ABSTRACT

Methylene blue adsorption on *Sargassum muticum*, an invasive macroalga in Europe, has been investigated using visible absorption spectroscopy. Different pre-treatments, protonation and chemical cross-linking with CaCl2 or H2CO, have been tested in order to improve the stability as well as the adsorption capacity of the algal biomass. The equilibrium binding has been described in terms of Langmuir or Freundlich isotherms depending on the algal pre-treatment; from the maximum adsorption capacity values, an estimation of the algal specific surface area was made. Moreover, it has been found that adsorption kinetics can be described according to the first order Lagergren model, from which the rate constant and the adsorption capacity were determined. Finally, simple empirical equations were obtained to evaluate the amount of methylene blue removed at any initial concentration and reaction time. The results obtained have shown that this type of material has a high adsorption capacity for methylene blue dye, this feature together with the short times needed to reach the equilibrium suggest that *Sargassum muticum* can be used as a low-cost biosorbenent in wastewater treatments.

**Keywords:** Biosorption, dye adsorption, *Sargassum muticum*, isotherms, adsorption kinetics.

1 INTRODUCTION

Biosorption processes have attached a great importance from an environmental point of view as they can be used to remove toxic compounds from industrial wastewaters. Many industries use dyes to colour their final products and their discharge into natural waters causes severe problems because they are toxic to aquatic life and damage the aesthetic nature of the environment. Moreover, these
Effluents are rather difficult to treat by conventional biological and physical-chemical techniques due to the complex structure of the dyes. Therefore, adsorption processes provide an attractive alternative for the treatment of coloured waters. Activated carbon is the most popular and widely used adsorbent, but there are certain problems with its use since it is expensive and its regeneration is difficult. For this reason, interest has been recently focused on low-cost materials, ranging from waste products from other industries to naturally abundant biomass: sewage sludge and peanut shell, silk cotton hull, coconut tree saw dust and coir pith, moss, banana pith and water hyacinth roots, parthenium plant, bacteria and fungi. In particular, marine algae are very promising materials to be used as biosorbents in wastewater treatment because they represent a cheap source of biosorbent, as they are readily available in large quantities, and it has been shown that they display a high metal binding capacity, mainly due to carboxylic and sulfonate groups from the algal polysaccharides.

The present work deals with the adsorption of methylene blue, a dye often used to characterize the capacity of an adsorbent, by Sargassum muticum, an alga which is a pest fouling organism that competes with the local fucalean species and may also interfere with the “sea industry”. For this reason, it would constitute an ideal material to be used as biosorbent. In addition, to the best of our knowledge, studies of dye adsorption by algae are not available; therefore, to explore this promising field of biosorption is desirable.

In order to perform the adsorption experiments, different pre-treatments for the chemical modification of the biomass, among them protonation and chemical cross-linking with CaCl₂ and H₂CO, have been tested to improve its stability as well as its adsorption capacity, making it suitable for industrial use. The effect of the solution pH on the adsorption capacity of the alga has been examined to carry out the adsorption experiments at a suitable value of pH. The equilibrium and kinetics of the adsorption process were then evaluated and it was found that both rely on the pre-treatment made to the biomass. Therefore, the equilibrium binding has been described in terms of Langmuir or Freundlich isotherms, depending on the algal pre-treatment, and kinetic data were fitted according to the first order Lagergren model, from which the rate constant of sorption and the equilibrium capacity were determined. These two parameters are dependent on the initial dye concentration, and taking into account these dependencies, simple empirical equations were derived to evaluate the amount of methylene blue removed at any initial concentration and reaction time.
2 EXPERIMENTAL

2.1 Preparation of the adsorbent

The adsorbent used was alga Sargassum muticum collected in La Coruña (Galicia, NW Spain). 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 size pore range from 0.5 to 1 mm. Finally, the biomass was chemically modified by means of different treatments, which were carried out as follows.

