BIOSORPTION OF CRYSTAL VIOLET BY CHAETOPHORA ELEGANS ALGA

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ABSTRACT

Adsorptive removal capacities of renewable and highly available Chaetophora elegans alga have been investigated in this study. To assess the use of this soft water alga to remove organic pollutants from aqueous solution, crystal violet (CV) dye was used as a cationic model molecule. The effect of dye concentrations, pH, adsorbent mass, temperature, and salinity have been evaluated. The algal biomass showed quite interesting adsorption capacity under optimized operating conditions (158.7 mg of dye per gram of biomass at 25°C). The pseudo-first and pseudo-second order kinetic models were applied to the adsorption dynamic data. Pseudo second order model was well in line with the experimental data, suggesting therefore, a probable chemically-based sorption process. Several isotherm models were investigated to monitor the adsorption behavior. The Langmuir-Freundlich isotherm model fitted better the experimental data. The inhibition of the dye adsorption in the presence of different salts suggests that the salt inhibition is rather via an electric double layer. The adsorption thermodynamic parameters ΔG°, ΔH° and ΔS° were calculated. From the values of the thermodynamic parameters, we concluded that the adsorption is endothermic, less ordered and spontaneous.

Keywords: Chaetophora algae, crystal violet, adsorption isotherms, kinetics, salinity, thermodynamics.

INTRODUCTION

Water pollution mostly comes from wastewater which contains industrial and environmental pollutants. Dyes manufacturing causes serious problems in wastewaters. They affect biodegradation, light penetration and photosynthesis. Minor releases of colorants impact the aesthetics and health disorders to organisms exposed to them. Furthermore, some of these dyes on passage to drinking water cause damage to human life. Crystal violet (CV), a basic dye (belonging to the triphenyl carbocation dye group) is most widely used for the dyeing of cotton, wool, silk, nylon, paper, leather [1]. Crystal violet is also used for various purposes e.g. biological staining, as a dermatological agent, in veterinary medicine [2]. In fact, basic dyes, such as crystal violet, are the brightest class of soluble dyes whose tinctorial values are very high; it has been linked to increased risk of human bladder cancer and to cancer in the digestive system of other animals.

It is necessary to remove these dyes from a textile effluent before it is discharged into receiving water bodies. Possible treatments such as filtration, oxidation, sedimentation, biodegradation and adsorption for cotton textile wastes and their associated advantages and disadvantages are presented in the literature [3]. Adsorption techniques for wastewater treatment have become more popular due to their efficiency. The idea used to dye cotton and paper is employed to remove dyes from aqueous solution. Activated carbon is mainly used to remove dyes from aqueous solutions, but it is very expensive and its regeneration efficiency with the
increase of the sorption desorption cycles is not so good [4, 5]. Many reviews appeared in the literature on low cost adsorbents [5]. To remove dyes from aqueous solution, the adsorbent can be from agricultural waste like sugarcane bagasse pith [6], dates stones [7], industrial waste products including fly ash [8], and natural inorganic materials [9-11]

Many researchers studied the ability of algae to remove toxic dyestuff including Cystoseira baccata brown algae [12], Spirogyra [13], Pithophora sp. [14], and Enteromorpha sp. [15], from simulated industrial effluents. The ability of algae to remove mainly cationic dyes is due to the functional groups present in the principal organic constituents of algae such as polyphenols, polysaccharides, and alginic acid [16].

In this work, a batch-based adsorption study on Chaetophora elegans alga is undertaken for the removal of crystal violet from synthetic wastewater. The effect of pH, initial dye concentration, temperature, and matrix composition were tested in order to optimize the adsorption process. A comparison between linear and non-linear regression to predict the best sorption kinetics and to obtain more realistic set of dynamic parameters has been made.

