Macrophagia of *Iridaea cordata* as an efficient biosorbent to remove hazardous cationic dyes from aqueous solutions

Leticia Belén Escudero, Patricia Nora Smichowski and Guilherme Luiz Dotto

**ABSTRACT**

In the present work, *Iridaea cordata* (IC), a red marine macroalgae, was used as an efficient biosorbent for the removal of crystal violet (CV) and methylene blue (MB) dyes from aqueous solutions. The effects of pH (5, 7, and 9) and IC concentration (1, 3, and 5 g L\(^{-1}\)) on the biosorption were studied through a 3\(^2\) full factorial design. Under the optimal conditions (pH: 7, biosorbent concentration: 1 g L\(^{-1}\)), biosorption kinetic studies were developed and the obtained experimental data were evaluated by pseudo-first order and pseudo-second order models. The results showed that the pseudo-second order model was in agreement with the experimental kinetic data for both dyes. Equilibrium studies were also carried out, and results exhibited good concordance with the Brunauer–Emmett–Teller isotherm. The biosorption capacities were 36.5 and 45.0 mg g\(^{-1}\) for CV and MB dyes, respectively. The dye removal percentages were around 75% for CV and 90% for MB. Thermodynamically, the biosorption process proved to be exothermic, spontaneous, and favorable. These results showed that IC biomass is a promising biosorbent for removal of CV and MB dyes from aqueous solutions.

**Key words** | algae, biosorption, cationic dyes, kinetic, thermodynamic

**INTRODUCTION**

Crystal violet (CV) and methylene blue (MB) dyes are contaminants that are introduced into the environment mainly as waste from textile industries. These dye molecules remain in the environment for a long period, causing several disorders for human health, including eyes burn, allergy, cyanosis, and skin irritation (Mittal *et al.* 2010). Their ingestion can cause irritation in the gastrointestinal tract, increase the heart rate, and cause headache, nausea, and mental confusion (Rafatullah *et al.* 2010). Furthermore, these organic compounds are potentially hazardous for the aquatic ecosystems, as they cause inhibition of the photosynthesis, thus generating consequences such as a decrease in the growth speed or even the death of aqueous flora (Yang *et al.* 2013). Therefore, considerable interest in developing more studies devoted to the removal of MB and CV dyes from aqueous media has arisen in the research field.

Operations based on biological treatment (Yahiaoui *et al.*, 2013), coagulation and electrocoagulation (Anantha Singh & Ramesh 2013; Mbacké *et al.*, 2016), membrane filtration (Cheng *et al.*, 2011; Liang *et al.*, 2011), oxidation (Jana *et al.* 2010; Ünnü *et al.*, 2016), electrochemical oxidation (Zhang *et al.*, 2010; Yao *et al.*, 2013), and adsorption/biosorption (Sharma *et al.*, 2011; Ahmed 2016; Umpieres *et al.*, 2017) have been applied for the removal of MB and CV from contaminated wastewaters. Among them, biosorption is one of the most convenient methods to remove contaminants due to being a low-cost, simple, and efficient operation. In the case of adsorption, activated carbon is the most common adsorbent used for dye removal due its outstanding properties, such as good pore structures and high specific surface area. However, the treatment of contaminated water with activated carbon is not always feasible due to its high cost (Moreno-Castilla & Rivera-Utrilla 2001). For this reason, cheaper and effective alternatives need to be explored.