Pre-treatment with CaCl₂

A sample of 2.5 g of dried biomass was treated with 100 mL of 0.2 mol dm⁻³ CaCl₂ solution, keeping the solution pH constant at a value of 5.0, because it is the optimum pH value for calcium activation of biomass. 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°C for 24 h.¹¹

Pre-treatment with HCl

A constant mass of Sargassum muticum (2.5 g) was treated with 100 mL of 0.1 mol dm⁻³ HCl solution for 3h at room temperature. The biomass was then filtered off followed by washing with deionised water and it was dried overnight at 60°C. Then, 400 mL of 0.1 mol dm⁻³ HCl solution were added to the dried biomass and the previous procedure was repeated.¹²

Formaldehyde cross-linking

2.5 g of dried biomass were added to a mixture of 17 mL 36% formaldehyde and 33 mL of 0.1 mol dm⁻³ HCl solution. The mixture was left at room temperature for 1 h under gentle mixing. The biomass was then filtered off followed by sequential distilled water, 0.2 mol dm⁻³ Na₂CO₃ and final distilled water washes. It was dried overnight at 60°C and finally 2 h at 110°C.¹³

Pre-treated biomass was kept in plastic containers refrigerated at 4°C for further use.

2.2 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 Fig 1.

Stock solutions of methylene blue, without further purification, were prepared by dissolving accurately weighed dye in deionised water at a concentration of 1000 mg L⁻¹ and they were diluted when necessary.
2.3 Dye adsorption experiments

In order 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 were added to it. The mixture was shaken at 175 rpm and room temperature for 2 h, when the equilibrium was reached. Then, algae were separated by decantation and the dye concentration was analysed using a spectrophotometer UV/VIS (Varian Cary 100 Bio) at $\lambda_{\text{max}}$ 665 nm. The solutions involved were diluted to proper concentrations, to give absorbencies in the range 0.1-1, before making the measurements.

Firstly, the effect of the solution pH 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, the binding capacity of the sorbent was determined varying dye concentration within the range 10-1000 mg L$^{-1}$ and adjusting the pH to a value of 5.5. 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 the equilibrium dye concentrations (mg L$^{-1}$), $V$ is the volume of 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. Aliquots were withdrawn at various time intervals for 4 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 by:

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

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

3 RESULTS AND DISCUSSION

3.1 Equilibrium of sorption

As it is shown in Fig 2, the uptake was unaffected in the pH range of 4-10 and for pH values below 2, sorption of methylene blue was less favourable. However, the adsorption capacity for protonated alga, which is the most pH dependent, at the lower pH is still about 45 mg g$^{-1}$. For the adsorption of Cd$^{2+}$ on Sargassum 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.\textsuperscript{15} in a detailed study about the acid-base behaviour of \textit{Sargassum muticum} biomass directly, and also in connection with the protonation of the most important component of the alga: the alginic acid.\textsuperscript{16} In the case of methylene blue, a pure electrostatic interaction between the negative charge of the alga and the positive charge of the dye cannot be considered the unique mechanism of adsorption. A different type of interaction 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 two pH units below the algal pK\textsubscript{a}, which is 3.85 for a degree of dissociation of 0.5.\textsuperscript{14} These facts suggest the existence of hydrophobic interactions which have been reported by different authors to contribute to the description of the interaction of methylene blue with different kind of surfaces.\textsuperscript{17-20}

The equilibrium binding was described in terms of Langmuir and Freundlich isotherms.\textsuperscript{21,22} 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, a saturation point is reached beyond which no further adsorption can occur and the saturation monolayer can be then represented by the following expression:

\[
q_a = \frac{q_{\text{max}} b C_e}{1 + b C_e}
\]  

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

The Freundlich model assumes that the sorption takes place on heterogeneous surfaces and adsorption capacity depends on the concentration of methylene blue at equilibrium according to the exponential expression:

\[
q_a = (b C_e)^\beta
\]  

where \(\beta\) is a heterogeneity factor.

Equation (4) can be linearised as follows:

\[
\log q_a = \beta \log b + \beta \log C_e
\]  

So, the plot of \(\log q_a\) against \(\log C_e\) of eqn (5) should give a linear relationship, from which \(\beta\) and \(b\) can be determined from the slope and the intercept respectively.

