is little or no external film control.

Table 3 contains the intraparticle diffusion parameters for the various chemically modified algal biomasses at different initial dye concentrations. As can be seen there is an increase of intraparticle diffusion constant values with initial dye concentration; that is, increasing the dye concentration in the solution promotes the diffusion in the particles. This increasing trend of intraparticle rate constant values with initial adsorbate concentration was reported previously by various authors.[30−33]

For adsorption onto spherical particles with a constant diffusivity, in the earlier stages of the adsorption process, when $t$ is relatively small, $q_t$ can be expressed by[34]

$$q_t = \frac{6 q_e D_i^{0.5}}{\pi^{0.5} r} t^{0.5} \tag{7}$$

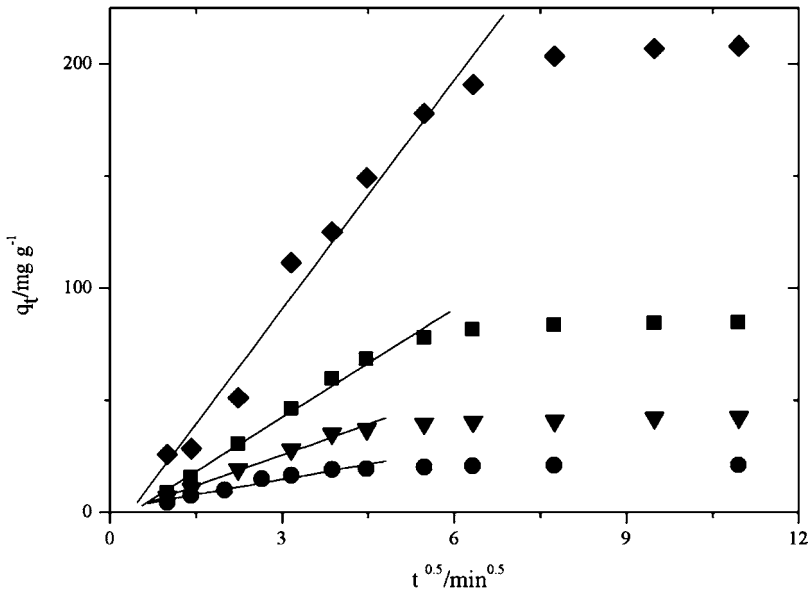


**Figure 5.** Intraparticle diffusion model of methylene blue sorption onto acetone-reflux-pretreated *S. muticum* with different initial concentrations of dye: ◆, $[MB]_o = 500$ mg·L$^{-1}$; ■, $[MB]_o = 200$ mg·L$^{-1}$; ▼, $[MB]_o = 100$ mg· L$^{-1}$; ●, $[MB]_o = 50$ mg·L$^{-1}$.

**Table 3. Intraparticle Diffusion Parameters Obtained Using the Weber−Morris Model for the Various Chemical Treatments and Different Methylene Blue Initial Concentrations**

| $[MB]_o$ / mg·L$^{-1}$ | $k_i$ / mg·g$^{-1}$·min$^{-0.5}$ | $R^2$ |
|---|---|---|
| | $CHCl_3$/MeOH | |
| 50 | 5.9 ± 0.4 | 0.993 |
| 100 | 10.5 ± 0.0.9 | 0.989 |
| 200 | 22 ± 1 | 0.991 |
| 500 | 50 ± 1 | 0.999 |
| 1000 | 66 ± 2 | 0.997 |
| | $Me_2CO$ Reflux | |
| 50 | 5.2 ± 0.4 | 0.990 |
| 100 | 9.1 ± 0.5 | 0.995 |
| 200 | 16.1 ± 0.7 | 0.995 |
| 500 | 34 ± 2 | 0.987 |
| | $Me_2CO$ | |
| 50 | 6.5 ± 0.3 | 0.997 |
| 100 | 11.4 ± 0.5 | 0.997 |
| 200 | 20 ± 1 | 0.991 |
| 500 | 48 ± 3 | 0.994 |
| 1000 | 74 ± 5 | 0.991 |
| | MeOH | |
| 50 | 4.8 ± 0.2 | 0.996 |
| 100 | 8.4 ± 0.5 | 0.991 |
| 200 | 15.4 ± 0.7 | 0.995 |
| 500 | 37 ± 1 | 0.996 |
| | MeOH/$H^+$ | |
| 50 | 3.7 ± 0.3 | 0.983 |
| 100 | 6.5 ± 0.0.5 | 0.986 |
| 200 | 13.9 ± 0.8 | 0.992 |
| 500 | 27.1 ± 0.4 | 0.999 |

where $D_i$ is the intraparticle diffusion coefficient and $r$ is the radius of the adsorbent particles, assumed to be spherical.