Several works have reported the use of dead macroalgae for the removal of contaminants (Rubin *et al.*, 2010; Esmaeili...
& Darvish 2014; Anastopoulos & Kyzas 2015; Devi & Murugappan 2016; Castro et al. 2017; Dadwal & Mishra 2017). This kind of biosorbent shows outstanding properties, including a large area/volume ratio, low cost, and relatively simple growth (Suresh & Ravishankar 2004; Escudero et al. 2016). To date, there are no biosorption studies reported in the literature using *Iridaea cordata* (IC) biomass for the removal of toxic compounds. This biomass is a cold- and dry-adapted red alga occurring in North and South America, Australia, New Zealand, and Antarctica (Navarro et al. 2010; Rautenberger et al. 2015). As for all red algae, the cell wall of IC is composed of agar, carrageenan, xylans, lectin and cellulose. The wide variety of functional groups present in these molecules could be involved in the biosorption process. Moreover, this alga is abundant and has the ability to maintain its functioning photosynthetic apparatus even in darkness and winter (Weykam et al. 1997). *Iridaea cordata* has been defined as an opportunistic life strategist and hence it is easy to cultivate under different laboratory conditions (Weykam et al. 1997). For these reasons, the aim of our work is to contribute novel information through the evaluation of the biosorptive potential of IC biomass for the removal of hazardous cationic dyes from aqueous solutions. This work opens the door for new studies in this field. The algae can be cultivated under different conditions, which generates biomasses with different functional groups and, hence, the possibility of its use to remove specific contaminants from aqueous media. In this study, the IC biosorbent was evaluated for removal of CV and MB dyes. The characteristics of the biosorbent were evaluated by the point of zero charge (pH<sub>PZC</sub>), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy X-ray dispersive spectroscopy (EDS). A 2<sup>5</sup> full factorial design was developed to optimize the pH and biosorbent concentration. The biosorption kinetic data were evaluated by the pseudo-first order and pseudo-second order model. The Brunauer–Emmett–Teller (BET) model was used to fit the biosorption equilibrium data. Thermodynamic parameters of standard Gibbs free energy change, standard enthalpy change, and standard entropy change were also estimated.

### MATERIALS AND METHODS

#### Solutions and reagents

CV dye (tris(4-(dimethylamino)phenyl)methylmethyl chloride; C.I. 42555; λ<sub>max</sub> = 583 nm; molecular formula C<sub>25</sub>H<sub>30</sub>N<sub>3</sub>; molecular weight 407.99 g mol<sup>−1</sup>) was obtained from Vetec (Brazil). MB dye (3,7-bis(dimethylamino)-phenothiazine-5-iium chloride; C.I. 52030; λ<sub>max</sub> = 664 nm; molecular formula C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl; molecular weight 319.8 g mol<sup>−1</sup>) was obtained from Merck Ltda (Brazil). Stock standard solutions of 1,000 mg L<sup>−1</sup> were prepared from an accurate weight of CV and MB dissolved in deionized water. Working standard solutions were prepared by appropriate dilution with deionized water. The pH of the solution was adjusted with 0.1 mol L<sup>−1</sup> NaOH and HCl solutions using a pH meter (Digimed, DM 20, Brazil) for the measurements.

#### Preparation of algal absorbent

The algal biomass was collected at locations in the vicinity of Casey Station in the Windmill Islands, East Antarctica. Macroalgae were transported in polyethylene containers to the laboratory, where they were first washed with drinking water and then rinsed with distilled water several times to remove extraneous and salts. After, the biomass was oven dried at 50 °C for 24 h, and stored in a desiccator. Finally, it was ground in a blender until particles with an average size of 1 mm, a BET surface area of 45 m<sup>2</sup> g<sup>−1</sup> and pore volume of 0.092 cm<sup>3</sup> g<sup>−1</sup> were obtained.

#### Methodologies used for macroalgae characterization

In order to know the surface charge of the biosorbent as a function of pH, pH<sub>PZC</sub> was determined following a procedure similar to that reported by Rivera-Utrilla et al. (2000). Initially, 50 mL of 0.01 mol L<sup>−1</sup> NaCl solutions was placed in closed Erlenmeyer flasks. The pH values were adjusted to 2, 4, 6, 8, 10, and 12 by the addition of 0.1 mol L<sup>−1</sup> NaOH or HCl solutions. Then, an amount of 0.15 g of the biosorbent was added and the final pH was determined after 48 h under agitation at room temperature. The pH<sub>PZC</sub> is the point where the curve of pH<sub>final</sub> vs. pH<sub>initial</sub> intersects the line pH<sub>initial</sub> = pH<sub>final</sub>.

FTIR spectroscopy (Shimadzu, Prestige 21, Japan) was used for the identification of functional groups present in the biosorbent (Silverstein et al. 2007). Samples were analyzed using potassium bromide (KBr) pellets (~0.5 mg sample with 100 mg KBr and compressing the mixture into a 13-mm diameter pellet).

The morphology of the biosorbent and the main elements present on the alga surface were evaluated by SEM coupled to EDS (Jeol, JSM-6610LV, Japan). Before analysis, samples were coated with a 15-nm thick Au/Pd layer with a sputter coating system. Both FTIR and SEM
analytical techniques were performed before and after the biosorption process in order to identify possible changes on the biosorbent surface.