In the case of Langmuir isotherm, there are two possibilities for the linearisation, each one
giving different outcomes, besides, these transformations implicitly alter the error structure of data. In view of these considerations, a non-linear fit of experimental data to eqn (3) was done for the sorption of methylene blue on *Sargassum muticum* treated with CaCl₂ and HCl. Figure 3 shows these fits and the linear fit in the inset; adsorption parameters calculated from the non-linear plots are given in Table 1. On the other hand, data for H₂CO treatment show a better compliance with the Freundlich isotherm (Fig 4). Parameters b and β calculated from the linear fit of experimental data are given in Table 1.

Table 2 compares methylene blue sorption using different sorbents and reveals the large adsorption capacity of *Sargassum muticum*, suggesting that this invasive alga in Europe could be used as a quite effective biosorbent for removing cationic dyes as methylene blue.

### 3.2 Determination of the specific surface area

Moreover, from the maximum adsorption capacity values (Table 1), it is possible to determine the specific surface area of *Sargassum muticum* biomass according to the following expression²³

\[
S_s = \frac{X_m NA_m}{MW} \times 10^{-20}
\]

where: 
- \(S_s\) = specific surface area of the adsorbent (m²/g);
- \(X_m\) = monolayer capacity (g solute/g solid);
- \(N\) = Avogadro's constant (=6.02x10²³);
- \(A_m\) = ionic cross-sectional area of solute ((D)²);
- \(MW\) = molecular weight of the solute.

The methylene blue molecular cross section, \(A_m\), is difficult to assess. In the concentration range used in this work, there is an equilibrium between the monomeric and the dimeric forms of methylene blue in the bulk solution.²⁴ On the other hand, when cationic dyes are placed in solutions containing anionic polyelectrolytes they may be adsorbed as induced aggregates.²⁵ Assuming that the dimer is formed by monomer units lying flat on the surface,²⁶ it would occupy double area than the monomer and the specific surface area should be the same independently of the aggregation. However, if the monomer units are joined in a sandwich structure, with the principal molecular axes parallel,²⁴ the specific surface area would be a half of that calculated assuming the adsorption of the monomer. A different value should be obtained if it is considered that methylene blue adsorbed molecules are perpendicular to the surface, as has been reported for adsorption on clays.²⁷

Different values for the methylene blue cross section have been given in the literature, Hang
and Brindley, in a study on the adsorption of methylene blue by clay minerals,\textsuperscript{26} considered that the projected areas of the molecule remain between 55 and 130 (D)\textsuperscript{2}, depending on the methylene blue orientation. He and Tebo,\textsuperscript{28} use a value of 55 (D)\textsuperscript{2}, previously employed with clay minerals, in the determination of surface area of spores of the Marine Bacillus sp. Strain SG-1. Results shown in Table 1 were obtained using a value of 108 (D)\textsuperscript{2} for the ionic cross-sectional area of methylene blue, which was proposed by van den Hul and Lyklema\textsuperscript{29} in a critical study on the determination of specific surface areas by different methods. It is noticeable that these values are much higher than that found using the B.E.T. method (2.86 m\textsuperscript{2}/g). The reason for this discrepancy may be a different sorption mechanism for nitrogen and dye molecules since in the water-wet state, the alga is swollen and there is a water-filled porous structure.

3.3 Kinetics of the sorption process

As far as kinetics are concerned, it was found that the necessary contact time to reach the equilibrium depends on the initial dye concentration and the adsorption capacity increases with the initial dye concentration in all cases.

In order to elucidate the mechanism of the adsorption process several models were tested. A simple kinetic analysis is the first order Lagergren equation\textsuperscript{30} in the form:

$$\frac{dq_i}{dt} = k_1(q_e - q_i)$$ \hspace{1cm} (6)

Integrating this equation for the boundary conditions $q_i=0$ at $t=0$ and $q_i=t$ at $t=t$ gives:

$$\ln(q_e - q_i) = \ln q_e - k_1t$$ \hspace{1cm} (7)

which is the integrated rate law for a first order reaction. Where $q_e$ and $q_i$ are the sorption capacity at equilibrium and at time $t$, respectively (mg g\textsuperscript{-1}) and $k_1$ is the equilibrium rate constant of pseudo-first order sorption (min\textsuperscript{-1}).