**EXPERIMENTAL**

**Adsorbent**

The soft water algae Chaetophora elegans were collected from the pond in Amnik’s reserve in Bekaa valley, Lebanon (in June 2010). The material was first washed several times with tap water to remove dirt and small aquatic organisms. Afterwards, it was washed several times with distilled water. The material was dried at room temperature then rubbed by hands to turn it into a fine powder. The obtained powder was dried at 100 °C for 12 h. The distribution of particle size determined by Laser scattering particle size distribution analyzer (Horiba, Partica, LA-950V2) was 7 μm < d < 1900 μm and the mean size was 371 μm. The dried powder was characterized by FTIR (spectrophotometer Thermo, Nicolet IR 200, dilution with KBr) to identify the functional groups that might intervene in the adsorption process.

Crystal violet is a triphenylmethyl cation (C_{25}H_{31}N_3Cl; molecular mass 407.99 g). It was used in this study as a model molecule for organic pollutants in general and basic dyes in particular. The three phenyl rings of CV are substituted with dimethylamino groups.

Accurately weighted quantities of CV were dissolved in ultra pure water to prepare the stock solutions. The working solutions were prepared by diluting the stock solution to give the appropriate concentrations.

**Adsorption and Analysis**

All adsorption experiments were carried out by agitating the alga powder of a required amount with a certain volume of dye solution of desired concentration at constant temperature in a water bath shaker (Wisebath) at 215 rpm. Temperature control was provided by the water bath shaker unit.

Several operating conditions affecting the dye uptake were studied in order to optimize the overall adsorption process. Thus, the experiments were carried out for various alga mass, pH, contact time, salt concentration, temperature and different initial dye concentrations. The effect of pH on adsorption was investigated by varying the initial pH solution from 2 to 10. The solution pH was adjusted with diluted solution of HCl or NaOH. The effects of the salt concentrations and the ionic strength of NaCl, CaCl₂ solutions (0.05, 0.1, 0.5 and 1 M) on the dye uptake were then examined. After a predetermined time interval (for kinetics) or at equilibrium time (for isotherms), a small volume of the solution was extracted and analyzed for residual dye concentration via the spectro-photometric technique. The concentration of the dye was determined by double beam UV-Visible, Specord 200, Analytical Jena spectrophotometer.

The amount of dye adsorbed per g of alga at equilibrium; \( q_e \) (mg g⁻¹) or at time \( t \); \( q_t \) (mg g⁻¹) were calculated according to the following relations

\[
q_e = (C_o - C_e) \times \frac{V}{m} \tag{1}
\]

and

\[
q_t = (C_o - C_t) \times \frac{V}{m} \tag{2}
\]

\( C_o \) and \( C_e \) are the initial and equilibrium concentrations of dye (mg dm⁻³), respectively. \( V \) is the volume of
the dye solution (dm$^3$) and m is the amount of the adsorbent used (g). To determine the percentage of dye removal equation (3) is used:

$$\text{% removed} = \left(\frac{C_0 - C_f}{C_0}\right) \times 100 \quad (3)$$

**Desorption**

In order to clarify the mechanism of adsorption, desorption studies were also performed. Initially, batch equilibrium experiments were carried out, and then the dye-loaded adsorbent was filtered through filter paper and dried. Afterwards, 0.1 g of dye-loaded adsorbents was added into 40 ml of several concentrations of NaCl (0.1 to 1.0 M) or HCl (0.01 M- 0.1 M), and the mixtures were agitated for 4 h at 215 rpm. The desorbed dye was estimated as described in the adsorption experiments.

**RESULTS AND DISCUSSION**

**FT-IR Spectrum Analysis of Chaetophora Elegans**

The infrared spectrum, shown in Fig. 1, displays a number of absorption peaks, indicating the complex nature of the Chaetophora algae. Several bands were found at 3350 cm$^{-1}$ (-OH or NH$_2$), 2915 cm$^{-1}$ (-CH or COOH), 1620 cm$^{-1}$ (>C=O), 1424 cm$^{-1}$ (aromatic ring) and 1060 cm$^{-1}$ (C-O or S=O). Quite similar spectra were found in the literature for other algae such as Cystoseira baccata [12] and Cystoseira barbatula [17]. The FTIR spectrum of pure CV shows several characteristic peaks at 1584.24, 1361.5 and 1165.76 cm$^{-1}$. New peaks appeared after adsorption of CV onto algae at 1581.44 and 1356.62 cm$^{-1}$ which are attributed to C=C in an aromatic ring and to CN stretch in an aromatic tertiary amine, respectively (Fig. 1).