**Biosorption experiments**

The biosorption experiments used to perform the experimental design were carried out as follows. Erlenmeyer flasks containing 25 mL of 50 mg L\(^{-1}\) CV or MB solutions were prepared. The pH of each dye solution was adjusted to different pH values (3, 5, and 7). Then, different amounts of the algal biosorbent (25, 50, and 125 mg) were individually added to the previous solutions. The flasks were stirred at 200 rpm in a thermostatic agitator (Marconi, MA 093, Brazil) for 90 min at room temperature. Finally, the solid phase was separated from the supernatant using a centrifuge (Centribio, 80-2B, Brazil) at 3,500 rpm for 10 min.

Subsequently, the kinetic experiments were carried out under the optimal conditions (above determined). Thus, 25 mL of dye solution (CV or MB), with initial dye concentrations of 50 and 100 mg L\(^{-1}\) were used. The pH was adjusted to 7. An amount of 25 mg of biosorbent was added to each solution. Contact times from 0 to 120 min were assayed (samples were withdrawn at different time intervals), at room temperature and under stirring rate of 200 rpm.

The equilibrium experiments were assayed in a thermostatic agitator at 298, 308, 318, and 328 K. Erlenmeyer flasks containing 25 mL of CV or MB solution with initial dye concentrations of 25, 50 mL of 100, 150, 200, and 300 mg L\(^{-1}\) were prepared and the pH of each solution was also adjusted to 7. The flasks were placed in the thermostatic agitator to reach the suitable temperature. Then, 25 mg of IC biosorbent was added to each flask. The flasks were stirred at 200 rpm until the equilibrium. Finally, the solid phase was separated by centrifugation.

For all experiments, the CV and MB concentrations were determined in the upper aqueous phase by spectrophotometry (Biospectro SP-22, Brazil), at the maximum wavelength for each dye. Calibration was performed against aqueous standards and blank solutions. The dye removal percentage (R, %) was calculated by Equation (1). Biosorption capacity at any time (\(q_t\) (mg g\(^{-1}\))) and at equilibrium (\(q_e\) (mg g\(^{-1}\))) were calculated by Equations (2) and (3), respectively (Crini & Badot 2008):

\[
R = \frac{(C_0 - C_e)}{C_0} \times 100
\]  

\[
q_t = \frac{V(C_0 - C_t)}{m}
\]  

\[
q_e = \frac{V(C_0 - C_e)}{m}
\]

where \(C_0\) is the initial dye concentration in liquid phase (mg L\(^{-1}\)), \(C_t\) is the dye concentration in liquid phase at any time \(t\) (mg L\(^{-1}\)), \(C_e\) is the equilibrium dye concentration in liquid phase (mg L\(^{-1}\)), \(m\) is the amount of adsorbent (g) and \(V\) is the volume of solution (L).

**Experimental design and optimization of variables**

As pH and biosorbent dosage play an important role in the biosorption process, the effects of pH (5, 7, and 9) and biomass concentration (1, 3, and 5 g L\(^{-1}\)) on the biosorption capacity were evaluated through a three-level two-factor 3\(^2\) full factorial design. The biosorption capacity \((q)\) was represented as a function of independent variables, through the polynomial quadratic equation expressed in Equation (4):

\[
q = a + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j
\]

where, \(a\) is the constant coefficient, \(b_i\) are the linear coefficients, \(b_{ii}\) are the interaction coefficients, \(b_{ij}\) are the quadratic coefficients, and \(x_i\) and \(x_j\) are the coded values of the variables. The statistical significance of the nonlinear regression was determined by Student’s t-test, the second order model equation was evaluated by Fisher’s test and the proportion of variance explained by the model obtained was given by the coefficient of determination, \(R^2\). Experimental runs were performed at random and the results were analyzed using Statistica version 9.1 (StatSoft Inc., USA) software.