Equation (7) can be expressed as follows:

$$q_i = q_e (1 - e^{-k_1t})$$ \hspace{1cm} (8)

In addition, a pseudo-second order equation\textsuperscript{31-33} based on adsorption equilibrium capacity, was tested:

$$\frac{dq}{dt} = k_2 (q_e - q_i)^2$$ \hspace{1cm} (9)

After integration, applying boundary conditions $q_i=0$ at $t=0$ and $q_i=t$ at $t=t$ the eqn (9) becomes:
which is the integrated rate law for a pseudo-second order reaction. 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$^{-1}$).

Equation (10) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_{o}t}$$

If pseudo-second order kinetics are applicable, the plot of $t/q_t$ against $t$ of eqn (11) should give a linear relationship, from which $q_e$ and $k_2$ can be determined from the slope and the intercept respectively.

The experimental data were fitted to first order and pseudo-second order equations. It was found that the adsorption of methylene blue on *Sargassum* treated with CaCl$_2$ follows first order kinetics while those for HCl and H$_2$CO treatments show a better compliance with the pseudo-second order equation. However, the equilibrium adsorption capacity values obtained from this equation are not reasonable which suggests that the sorption process is not a pseudo-second order process. The kinetic parameters were calculated by fitting the experimental data to eqn (8) using the non-linear Marquardt algorithm. A non-linear fit was chosen as it has the advantage of providing a value for $q_e$, which has to be fixed in case of using eqn (7). The values obtained are listed in Table 3 together with the correlation coefficients. The equilibrium adsorption capacity increases with an increase in the initial concentration of methylene blue while the rate constant decreases.

The corresponding linear plots of the values of $q_e$ and $k$ against $C_i$ (initial dye concentration) were regressed to obtain empirical expressions for these values in terms of $C_i$. The best fits were found with the following expressions:

$$q_e = dC_i$$

$$k = aC_i^b$$

The parameters calculated from these plots are summarised in Table 4 for each treatment of the biomass.

Substituting the expressions above in eqn (8), the rate law for a first order reaction and the relationship between $q_p$, $C_i$ and $t$ can be represented as:
\[ q_i = \text{d}C_{\text{eq}}[1 - \exp(-aC_{\text{eq}}^t)] \] (14)

This equation can be used to determine in advance the amount of methylene blue removed at any initial concentration and reaction time. The plots of \( q_i \) vs. \( t \) are shown in Figs 5, 6 and 7, where symbols represent experimental data and lines are the modelled results according to eqn (14), whose parameters are given in table 4. It is noticeable that experimental data show a good compliance with the proposed equation.

4 CONCLUSIONS

In this paper the adsorption behaviour of methylene blue on \textit{Sargassum muticum} has been evaluated. The equilibrium binding has been described in terms of Langmuir and Freundlich isotherms, depending on the biomass pre-treatment. It is remarkable that the percentage of methylene blue removed is up to 90%, which is higher than that found for other biosorbents and it could be even compared with activated carbon (99.8% uptake).\textsuperscript{34} Biosorption kinetics have been described by means of the first order Lagergren equation, from which the corresponding kinetics parameters were obtained. These results have led to simple empirical equations, which are very useful to derive the amount of methylene blue removed at any initial concentration and reaction time. It is noteworthy that the equilibrium was achieved, depending on the algal pre-treatment, in 30-60 min, which is similar to values found by other authors for methylene blue sorption on different biosorbents and, in the case of the H\textsubscript{2}CO pre-treated alga, it can be compared with the optimum contact time determined for activated carbon (35 min).\textsuperscript{34}

Therefore, this work shows that the invasive alga in Europe, \textit{Sargassum muticum}, constitutes a promising material to be used as biosorbent which could compete with commercial biosorbents because of its low cost, ready availability and high adsorption capacity. In the future, it could be applied in wastewater treatments, especially of textile effluents.

ACKNOWLEDGEMENTS

This work was funded by the projects BQU2002-02133 (from the Ministerio de Ciencia y Tecnología of Spain) and PGDIT02TAM10302PR (from the Xunta de Galicia).
Table 1. Results of methylene blue adsorption isotherm analysis and specific surface areas of the biomass.