**Effect of adsorbent dosage**

The effect of adsorbent dosage on CV adsorption is shown in Fig. 2. The tested adsorbent amounts were between 0.02 and 0.20 g, for an initial dye concentration of 100 mg dm$^{-3}$. The results showed that as the adsorbent dosage increases, the residual dye concentration decreases from 8.4 to 0.74 mg dm$^{-3}$, which is due to the increase in the number of adsorption sites with the augmentation of the algae quantity and causes higher adsorption of dye. The sorption capacity calculated according to Eq.1 went down from 102.9 mg g$^{-1}$ using 0.02 g of algae to 19.2 mg g$^{-1}$ using 0.2 g of biomass. Similar results were obtained for dye removal using Brown alga Cystoseira barbatula [17] and spent tea leaves [18]. 0.1 g of algae was selected for the further experiments.

**Effect of initial pH**

Basically, the pH of the solution affects the adsorbent surface charge through protonation /deprotonation. For the case of CV, the pH has a huge effect on the protonation of the amino groups located at the aromatic rings. The number of positive charge decreases from 3 to 1 with the increase of pH. The color of the dye depends on the acidity of the solution. For pH > 5 the dye has a blue-violet color with a $\lambda_{max}$ at 582 nm and a shoulder at 540 nm, and an extinction coefficient of

![Fig. 1. FTIR spectrum of raw Chaetophora elegans algae before and after adsorption of CV (40 ml of 40 mg dm$^{-3}$ of CV, temperature 22°C and pH$_o$ 5.6).](image1)

![Fig. 2. Variation of the CV uptake as a function of Chaetophora elegans algae (40 ml of 100 mg dm$^{-3}$ of CV, temperature 22°C and pH$_o$ 5.6).](image2)
Fig. 3. Effect of pH on the adsorption of CV onto Chaetophora elegans algae (40 ml of 100 mg dm\(^{-3}\) of CV, 0.1 g of algae, temperature 22°C).

0.172 dm\(^3\) mg\(^{-1}\) at 582 nm. At a pH < 2 the dye is green with absorption maxima at 422 nm and 630 nm while in a strongly acidic solution (pH < 0.5), the dye is yellow with an absorption maximum at 420 nm. The different colors are a result of the different charged states of the dye molecule. In alkaline solutions (pH > 10), hydroxyl ions attack the electrophilic central carbon to produce the colorless triphenylmethanol. For this reason, the effect of pH on the CV adsorption was carried out for pH between 2 and 10. The effect of this parameter was evaluated for several dye concentrations. The variation of the uptake with initial pH follows the same behavior, so for simplicity, only the result with 100 mg dm\(^{-3}\) is shown in Fig. 3. For pH \(\leq 6\), the uptake of dye increased with the increase in pH, then for pH \(\geq 6\), the uptake of dye remained approximately constant. The moderate increase in CV uptake is mainly attributed to the electrostatic interactions between adsorbent and the positively charged cationic dye molecules, which is enhanced considering the negatively-charged biomass surface (i.e. gradual deprotonation as the pH increases) [18, 19].

**Effect of shaking**

The adsorption of dye was carried out by soaking and by shaking at 215 rpm. The results showed that the uptake of dye occurred in both cases, but the adsorption rate is much higher by shaking due to the increase in the transport material rate toward the adsorbent (Fig. 4). The equilibrium occurred by shaking during 30 min, but it takes 3 days by soaking. A similar result was obtained by the adsorption of methyl violet onto dead leaves of Posidonia Oceanica [20] and by the adsorption of MB onto feldspar [21].