**Kinetic studies**

Kinetic profiles of CV and MB biosorption on IC marine algae were developed by fitting the experimental data using the pseudo-first order (Lagergren 1898), and pseudo-second order (Ho & McKay 1998) models. These models are shown in Equations (5) and (6), respectively:

\[
q_t = q_1(1 - \exp(-k_1t))
\]  

\[
q_t = \frac{t}{(1/k_2q_e^2) + (t/q_2)}
\]
where \( k_1 \) and \( k_2 \) are the rate constants of pseudo-first order (min\(^{-1}\)) and pseudo-second order (g mg\(^{-1}\) min\(^{-1}\)) models, respectively; \( q_1 \) and \( q_2 \) are the theoretical values for the biosorption capacity (mg g\(^{-1}\)).

**Equilibrium models**

The BET model was tested aiming to represent the CV and MB biosorption on IC biomass. This model assumes sites with different energies on the surface of the adsorbent; consequently, multilayers can be formed in several parts of this surface. It is represented by Equation (7) (Brunauer et al. 1938):

\[
q_e = \frac{q_{BET}K_1C_e}{(1 - K_2C_e)(1 - K_2C_e + K_1C_e)}
\]  

where \( q_{BET} \) is the monolayer biosorption capacity (mg g\(^{-1}\)), \( K_1 \) and \( K_2 \) are the BET constants (L mg\(^{-1}\)).

**Thermodynamic studies**

The biosorption of CV and MB on IC alga was thermodynamically evaluated according to the standard values of Gibbs free energy change (\( \Delta G^0 \), kJ mol\(^{-1}\)), enthalpy change (\( \Delta H^0 \), kJ mol\(^{-1}\)), and entropy change (\( \Delta S^0 \), kJ mol\(^{-1}\) K\(^{-1}\)), which were estimated by Equations (8)–(10) (Milonjic 2007; Anastopoulos & Kyzas 2016):

\[
\Delta G^0 = -RT\ln(\rho K_e)
\]  

\[
\Delta G^0 = \Delta H^0 - \Delta S^0T
\]  

\[
\ln(\rho K_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\]

where \( K_e \) is the equilibrium constant (L g\(^{-1}\)) (based on the parameters of the best fit isotherm model), \( T \) is the temperature (K), \( R \) is 8.31 × 10\(^{-3}\) kJ mol\(^{-1}\) K\(^{-1}\) and \( \rho \) is the solution density (g L\(^{-1}\)).

**Modeling and parameter estimation**

The kinetic, equilibrium and thermodynamic parameters were determined by nonlinear regression using Statistic 9.1 software (Statsoft, USA). The fit quality was checked through \( R^2 \) and average relative error (ARE) (Equations (11) and (12)):

\[
R^2 = \left( \frac{\sum^n_{i=1} (q_{i,exp} - q_{i,model})^2 - \sum^n_{i=1} (q_{i,exp} - \bar{q}_{i,exp})^2}{\sum^n_{i=1} (q_{i,exp} - \bar{q}_{i,exp})^2} \right)
\]  

\[
ARE = \frac{100}{n} \sum^n_{i=1} \left| \frac{q_{i,model} - q_{i,exp}}{q_{i,exp}} \right|
\]

where \( q_{i,model} \) is each value of \( q \) predicted by the fitted model, \( q_{i,exp} \) is each value of \( q \) measured experimentally, \( \bar{q}_{i,exp} \) is the average of \( q \) experimentally measured, and \( n \) is the number of experimental points.

**RESULTS AND DISCUSSION**

**IC biomass characteristics**

*Iridaea cordata* biosorbent was characterized according to the pHpzc, FTIR spectroscopy, SEM, and EDS. The pHpzc of the marine algae was 6.80, which means that at pH values lower than 6.80, the surface charge of the biosorbent is positively charged. In contrast, if the pH is higher than 6.80, the surface of the algae is negatively charged.

FTIR spectroscopy was used in order to understand the possible interactions between the functional groups present in the biosorbent surface and the cationic dyes. As can be seen in Figure 1, the FTIR spectrum of IC biomass shows a broad band at 3,433 cm\(^{-1}\), which is mainly due to O–H and N–H stretching (Coates 2000). The band visualized at 3382 L. B. Escudero et al. | Macroalgae as biosorbent to remove hazardous cationic dyes Water Science & Technology | 76.12 | 2017