<table>
<thead>
<tr>
<th>Biomass pre-treatment</th>
<th>( q_{\text{max}} ) (mg g(^{-1}))</th>
<th>( b ) (mg L(^{-1}))</th>
<th>( \beta )</th>
<th>( r^2 )</th>
<th>( S_s ) (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl(_2) (Langmuir model)</td>
<td>237±12</td>
<td>0.06±0.01</td>
<td>___</td>
<td>0.9987</td>
<td>412±206(^a)</td>
</tr>
<tr>
<td>HCl (Langmuir model)</td>
<td>279±4</td>
<td>0.025±0.001</td>
<td>___</td>
<td>0.9985</td>
<td>485±242.5(^b)</td>
</tr>
<tr>
<td>H(_2)CO (Freundlich model)</td>
<td>___</td>
<td>2.51±0.02</td>
<td>0.997±0.005</td>
<td>0.9999</td>
<td>___</td>
</tr>
</tbody>
</table>

\(^a\) Monomers lying flat on the algal surface.

\(^b\) Dimers with the methylene blue molecules joined in a sandwich structure.

Table 2. Maximum adsorption capacity of methylene blue on various biosorbents at optimum pH values and room temperature.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Sorption capacity (mg g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon</td>
<td>373.9</td>
<td>Dogan et al. 35</td>
</tr>
<tr>
<td><em>Sargassum muticum</em> seaweed</td>
<td>279.2</td>
<td>Present work</td>
</tr>
<tr>
<td>Cotton waste</td>
<td>240</td>
<td>McKay et al. 36</td>
</tr>
<tr>
<td><em>Hydrilla verticillata</em></td>
<td>198.0</td>
<td>Low et al. 37</td>
</tr>
<tr>
<td>Moss</td>
<td>185.0</td>
<td>Low et al. 5</td>
</tr>
<tr>
<td>Perlite</td>
<td>162.3</td>
<td>Dogan et al. 35</td>
</tr>
<tr>
<td><em>Spirodea polyrrhiza</em> (duckweed)</td>
<td>144.93</td>
<td>Waranusantigul et al. 38</td>
</tr>
<tr>
<td>Water hyacinth root</td>
<td>128.9</td>
<td>Low et al. 5</td>
</tr>
<tr>
<td>Hexane-extracted spent bleaching earth</td>
<td>120.5</td>
<td>Lee et al. 39</td>
</tr>
<tr>
<td>Carbonized spent bleaching earth</td>
<td>94.5</td>
<td>Lee et al. 39</td>
</tr>
<tr>
<td>Date pits</td>
<td>80.3</td>
<td>Banat et al. 40</td>
</tr>
<tr>
<td>Zeolite</td>
<td>53.1</td>
<td>Dogan et al. 35</td>
</tr>
</tbody>
</table>
Table 3. Kinetic parameters obtained from the first order equation for the sorption of methylene blue on *Sargassum muticum*.