**Effect of contact time**

Results of the effect of exposure time for CV adsorption under shaking onto soft water Chaetophora alga is shown in Fig. 5. It can be observed that, the rate of adsorption was very fast in the first 3 minutes (exponential phase). Then it gradually slowed down from 3 to 15 minutes (transition phase) until the equilibrium was reached (saturation phase). The results show that the equilibrium states were attained after almost 15 to 20 minutes within the experimental concentration range. Furthermore, raising the dye concentration from 40 to 100 mg dm\(^{-3}\) allows the fibers to increase their sorption
capacities from 17.6 mg g⁻¹ to nearly 38 mg g⁻¹ respectively at 22°C.

Hence, although 30 minutes seem to be sufficient to reach equilibrium for all studied CV concentrations, the isotherms experiments were left for 3 h to ensure full saturation. The visible spectrum of CV remained in solution after adsorption was little different from its spectrum before adsorption. The shoulder at 540 nm disappeared and there was a large band from 500 nm to 590 nm. The change in CV spectrum is due probably to interaction between the dye and the algae allowing a little change in the electronic resonance.

**Kinetic modeling analysis**

Kinetic studies are widely used for interpreting the dynamic interaction between adsorbent and adsorbate. Different kinetic models were used to predict the mechanism involved in the sorption process, namely a Lagergren pseudo-first order model and a pseudo-second order model for prediction of batch sorption kinetics.

In the present study, a comparison between a linear and a non-linear regression method has been used to predict the best sorption kinetic model and also to obtain reliable kinetic parameters. The kinetic parameters were evaluated by linear and non-linear regression analysis by using Excel and OriginPro® 7.0.

The Lagergren first order kinetic expression was used mostly in the literature to show adsorption capacity on different adsorbents [22]. The pseudo-first order equations are:

**Linear form:**

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.3} t
\]

**Non-Linear form:**

\[
q_t = q_e (1 - e^{-K_1 t})
\]

The first order rate constant \(K_1\) can be obtained from the slope of the plot of \(\log (q_e - q)\) versus time \(t\). The pseudo-second order model is based on the assumption that the adsorption follows second order chemisorption [23, 24]. The pseudo-second order model can be expressed as:

**Linear form:**

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}
\]

**Non-linear form:**

\[
qu = \frac{q_e^2 \times K_2 \times t}{1 + K_2 \times q_e \times t}
\]

where \(t\) is the contact time (min), \(q_e\) (mg g⁻¹) and \(q_t\) (mg g⁻¹) are the amounts of dye adsorbed at equilibrium and at any time, \(t\). A plot between \(t/q_t\) versus \(t\) gives the value of the constants \(K_2\) (g mg⁻¹ min⁻¹) and \(q_e\) (mg g⁻¹).

However, there is a limitation in this approach. Indeed, the transformation of data required for linearization can result in modifications of error structure, introduction of error into the independent variable and alteration of the weight placed on each data point. This will lead to difference in fitted parameter values between a linear and a non-linear version of the kinetic model. The dynamic sorption behavior of CV onto the Chaetophora elegans' surface under several initial dye concentrations was monitored and modeled using both linear and non linear regression analyses. The related kinetic parameters and error derivation values are presented in Tables 1 and 2 for linear and non linear regressions, respectively. For linear regression analysis, the \(R^2\) values clearly showed that the pseudo-second order model is the most suitable one to satisfactorily fit the experimental data for all dye concentrations.

Using the non linear regression analysis, the pseudo-second order model still fits well the kinetic data with \(R^2\) between 0.994 and 0.999. However, the Lagergren pseudo-first model showed a clear and significant improvement in complying with the experimental data. For instance, the \(R^2\) values, for a CV concentration of 40 mg dm⁻³, went from 0.75 with a linear analysis, up to 0.99 when using a non linear regression analysis. Thus, it is clear that when the pseudo-first order equation is applied to fit kinetic data using its linear form, there is a serious error in estimation its fitting aptitude. This seems not to be the case for the pseudo-second order model. Based on the comparison that we have done (at least for the present sorption system), we have demonstrated that the linear approach drastically diminishes the fitting aptitude of the first-order model. Hence, to come up with a more realistic and reliable kinetic modeling study, non linear regression analysis should always be the choice, especially since the analysis itself is quite easy considering the availability of many mathematical software programs.
Table 1. Pseudo first and pseudo second order adsorption kinetic parameters and error estimation, deduced from linear regression analysis.