*Figure 1* | FTIR spectra of IC biomass before (1) and after CV (2) and MB (3) biosorption.
2,930 cm\(^{-1}\) is assigned to stretching vibrations of the C–H bond of the aliphatic groups (Coates 2000). The band found at 1,640 cm\(^{-1}\) can be attributed to stretching of the conjugated carbonyl bond in the lignin that is present in IC biomass (Chen et al. 2011; Song et al. 2011). The bands at 1,644 and 1,546 cm\(^{-1}\) can be attributed to C=O stretching vibration and a combination of N–H bending and C–N stretching vibrations in amide compounds (Duygu et al. 2012). The bands at 1,230 to 1,265 cm\(^{-1}\) are assigned to the aryl–O stretching of the aromatic ethers (Coates 2000). The bands at 1,042 and 1,153 cm\(^{-1}\) could be attributed to C–O–C stretching of ether (Coates 2000). The bands at 929 and 842 cm\(^{-1}\) could represent the j-carrageenans present in IC algae (Vijayaraghavan et al. 2015). The band at 847 cm\(^{-1}\) may correspond to the S=O stretching (Coates 2000). The weak band found at 620 cm\(^{-1}\) could be due to C–S and C=S stretching (Kannan 2014). The analysis of the IC spectrum reveals that the biosorbent contains several functional groups that could interact with CV and MB dyes. The spectra after biosorption with CV and MB (Figure 1) did not show significant changes with respect to the spectra of raw biomass. It means that no chemical links were formed or broken during the biosorption process, indicating that a physical process occurred.

Figure 2 shows the SEM images of IC biosorbent before (Figure 2(a) and 2(b)) and after the biosorption of CV (Figure 2(c)) and MB (Figure 2(d)). It can be observed that IC biomass is composed of amorphous particles dispersed on the rough surface (Figure 2(a) and 2(b)). This morphology is suitable to accommodate the molecules of CV and MB on the surface of the biomass. After biosorption of CV (Figure 2(c)) and MB (Figure 2(d)), a change (smoothing) in the surface texture of the biosorbent can be observed, which manifests the biosorption of the colored solutions on the algae surface.

Figure 3 exhibits the EDS spectra of IC biosorbent before (Figure 3(a)) and after biosorption process for CV (Figure 3(b)) and MB (Figure 3(c)) dyes. It can be observed that the marine algae contain elements such as C, O, Fe, Na, Mg, Al, Si, P, S, Cl, K, and Ca, which is in concordance with the biological matrix. After biosorption of dyes, some elements
cannot be observed in the spectra. In both cases, Fe is not present after the biosorption process. It could suggest that an ion-exchange could be one of the mechanisms involved in dye removal. In the case of MB biosorption, chloride is also absent, and the percentage of sulfur is higher in comparison with the raw biomass. This suggests the insertion of sulfhydryl groups of the organic molecule on the adsorbent surface.

**Optimization of cationic dye biosorption**

Table 1 shows the experimental design matrix and the results obtained through the $3^2$ full factorial design.

The significance of pH and biosorbent concentration on the biosorption capacity was evaluated by the Pareto charts, shown in Figure 4.

In the Pareto charts, the independent variables (represented by horizontal bars) are in the y axis and the standardized effects are in the x axis. The significance level ($p = 0.05$) is represented by a vertical dashed line. If the horizontal bars cross the vertical dashed line, then the independent variable significantly affects the response (biosorption capacity for each dye). Furthermore, if the horizontal bars have positive values, then the independent variable affects the response by a directly proportional

**Figure 3 | EDS spectra of IC biosorbent before (a) and after the biosorption process for CV (b) and MB (c).**

Table 1 | Experimental design matrix and results for CV and MB biosorption by IC biomass