Comparing eqs 6 and 7, a linear dependence of the intraparticle rate constant on the equilibrium dye uptake can be obtained as follows:

$$k_i = \frac{6D_i^{0.5}}{\pi^{0.5} r} q_e \tag{8}$$

The plot of $k_i$ versus $q_e$, for the different chemically modified algae biomasses, is shown in Figure 6. The obtained straight line results in an intraparticle diffusion coefficient of $5.46 \cdot 10^{-8}$ cm$^2$·s$^{-1}$. In these calculations, it has been assumed that the solid phase consists of spherical particles with an average radius between the radii corresponding to the upper and lower size fractions. Other values found in the literature for the methylene blue intraparticle diffusion coefficient are $8.04 \cdot 10^{-6}$ cm$^2$·s$^{-1}$ for modified wheat straw[35] and $5.37 \cdot 10^{-10}$ cm$^2$·s$^{-1}$ for sepiolite.[28]

***Surface Area Data.*** From the maximum adsorption capacity values, $q_{max}$, the specific surface area of *S. muticum* biomass can be calculated according to the following expression:

$$S_s = \frac{q_{max} N_A A_m}{MW} \cdot 10^{-20} \tag{9}$$

where $S_s$ is the specific surface area of the adsorbent (m$^2$·g$^{-1}$), $q_{max}$ is the monolayer capacity [(g of solute)·(g of solid)$^{-1}$], $N_A$ is Avogadro's constant ($=6.02 \cdot 10^{23}$), $A_m$ is the ionic cross-sectional area of solute (Å$^2$), and MW is the molecular weight of the solute.

The results shown in Table 4 were obtained using the value 108 Å$^2$ for the ionic cross-sectional area of methylene blue, which was proposed by van den Hul and Lyklema[36] in a critical study on the determination of specific surface areas by different methods.

As the uncertainty in the assumption of the covered area can strongly affect the estimation of the specific surface, the results can only be used for comparison among different adsorbents, as pointed out in previous work on algal surfaces.[8,9] However, results obtained by the methylene blue method lead to specific areas much higher than that found using the Brunauer−Emmett−Teller (BET) method[9,14] and are the same magnitude as those obtained by mercury porosimetry. This last method gives higher pore volumes than $N_2$ adsorption, suggesting that the BET method cannot be applied to this kind of material,[8] and consequently, the methylene blue method is, with limitations, the best approach.

## Conclusions

*S. muticum* shows a high adsorption capacity of methylene blue in aqueous solution. Chemical modification of the biomass

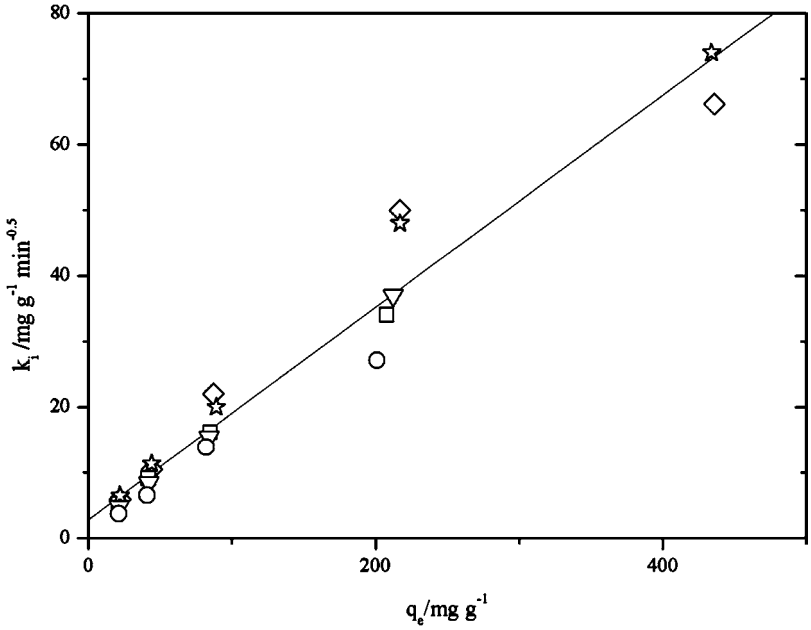


**Figure 6.** Intraparticle diffusion parameters for the various chemical treatments against different equilibrium dye uptakes: ◇, $CHCl_3$/MeOH; □, $Me_2CO$ reflux; ☆, MeOH; △, EtOH; ○, MeOH/$H^+$.