<table>
<thead>
<tr>
<th>[CV]₀ (mg dm⁻³)</th>
<th>qₑ exp. (mg g⁻¹)</th>
<th>qₑ calc. (mg g⁻¹)</th>
<th>Kᵢ (min⁻¹)</th>
<th>R²</th>
<th>qₑ calc. (mg g⁻¹)</th>
<th>K₂ (g mg⁻¹ min⁻¹)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>17.7</td>
<td>1.1</td>
<td>0.0347</td>
<td>0.753</td>
<td>17.79</td>
<td>0.117</td>
<td>0.9993</td>
</tr>
<tr>
<td>50</td>
<td>19.3</td>
<td>7.4</td>
<td>0.092</td>
<td>0.891</td>
<td>19.50</td>
<td>0.0546</td>
<td>0.9998</td>
</tr>
<tr>
<td>75</td>
<td>28</td>
<td>12.6</td>
<td>0.061</td>
<td>0.863</td>
<td>28.10</td>
<td>0.0259</td>
<td>0.9992</td>
</tr>
<tr>
<td>100</td>
<td>38.37</td>
<td>18</td>
<td>0.083</td>
<td>0.623</td>
<td>36.6</td>
<td>0.0274</td>
<td>0.9974</td>
</tr>
</tbody>
</table>

Table 2. Pseudo first and pseudo second order adsorption kinetic parameters and error estimation, deduced from non linear regression analysis.

<table>
<thead>
<tr>
<th>[CV]₀ (mg dm⁻³)</th>
<th>qₑ exp. (mg g⁻¹)</th>
<th>qₑ calc. (mg g⁻¹)</th>
<th>Kᵢ (min⁻¹)</th>
<th>R²</th>
<th>qₑ calc. (mg g⁻¹)</th>
<th>K₂ (g mg⁻¹ min⁻¹)</th>
<th>R²</th>
<th>χ²</th>
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</thead>
<tbody>
<tr>
<td>40</td>
<td>17.7</td>
<td>17.17</td>
<td>0.83</td>
<td>0.989</td>
<td>0.35</td>
<td>17.67</td>
<td>0.118</td>
<td>0.986</td>
</tr>
<tr>
<td>50</td>
<td>19.3</td>
<td>18.65</td>
<td>0.48</td>
<td>0.976</td>
<td>0.87</td>
<td>19.53</td>
<td>0.044</td>
<td>0.994</td>
</tr>
<tr>
<td>75</td>
<td>28</td>
<td>26.49</td>
<td>0.415</td>
<td>0.960</td>
<td>3.1</td>
<td>28.04</td>
<td>0.0237</td>
<td>0.998</td>
</tr>
<tr>
<td>100</td>
<td>38.37</td>
<td>35.6</td>
<td>0.393</td>
<td>0.960</td>
<td>5.3</td>
<td>37.79</td>
<td>0.0178</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The activation energy was determined, from the slope of the Arrhenius plot of ln Kᵢ versus 1/T in the range of temperature between 20 and 40°C, and was found to be 34.5 kJ mol⁻¹ (with R²: 0.975 for 40 mg dm⁻³ of CV).

Isotherm modeling analysis

The analysis of the sorption equilibrium data is quite important in order to accurately monitor the adsorption behavior and exploit the isotherm data for design purposes. Several isotherm models are used in the literature to find the relationship between qₑ and Cₑ. The experimental data related to the adsorption of CV molecules onto the algal biomass at different temperatures were fitted using Langmuir [25], Freundlich [26], Temkin [27] and combined Langmuir-Freundlich equations [28]. In this study, the theoretically predicted isotherm data were determined using a non-linear regression analysis with the Origin software (in order to avoid the error induced using the linerized forms, as discussed in the kinetic section).