<table>
<thead>
<tr>
<th>Experiment</th>
<th>pH [coded form]</th>
<th>IC concentration (g L$^{-1}$) [coded form]</th>
<th>CV</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$R$ (%)$^a$</td>
<td>$q$ (mg g$^{-1}$)</td>
<td>$R$ (%)$^a$</td>
</tr>
<tr>
<td>1</td>
<td>5 [-1]</td>
<td>1 [-1]</td>
<td>71.2 ± 2.5</td>
<td>34.9 ± 2.8</td>
<td>90.1 ± 3.1</td>
</tr>
<tr>
<td>2</td>
<td>5 [-1]</td>
<td>3 [0]</td>
<td>72.1 ± 2.9</td>
<td>11.9 ± 1.8</td>
<td>89.4 ± 2.7</td>
</tr>
<tr>
<td>3</td>
<td>5 [-1]</td>
<td>5 [+1]</td>
<td>75.8 ± 3.4</td>
<td>7.60 ± 2.1</td>
<td>89.5 ± 2.5</td>
</tr>
<tr>
<td>4</td>
<td>7 [0]</td>
<td>1 [-1]</td>
<td>73.0 ± 3.1</td>
<td>36.5 ± 3.1</td>
<td>90.8 ± 3.0</td>
</tr>
<tr>
<td>5</td>
<td>7 [0]</td>
<td>3 [0]</td>
<td>73.8 ± 3.1</td>
<td>12.0 ± 1.8</td>
<td>89.8 ± 3.1</td>
</tr>
<tr>
<td>6</td>
<td>7 [0]</td>
<td>5 [+1]</td>
<td>76.4 ± 2.6</td>
<td>7.60 ± 2.1</td>
<td>89.1 ± 2.8</td>
</tr>
<tr>
<td>7</td>
<td>9 [+1]</td>
<td>1 [-1]</td>
<td>72.4 ± 3.2</td>
<td>34.3 ± 2.7</td>
<td>90.0 ± 2.7</td>
</tr>
<tr>
<td>8</td>
<td>9 [+1]</td>
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<td>73.9 ± 2.9</td>
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<tr>
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<td>9 [+1]</td>
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<td>75.5 ± 3.3</td>
<td>7.52 ± 1.7</td>
<td>89.9 ± 3.3</td>
</tr>
</tbody>
</table>

$R$: dye removal percentage; $q$: biosorption capacity.

$^a$Mean ± standard deviation (n = 3).
manner. In the same way, if the bars have negative values, the influence is inversely proportional. For the biosorption capacity of CV (Figure 4(a)), it can be seen that linear and quadratic effects belonging to algae concentration were highly significant ($p \leq 0.05$). Regarding pH, only the quadratic effect was slightly significant ($p \leq 0.05$). For the biosorption capacity of MB, all the linear and quadratic effects and the interaction effects were significant ($p \leq 0.05$). However, it is clear that the effect of IC concentration was the most significant factor, whereas pH showed minimal effects.

The biosorption capacities of CV and MB as function of IC concentration ($x_1$) and pH ($x_2$) are depicted in Equations (13) and (14), respectively:

$$q_{CV} = 12.4 + 9.2 x_1^2 - 0.5 x_2^2 - 13.8 x_1$$  (13)

$$q_{MB} = 14.9 + 11.4 x_1^2 - 0.4 x_2^2 - 17.2 x_1 + 0.6 x_2$$
$$- 0.8 x_1 x_2$$  (14)

In order to verify the prediction and significance of the models, analysis of variance and Fisher F-test were used. The
biosorption model for CV proved to be significant and predictive, since calculated Fisher ($F_{\text{calc}} = 3.740$) was more than 1,000 times greater than the standard Fisher ($F_{\text{std}} = 3.34$), with $R^2$ of 0.99. The model for MB was also significant and predictive, with a calculated Fisher ($F_{\text{calc}} = 2.561$) 800 times higher than standard Fisher ($F_{\text{std}} = 3.1$), with $R^2 = 0.99$.

Response surface methodology is an interesting tool for multivariate optimization because it combines statistical experimental designs that can be used to describe the individual and cumulative effect of the evaluated variables on a response and determines the mutual interactions between the evaluated variables and their subsequent effect on the response. In this work, a representation of biosorption capacities vs. IC concentration and pH variables through graphics of response surface is shown in Figure 5. For both dyes, a marked negative effect of IC concentration on the biosorption capacity can be observed. It means that an increase of biomass concentration provokes a decrease of the biosorption capacity. Regarding pH, it does not show any effect on the biosorption capacity. It is important to highlight that the variable $q$ was selected since the removal percentages remained practically constant (see Table 1). The dye removal percentages were around 75% for CV and 90% for MB. The optimal conditions for textile dye biosorption onto the biosorbent were obtained by determining the maximum point of surface responses (Figure 5). This way, the optimal process conditions for biosorption of CV were an IC concentration of 1 g L$^{-1}$, and as pH does not show any effect on the test response, pH 7 was selected for further experiments because at this pH value it was not necessary to use additional reagents to adjust the pH of medium. Under these conditions, the biosorption capacity was 36.5 mg g$^{-1}$. The optimal process conditions for biosorption of MB onto IC biomass were also 1 g L$^{-1}$ IC concentration and pH 7, reaching a biosorption capacity of 45 mg g$^{-1}$.