<table>
<thead>
<tr>
<th>[MB](mg L⁻¹)</th>
<th>MB removed %</th>
<th>qₑ(mg g⁻¹)</th>
<th>k₁(min⁻¹)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>97.4</td>
<td>19.2±0.2</td>
<td>0.106±0.004</td>
<td>0.9968</td>
</tr>
<tr>
<td><em>Sargassum muticum</em> treated with CaCl₂</td>
<td>100</td>
<td>96.4</td>
<td>39.1±0.2</td>
<td>0.075±0.001</td>
</tr>
<tr>
<td>200</td>
<td>94.2</td>
<td>78.8±0.5</td>
<td>0.067±0.001</td>
<td>0.9994</td>
</tr>
<tr>
<td>500</td>
<td>90.0</td>
<td>197±6</td>
<td>0.041±0.003</td>
<td>0.9948</td>
</tr>
<tr>
<td>50</td>
<td>98.2</td>
<td>15.9±0.9</td>
<td>0.08±0.01</td>
<td>0.9290</td>
</tr>
<tr>
<td><em>Sargassum muticum</em> treated with HCl</td>
<td>100</td>
<td>97.4</td>
<td>27±1</td>
<td>0.07±0.01</td>
</tr>
<tr>
<td>200</td>
<td>94.9</td>
<td>71±2</td>
<td>0.054±0.004</td>
<td>0.9935</td>
</tr>
<tr>
<td>500</td>
<td>92.9</td>
<td>131±5</td>
<td>0.044±0.004</td>
<td>0.9924</td>
</tr>
<tr>
<td>50</td>
<td>98.0</td>
<td>19.4±0.4</td>
<td>0.32±0.05</td>
<td>0.9715</td>
</tr>
<tr>
<td><em>Sargassum muticum</em> treated with H₂CO</td>
<td>100</td>
<td>97.0</td>
<td>37±1</td>
<td>0.14±0.02</td>
</tr>
<tr>
<td>200</td>
<td>95.1</td>
<td>79±2</td>
<td>0.10±0.01</td>
<td>0.9830</td>
</tr>
<tr>
<td>500</td>
<td>92.5</td>
<td>196±2</td>
<td>0.113±0.004</td>
<td>0.9979</td>
</tr>
</tbody>
</table>

Table 4. Parameters calculated from equations (12-13) and the corresponding rate law for each treatment of the biomass.

<table>
<thead>
<tr>
<th>Pre-treatment</th>
<th>Equation parameters</th>
<th>Rate law</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>qₑ = (0.3938 ± 0.0006)Cᵢ  ( r² = 1 )   ( qₜ = 0.3938Cᵢ[1 - \exp(-0.38Cᵢ^{0.39})] )  ( k = (0.5 ± 0.1)Cᵢ^{(-0.38±0.05)} )  ( r² = 0.9703 )</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>qₑ = (0.28 ± 0.02)Cᵢ  ( r² = 0.9724 )   ( qₜ = 0.28Cᵢ[1 - \exp(-0.23Cᵢ^{0.27})] )  ( k = (0.23 ± 0.03)Cᵢ^{(-0.27±0.02)} )  ( r² = 0.9845 )</td>
<td></td>
</tr>
<tr>
<td>H₂CO</td>
<td>qₑ = (0.392 ± 0.002)Cᵢ  ( r² = 0.9998 )   ( qₜ = 0.392Cᵢ[1 - \exp(-1.5Cᵢ^{0.45})] )  ( k = (1.5 ± 0.2)Cᵢ^{(-0.45±0.03)} )  ( r² = 0.7416 )</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Figure 1. Chemical structure of methylene blue dye.

Figure 2. Effect of pH on sorption of methylene blue by *Sargassum muticum* with different treatments.

Figure 3. Langmuir isotherms for the sorption of methylene blue by *Sargassum muticum* treated with CaCl₂ and HCl. Symbols represent experimental points; lines are modelled results according to equation (3).

Figure 4. Freundlich isotherm for the sorption of methylene blue by *Sargassum muticum* treated with H₂CO. Symbols represent experimental points; the solid line corresponds to the modelled results according to equation (4).

Figure 5. Kinetics for methylene blue uptake by *Sargassum muticum* treated with CaCl₂ at different initial dye concentrations: 50 mg L⁻¹ (□), 100 mg L⁻¹ (○), 200 mg L⁻¹ (●), and 500 mg L⁻¹ (●). Symbols represent experimental points; lines are modelled results according to equation (14).

Figure 6. Kinetics for methylene blue uptake by protonated *Sargassum muticum* at different initial dye concentrations: 50 mg L⁻¹ (□), 100 mg L⁻¹ (○), 200 mg L⁻¹ (●), and 500 mg L⁻¹ (●). Symbols represent experimental points; lines are modelled results according to equation (14).

Figure 7. Kinetics for methylene blue uptake by *Sargassum muticum* treated with H₂CO at different initial dye concentrations: 50 mg L⁻¹ (□), 100 mg L⁻¹ (○), 200 mg L⁻¹ (●), and 500 mg L⁻¹ (●). Symbols represent experimental points; lines are modelled results according to equation (14).
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