**Table 4. Specific Surface Areas for the Sorption of Methylene Blue on Chemically Modified *S. muticum***

| pretreatment | $q_{max}$ / mg·g$^{-1}$ | $S_s{}^a$ / m$^2$·g$^{-1}$ | $S_s{}^b$ / m$^2$·g$^{-1}$ |
|---|---|---|---|
| $HNO_3$ | 279 | 485 | 242 |
| $CHCl_3/CH_3OH$ | 841 | 1462 | 731 |
| $Me_2CO$ reflux | 860 | 1495 | 747 |
| $Me_2CO$ | 402 | 699 | 349 |
| MeOH | 416 | 723 | 361 |
| EtOH | 436 | 758 | 379 |
| MeOH/$H^+$ | 358 | 622 | 311 |

[a] Monomers lying flat on the algal surface. [b] Dimers with the methylene blue molecules joined in a sandwich structure.

increases the sorption capacity, especially if the lipid fraction is removed from the algae.

The solution pH affects adsorption of methylene blue by the alga. Maximum uptakes were found in the pH range of 4 to 10, and for pH values below 4 there is a decrease in methylene blue adsorption as the solution becomes more acidic. The fact that at the low pH the dye uptake is not negligible, together with the increase of dye sorption after methylation of the carboxylic groups in the algae, suggests the existence of hydrophobic interactions to account for the algae−dye binding.

The sorption equilibrium can be described in terms of the Langmuir isotherm model. The maximum dye uptake was obtained for the acetone under reflux treatment, with a $q_e$ value of 860 mg·g$^{-1}$.

The kinetics of the methylene blue adsorption is relatively fast; the equilibrium was achieved, depending on the alga pretreatment, in (30 to 60) min. A pseudo-first-order empirical model best describes the process. An intraparticle diffusion model can also account for the adsorption process, at the initial stages, and allows the intraparticle diffusion coefficient for methylene blue in *S. muticum* to be obtained.

The existence of an uncertainty in the assumption of the covered area can strongly affect the estimation of the specific surface, and the results for the specific surface area can be useful for comparison among different adsorbents but not in an absolute sense.

## Literature Cited


(1) Wainwright, M. Dyes in the development of drugs and pharmaceuticals. *Dyes Pigm.* **2008**, *76*, 582–589.
(2) Oz, M.; Lorke, D. E.; Petroinau, G. A. Methylene blue and Alzheimer's disease. *Biochem. Pharmacol.* **2009**, *78*, 927–932.
(3) Wu, Y.; Zhang, L.; Gao, C.; Ma, J.; Ma, X.; Han, R. Adsorption of copper ions and methylene blue in a single and binary system on wheat straw. *J. Chem. Eng. Data* **2009**, *54*, 3229–3234.
(4) Mills, A.; McFarlane, M. Current and possible future methods of assessing the activities of photocatalyst films. *Catal. Today* **2007**, *129*, 22–28.
(5) Fetterolf, M. L.; Patel, H. V.; Jennings, J. M. Adsorption of methylene blue and acid blue 40 on titania from aqueous solution. *J. Chem. Eng. Data* **2003**, *48*, 831.
(6) Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A. Adsorption of methylene blue on low-cost adsorbents: A review. *J. Hazard. Mater.* **2010**, *177*, 70–80.
(7) McKay, G. *Use of Adsorbents for the Removal of Pollutants from Wastewaters*; CRC Press: Boca Raton, FL, 1996.
(8) Vilar, V. J. P.; Botelho, C. M. S.; Boaventura, R. A. R. Methylene blue adsorption by algal biomass based materials: Biosorbents characterization and process behaviour. *J. Hazard. Mater.* **2007**, *147*, 120–132.
(9) Rubin, E.; Rodríguez, P.; Herrero, R.; Cremades, J.; Bárbara, I.; Sastre de Vicente, M. E. Removal of methylene blue from aqueous solutions using as a biosorbent *Sargassum muticum*: An invasive macroalga in Europe. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 291–298.
(10) Crithley, A. T.; Fanaham, W. F.; Yoshida, T.; Norton, T. A. A bibliography of the invasive alga *Sargassum muticum*. *Bot. Mar.* **1990**, *33*, 551–562.
(11) Fu, Y.; Viraraghavan, T. Dye biosorption sites in *Aspergillus niger*. *Bioresour. Technol.* **2002**, *82*, 139–145.
(12) Bai, R. S.; Abraham, T. E. Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. *Water Res.* **2002**, *36*, 1224–1236.
(13) Colla, L. M.; Oliveira Reinehr, C.; Reichert, C.; Costa, J. A. V. Production of biomass and nutraceutical compounds by *Spirulina platensis* under different temperature and nitrogen regimes. *Bioresour. Technol.* **2007**, *98*, 1489–1493.
(14) Lodeiro, P.; Cordero, B.; Grille, Z.; Herrero, R.; Sastre de Vicente, M. E. Physicochemical studies of cadmium (II) biosorption by the invasive alga in Europe, *Sargassum muticum*. *Biotechnol. Bioeng.* **2004**, *88*, 237–247.
(15) Volesky, B. *Sorption and Biosorption*; BV Sorbex: St. Lambert, Quebec, Canada, 2003.