**Kinetic models evaluation**

Figure 6 shows the biosorption kinetic curves of CV and MB on IC biomass at initial dye concentrations of 50 and 100 mg L$^{-1}$. A marked increase of biosorption capacity during the first minute can be observed, and after that, the increase of biosorption capacity was less than the previous one. The equilibrium was attained at around 90 min. Additionally, Figure 6 shows a higher biosorption capacity for MB than for CV dye, which could be related to steric effects from CV due to its size and distribution.

In order to obtain a suitable model that represents the kinetic results obtained experimentally, pseudo-first order and pseudo-second order models were fitted to experimental data. The selection of the more adequate model was based on the evaluation of $R^2$ and ARE. The kinetic parameters are given in Table 2. The high $R^2$ and the low ARE values show that the pseudo-second order model was the more suitable
to represent the biosorption kinetic of CV and MB onto IC marine algae. The $q_2$ parameter shows higher values for MB than for CV, which is in accordance with observations derived from Figure 6. Moreover, the $q_2$ values increase from 50 to 100 mg L$^{-1}$ for both dyes, confirming that the biosorption capacity is higher at higher concentrations. The $h_0$ (initial biosorption rate) values also increased with the initial MB and CV concentration, indicating that at the initial stages, the biosorption was faster when an initial concentration of 100 mg L$^{-1}$ was used. On the other hand, it is important to mention the $q_2$ values are very close to the experimental data ($q_{exp}$), which confirms the predictive potentiality of the pseudo-second order model.

**Equilibrium and thermodynamic results**

Figure 7 exhibits the equilibrium isotherms of CV (Figure 7(a)) and MB (Figure 7(b)) dyes onto IC biomass under...
According to Ruthven, it can be deduced that the isotherm curves obtained for both dyes were type II (Ruthven 1984). Figure 7 shows that the temperature increase provokes a decrease of dye biosorption capacity. This aspect makes the overall biosorption process more economical and clean, as it can be carried out at room temperature. The BET isotherm model was evaluated to fit the equilibrium data of CV and MB dyes onto the algal biosorbent. This model postulates that the initial adsorbed layer may act as a substrate for further biosorption stages; hence, the isotherm will be able to increase indefinitely (Mahmoud et al. 2015). The isotherm parameters are shown in Table 3. Considering the high values of $R^2$ and the low values of ARE obtained by the proposed model, it can be assumed that this model fit well the experimental data. The values of $K_1$ and $K_2$ decreased with the increase of temperature, which means that the biosorption process was favored at room temperature. Moreover, the increase of temperature caused a decrease of $q_{BET}$ values from 65.9 to 56.1 and from 62.8 to 43.6 for CV and MB, respectively.

The thermodynamic parameters for the cationic dye biosorption onto IC algae are shown in Table 4. The $R^2$ values of the linear fit were 0.9567 and 0.9692 for CV and MB, respectively. In both cases, the negative values of $\Delta G^0$ indicate that the biosorption processes were favorable and spontaneous at all the temperatures assayed. The negative values of enthalpy changes ($\Delta H^0$) evidenced that the biosorption processes were exothermic. Furthermore, the magnitude of $\Delta H^0$ suggested that physical interactions were involved in the biosorption processes (Piccin et al. 2011). The positive $\Delta S^0$ values suggested the possibility of some structural changes or readjustments in the dye–macroalgae complex. This thermodynamic behavior has been also obtained by other authors (Dotto et al. 2015; Tabarak & Heidarizadi 2016).

### Comparison with adsorbents reported in the literature for CV and MB biosorption

It is important to mention that there are no biosorption studies reported in the literature for CV and MB onto IC red algae. A comparative study of some biosorption parameters allows us to show the strengths of the IC biosorbent with respect to other ones used and reported previously (Table 5). The studied biosorbent shows a biosorption capacity that is similar to or even better than that reported for other biosorbents used for biosorption of the same cationic dyes. Although two studies showed higher biosorption capacities than that of the present work, both

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**Table 3 | Isotherm parameters for CV and MB biosorption by IC biomass**