**The Langmuir model:** The Langmuir isotherm suggests that the CV adsorption is limited by monolayer coverage and there is no significant interaction among adsorbed species.

\[
qₑ = \frac{qₘₐₓ × b × Cₑ}{1 + b × Cₑ}
\]

(8)

where \(qₘₐₓ\) (mg/g) is the maximum sorbate uptake under the given conditions and \(b\) (dm³ mg⁻¹) is the sorption equilibrium constant, related to the affinity between the adsorbent and sorbate.

**The Freundlich model:** The Freundlich relationship is an exponential one expressed as follows:

\[
qₑ = k × Cₑⁿ
\]

(9)

where \(k\) is the Freundlich constant. The Freundlich isotherm exponent \(n\) is considered as a heterogeneity factor. In the literature, \(n\) values lower than 1 suggest a strong adsorption between adsorbent and sorbate.
**Temkin isotherm**: The Temkin isotherm deals with the heat of adsorption and the involved sorbent/sorbate interactions.

\[ q_e = \frac{RT}{b} \left( \ln K_T + \ln C_e \right) = A + B \times \ln C_e \quad (10) \]

where \( B \) is a factor related to the heat of adsorption and \( K_T \) is the Temkin equilibrium constant (dm\(^3\) mg\(^{-1}\)).

**Combined Langmuir-Freundlich**: Basically, it is an equation combining the previously mentioned Langmuir and Freundlich isotherms

\[ q_e = \frac{q_{\text{max}} \times b \times C_e^n}{1 + b \times C_e^n} \quad (11) \]

The experimental data related to the adsorption of CV molecules onto the algal biomass and the corresponding fitting models are shown in Fig. 6. The calculated isotherm constants by non linear methods are shown in Table 3. As seen, based on the highest \( R^2 \) (0.97 – 0.99) and the lowest \( \chi^2 \) (24 – 74) the best fitting equation is the Langmuir- Freundlich model for all four temperatures but the \( n \) values are not close to each other. If we fixed the value of \( n \) at 1.8, the isotherm parameters vary, for example at 30°C, \( R^2 \) decreased from 0.989 to 0.93 and \( b \) increased to 0.04. The high value of \( q_{\text{max}} = 140 \) mg g\(^{-1}\) at 20°C makes the Chaetophora elegans alga a very promising and highly performing biomaterial for basic dye removal from aqueous solutions. In the literature, the maximum sorptive capacity of CV reported (in mg g\(^{-1}\)) was 68 for Tendu (Diospyros melanoxylon) leaves [29], 47.3 for kaolin [30], and finally 45 for tea leaves refuse [18].

**Thermodynamic analysis**

The thermodynamic parameters for the adsorption of CV onto Chaetophora elegans algae were calculated by using the equations, given below:

\[ \ln K_{\text{dis}} = -\frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (12) \]

\[ \Delta G^\circ = \Delta H^\circ - T \times \Delta S^\circ \quad (13) \]

With

\[ K_{\text{dis}} = \frac{[CV]_{\text{ads}}}{[CV]_{\text{final}}} = \frac{C_v - C_e}{C_v} \quad (14) \]

where \( K_{\text{dis}} \) is equilibrium constant for adsorption, \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is temperature. The value of \( \ln K_{\text{dis}} \) was plotted versus \( 1/T \) (Fig. 7). The values of the enthalpy and the entropy change were calculated from the graph.

For an initial CV concentration of 40 mg dm\(^{-3}\), the Van’t Hoff equation is

\[ \ln k_{\text{dis}} = -2540.2 \times \frac{1}{T} + 11.67 \quad \text{(with } R^2 = 0.9877) \]

Thus, the calculated \( \Delta H^\circ \) was 21.08 kJ mol\(^{-1}\) > 0 (i.e. an endothermic phenomenon), \( \Delta S^\circ \) was 0.097 kJ mol\(^{-1}\) K\(^{-1}\)
Fig. 8. Variation of the % removed of CV vs final concentrations of NaCl and CaCl₂ for several concentrations of CV.