(16) Tremblay, L.; Kohl, S. D.; Rice, J. A.; Gagne, J. P. Effects of lipids on the sorption of hydrophobic organic compounds on geosorbents: A case study using phenanthrene. *Chemosphere* **2005**, *58*, 1609–1620.

(17) Kohl, S. D.; Rice, J. A. Contribution of lipids to the nonlinear sorption of polycyclic aromatic hydrocarbons to soil organic matter. *Org. Geochem.* **1999**, *30*, 929–936.

(18) Fourest, E.; Volesky, B. Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargasum fluitans*. *Environ. Sci. Technol.* **1996**, *30*, 277–282.

(19) Gong, R.; Sun, Y.; Chen, J.; Liu, H.; Yang, C. Effect of chemical modification on dye adsorption capacity of peanut hull. *Dyes Pigm.* **2005**, *67*, 175–181.

(20) Seki, H.; Suzuki, A.; Maruyama, H. Biosorption of chromium(VI) and arsenic(V) onto methylated yeast biomass. *J. Colloid Interface Sci.* **2005**, *281*, 261–266.

(21) Rey-Castro, C.; Lodeiro, P.; Herrero, R.; Sastre de Vicente, M. E. Acid−base properties of brown seaweed biomass considered as a Donnan gel. A model reflecting electrostatic effects and chemical heterogeneity. *Environ. Sci. Technol.* **2003**, *37*, 5159–5167.

(22) Rey-Castro, C.; Herrero, R.; Sastre de Vicente, M. E. Gibbs−Donnan and specific ion interaction theory descriptions of the effect of ionic strength on proton dissociation of alginic acid. *J. Electroanal. Chem.* **2004**, *564*, 223–230.

(23) Guy, R. D.; Narine, D. R.; Silva, S. Organocation speciation. I. A comparison of the interactions of methylene blue and paraquat with bentonite and acid humic. *Can. J. Chem.* **1980**, *58*, 547–554.

(24) Imamura, K.; Ikeda, E.; Nagayasu, T.; Sakiyama, T.; Nakanishi, K. Adsorption behavior of methylene blue and its congeners on a stainless steel surface. *J. Colloid Interface Sci.* **2002**, *245*, 50–57.

(25) Palit, D.; Moulik, S. P. Adsorption of the dyes (methylene blue and acridine orange and their mixtures) from aqueous solutions on cholesterol surface. *Colloid J.* **2003**, *65*, 383–390.

(26) Aharoni, C.; Sparks, D. L. Kinetics of soil chemical reactions−A theoretical treatment. *SSSA Spec. Publ.* **1991**, *27*, 1−18.

(27) Ho, Y. S.; Wase, D. A. J.; Forster, C. F. Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. *Environ. Technol.* **1996**, *17*, 71–77.

(28) Dogan, M.; Özdemir, Y.; Alkan, M. Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes Pigm.* **2007**, *75*, 701–713.

(29) Weber, W. J., Jr.; Asce, A. M.; Morris, J. C. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div., Am. Soc. Civ, Eng.* **1963**, *89*, 31–59.

(30) Ozer, A.; Akkaya, G.; Turabik, M. The biosorption of acid red 337 and acid blue 324 on *Enteromorpha prolifera*: The application of nonlinear regression analysis to dye biosorption. *Chem. Eng. J.* **2005**, *112*, 181–190.

(31) Koumanova, B.; Peeva, P.; Allen, S. J. Variation of intraparticle diffusion parameter during adsorption of *p*-chlorophenol onto activated carbon made from apricot stones. *J. Chem. Technol. Biotechnol.* **2003**, *78*, 582–587.

(32) Crini, G. Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer. *Dyes Pigm.* **2008**, *77*, 415–426.

(33) Choy, K. K. H.; Porter, J. F.; McKay, G. Intraparticle diffusion in single and multicomponent acid dye adsorption from wastewater onto carbon. *Chem. Eng. J.* **2004**, *103*, 133–145.

(34) Gerente, C.; Lee, V. K. C.; Le Cloirec, P.; McKay, G. Application of chitosan for the removal of metals from wastewaters by adsorption−Mechanisms and models review. *Crit. Rev. Environ. Sci. Technol.* **2007**, *37*, 41–127.

(35) Han, R.; Zhang, L.; Song, C.; Zhang, M.; Zhu, H.; Zhang, L. Characterization of modified wheat straw. Kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. *Carbohydr. Polym.* **2010**, *79*, 1140–1149.

(36) Van den Hul, H. J.; Lyklema, J. Determination of specific surface areas of dispersed materials. Comparison of the negative adsoption method with some other methods. *J. Am. Chem. Soc.* **1968**, *90*, 3010–3015.

Received for review June 18, 2010. Accepted November 6, 2010. We thank the Ministerio de Educación y Ciencia for its financial support through Research Project CTM 2006-03142.

JE100666V