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>CV</th>
<th></th>
<th></th>
<th>MB</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>298 K</td>
<td>308 K</td>
<td>318 K</td>
<td>328 K</td>
<td>298 K</td>
<td>308 K</td>
<td>318 K</td>
</tr>
<tr>
<td>BET</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_1$ (L mg$^{-1}$)</td>
<td>0.0767</td>
<td>0.0745</td>
<td>0.0637</td>
<td>0.0565</td>
<td>0.287</td>
<td>0.252</td>
<td>0.320</td>
</tr>
<tr>
<td>$K_2$ (L mg$^{-1}$)</td>
<td>0.0063</td>
<td>0.0056</td>
<td>0.0053</td>
<td>0.0047</td>
<td>0.0575</td>
<td>0.0303</td>
<td>0.0285</td>
</tr>
<tr>
<td>$q_{BET}$ (mg g$^{-1}$)</td>
<td>65.9</td>
<td>64.8</td>
<td>59.4</td>
<td>56.1</td>
<td>62.8</td>
<td>60.7</td>
<td>45.3</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99</td>
<td>0.96</td>
<td>0.95</td>
<td>0.98</td>
<td>0.88</td>
<td>0.81</td>
<td>0.94</td>
</tr>
<tr>
<td>ARE (%)</td>
<td>7.55</td>
<td>5.32</td>
<td>8.62</td>
<td>2.53</td>
<td>7.88</td>
<td>7.81</td>
<td>9.45</td>
</tr>
</tbody>
</table>

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**Table 4 | Thermodynamic parameters for CV and MB biosorption by IC biomass**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>CV dye</th>
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<th>MB dye</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G^0$ (kJ mol$^{-1}$)</td>
<td>$\Delta H^0$ (kJ mol$^{-1}$)</td>
<td>$\Delta S^0$ (kJ mol$^{-1}$ K$^{-1}$)</td>
<td>$\Delta G^0$ (kJ mol$^{-1}$)</td>
<td>$\Delta H^0$ (kJ mol$^{-1}$)</td>
<td>$\Delta S^0$ (kJ mol$^{-1}$ K$^{-1}$)</td>
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</tr>
<tr>
<td>298</td>
<td>-21.11</td>
<td>-13.58</td>
<td>0.03</td>
<td>-24.25</td>
<td>-9.89</td>
<td>0.05</td>
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<tr>
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<td>-21.69</td>
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<td></td>
<td>-24.64</td>
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<td></td>
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<td></td>
<td>-25.29</td>
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<td></td>
</tr>
<tr>
<td>328</td>
<td>-21.93</td>
<td></td>
<td></td>
<td>-25.64</td>
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</tr>
</tbody>
</table>
employed high concentrations of biosorbent for the biosorption of CV at concentrations similar to those used in this contribution (Chowdhury et al. 2014; Pavan et al. 2014). This work exhibits an outstanding advantage of the IC biosorbent in comparison with the others presented in Table 5, which is related to the low biosorbent concentration needed for biosorption of the cationic dyes, turning the complete process into a more economical alternative, because the consumption of reagents is considerably reduced.

**CONCLUSION**

For the first time, this work demonstrates the potential of IC for cationic hazardous dye removal from aqueous solutions, following the concept of ‘green chemistry’, minimizing the use of additional reagents and the generation of toxic residues to the environment. FTIR spectra suggested that no links were formed during the biosorption processes. SEM images showed changes in the texture of the biosorbent surface, indicating an accumulation of the cationic dyes on that surface. Three-level two-factor 3^2 full factorial design showed that the optimum conditions for CV and MB biosorption were pH 7 and 1 g L^{-1} algae concentration. Under these conditions, the biosorption capacities were 36.5 and 45.0 mg g^{-1} for CV and MB dyes, respectively. The dye removal percentages were around 75% for CV and 90% for MB. Kinetic and equilibrium studies were performed. The pseudo-second order was the most suitable to describe the experimental data of the biosorption processes (R^2 > 0.98 and ARE < 2.6). The BET isotherm model represented adequately the biosorption of CV and MB onto the marine biosorbent. Based on the thermodynamic parameters, the biosorption processes were demonstrated to be exothermic, favorable and spontaneous at all the temperatures assayed. To sum up, an efficient, cheap, and environmentally friendly biosorption process has been proposed and studied for removal of hazardous cationic dyes from aqueous solutions.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