Table 3. Isotherm modeling parameters related to the biosorption of CV onto Chaetophora elegans (non-linear approach).

<table>
<thead>
<tr>
<th>Models</th>
<th>Parameters</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
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<tr>
<td>Langmuir</td>
<td>( \chi^2 )</td>
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<td>0.945</td>
<td>0.96</td>
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<td></td>
<td>( R^2 )</td>
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<td>223</td>
<td>222</td>
<td>160</td>
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<tr>
<td></td>
<td>( Q_{\text{max}} ) (mg g(^{-1}))</td>
<td>0.105</td>
<td>0.074</td>
<td>0.084</td>
<td>0.135</td>
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<tr>
<td></td>
<td>( b )</td>
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<td>0.96</td>
<td>0.83</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>( Q_{\text{max}} ) (mg g(^{-1}))</td>
<td>161.23</td>
<td>223</td>
<td>222</td>
<td>160</td>
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<tr>
<td></td>
<td>( b )</td>
<td>99.5</td>
<td>0.96</td>
<td>0.83</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>( Q_{\text{max}} ) (mg g(^{-1}))</td>
<td>223</td>
<td>222</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( b )</td>
<td>223</td>
<td>222</td>
<td>160</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>222</td>
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<td>223</td>
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<td>( K )</td>
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<tr>
<td></td>
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<tr>
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<td>( A )</td>
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<td>53.4</td>
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<td>437</td>
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<tr>
<td></td>
<td>( B )</td>
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<td>0.88</td>
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<tr>
<td></td>
<td>( A )</td>
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\( > 0 \) (i.e. more randomness) and \( \Delta G^\circ \) at 298 K equals -7.8 kJ mol\(^{-1}\) < 0 (i.e. a spontaneous process).

**Desorption results**

Desorption experiments were performed in order to clarify the mechanism of adsorption, and the results showed insignificant desorption with different ionic strength of the medium. The desorption results confirmed the chemisorption characteristics of adsorption process. The same result was also observed for the desorption of methyl violet onto dead leaves of *Posidonia Oceanica* [20].
Salinity effect

Since industrial effluents are always contaminated with various additives such as inorganic salts, it is therefore important to study the effect of these ions on the adsorption property of dye solutions. It was demonstrated clearly that salinity had a significant impact on the adsorption of basic dyes [12, 30-32]. The ion strength becomes large at high salt concentration, and this reduces the active concentration of dyes and active binding sites at the adsorbent surface, thus reducing the adsorption capacity [21]. The effect of salt was identified in the presence of different concentrations of NaCl and CaCl₂ (Fig. 8). The results showed a decrease in the % removed of CV vs concentration of salt. Based on the salt concentration, the inhibition effect of CaCl₂ is higher than that of NaCl (Fig. 8). For example, for initial concentration of CV equal to 120 mg dm⁻³ and in the presence of 0.1 M Ca(II), the % removed is 72.8 but it is equal to 91.5 in presence of the same concentration of NaCl. But based on the ionic strength, the inhibition effect of both salts is similar. Thus, the inhibition of CV adsorption via the compression of an electric double layer which propels away the positive charged dye molecules is more probable.

CONCLUSIONS

The adsorption of CV onto Chaetophora elegans alga was investigated in order to find out the possibility of using this renewable and low cost biomass in removing organic molecules from aqueous media. The effects of several operating conditions were experimented. It was shown that the sorption process is dependent on the contact time, the adsorbent dose, the pH, the salinity and the initial dye concentration. As for the modeling section, experimental data of CV adsorption were best fitted by the combined Langmuir–Freundlich model for isotherms and a pseudo-second order for kinetics. Besides, the thermodynamic analysis revealed that the present adsorption process is endothermic and spontaneous. Thus, the high adsorption capacity (Q_max = 158.7 mg g⁻¹ at 25°C) and the fast uptake (equilibrium within the first 20 minutes) of Chaetophora elegans makes this algal biomass are very promising biomaterial for dye removal from aqueous media and eventually - for the treatment of industrial effluents containing basic dyes.

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