Removal of a basic dye from aqueous solution by *Gracilaria corticata*

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ABSTRACT

The potential of *Gracilaria corticata* towards the removal of crystal violet from aqueous solution was examined. The biosorption of crystal violet with respect to pH, biosorbent dosage and initial dye concentrations were studied. The maximum biosorption was recorded at pH 8, 5 g/L biosorbent dosage and 1000 mg/L initial dye concentration. The equilibrium isotherms were described using the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips adsorption models. According to the Langmuir model, *G. corticata* exhibited biosorption capacity of 193 mg/g for crystal violet. Scanning electron microscopy pictures and Fourier-transform infrared spectroscopy confirmed the dye biosorption mechanism as electrostatic interaction between the negatively charged seaweed surface and positively charged crystal violet. The results obtained in this study clearly indicated that *G. corticata* was an effective adsorbent for the removal of crystal violet from aqueous solution.

KEYWORDS

basic dye, biosorption, crystal violet, *Gracilaria corticata*, isotherm

1. INTRODUCTION

Dyes are organic compounds that are used to impart color to various products developed in textile, leather, fur, cosmetics, hair, drugs, paper, waxes, greases, plastics and some other industries. The global consumption of dyes and pigments were approximately 7×10^5 tons/year. Of these, the textile industry itself consumes about two-third of the world production (Chen and Yang, 2005; Maurya et al., 2006). It was evaluated that 10 to 15% of the total dye used by the industries are lost during the dyeing process and eventually released into the environment (Phang, 2006, Vijayaraghavan and Yun, 2008). The wastewater from the dye-based industries often consist of toxic dye compounds along with substances such as dispersants, acids, bases, salts, detergents, oxidants, etc (Ho et al. 2002). Therefore, discharge from textile industries were usually high in color content, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and suspended solids (Akar et al., 2009). The released dye contaminants cause major environmental pollution by affecting photosynthesis process, penetration of light and causes health issues to living organisms (Padmesh et al., 2005b). Therefore, proper treatment of dye-bearing wastewaters is of great importance. The use of conventional physical and chemical treatment such as ion exchange, flocculation, irradiation, coagulation, precipitation and adsorption or sometimes a combination of these methods for the decolorization of dyes are limited due to limitations such as operational costs, formation of hazardous byproducts and intensive energy requirement (Jarosz-wilkolazka et al., 2002, Soni et al., 2012). Thus the situation demands the development of cost effective and

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innovative strategies to remove the dye contaminants from the industrial wastewater to minimize the risk of environmental threat. In recent years, bioremediation has been claimed as one of the most economical and environmental friendly strategies to remove dye contaminants from wastewater (Vijayaraghavan and Yun, 2008). Studies on the biosorption and biodegradation have focused on the ability of the microorganisms such as bacteria and fungi. Both active and dead forms of microbial cells were used in the decolorization process (Padmesh et al., 2005b). In addition to the above biological materials, seaweeds are also shown excellent sorption capacity towards variety of metal ions and dyes. In adsorption process, seaweeds have inherent advantages such as high mechanical stability, macroscopic structure, low cost and variety of binding groups (Balakrishnan et al., 2013).

The main objective of the present study was to evaluate the sorption potential of *Gracilaria corticata* towards crystal violet in aqueous solution. Crystal Violet (CV) was selected as the sorbate since it is one of the most important and widely used basic dye in process industries. The changes in seaweed surface characteristics and pore structure before and after exposure of CV was studied using scanning electron microscopy analysis. The equilibrium isotherm data were fitted using the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips equations to determine the correlation between the isotherm models and experimental data. The kinetic parameters were calculated to determine the mechanism of adsorption.

2. MATERIALS AND METHODS

2.1. Biosorbent Preparation and Chemicals

Marine red seaweed (*G. corticata*) was collected from the beaches of Mandapam region, Tamilnadu, India. After collection, the seaweed was extensively washed with deionized water. The biomass was subsequently dried under sun and once again oven dried at 70 °C. It was then grounded in a blender and sieved to prepare particles with average particle size of 1.18 mm for subsequent usage in sorption experiments.

All the chemicals used were of analytical grade and purchased from Ranbaxy Fine Chemicals Ltd., India; whereas crystal violet (CV) was procured from Sigma-Aldrich Corporation, Bangalore, India.

2.2. Experimental procedure

The pH of the dye solutions were initially adjusted using 0.1 M HCl or 0.1 M NaOH. In all experiments, 0.5 g of seaweed biomass was contacted with 100 mL of the dye solution in 250 mL Erlenmeyer flasks. The contents of the flasks were then agitated in an incubated rotary shaker at 150 rpm for 2 h at 30 °C. Once equilibrium was reached, samples were centrifuged at 3500 rpm for 5 min and the supernatant liquid was analyzed in a spectrophotometer (UV-1800, Shimadzu, Japan) at 590 nm. The amount of dye biosorbed was calculated from the difference between the dye quantities initially added and the dye content of the supernatant using the following equation:

\[
Q = \frac{V}{M} \times \left( C_0 - C_f \right)
\]

(1)

where \( Q \) is the dye uptake (mg/g); \( C_0 \) and \( C_f \) are the initial and final dye concentrations in the solution (mg/L), respectively; \( V \) is the volume of dye solution (L); and \( M \) is the mass of biosorbent (g). For pH edge experiments, initial CV concentration was fixed at 100 mg/L and pH was varied from 2 – 9. In the case of isotherm experiments, initial CV concentrations were varied from 50 – 1000 mg/L.

2.3. Characterization of *G. corticata*

To understand the surface morphology and sorption removal mechanism of seaweed, the samples before and after adsorption of CV were dried, coated with thin layer of gold and analyzed by scanning electron microscopy (Hitachi S4800 EDX). For FTIR analysis, samples of *G. corticata* before and after CV sorption were dried and coated with KBr to form pellets and analyzed using FTIR-spectrometer ATR IR with 4 cm\(^{-1}\) resolution for crystal-ZnSe scan range of 500 to 4000 cm\(^{-1}\). At particular wavelengths, the basic structure of compounds can be determined by the spectral locations of their IR absorptions.

2.4. Isotherm Modelling

Five equilibrium isotherm models were used to describe the adsorption data (Ho et al. 2002):

Langmuir: 

\[
Q = \frac{Q_{max} \cdot b \cdot C_f}{1 + b \cdot C_f}
\]

(2)
3. RESULTS AND DISCUSSION

3.1. Effect of pH

The pH of the biosorption medium significantly influences the biosorption process as well as property of the biosorbent (Mithra et al., 2012). The pH is an important parameter in the biosorption medium which influences the overall biosorbent charges and behavior of the solute particles onto the surface of seaweeds (Aksu and Tezer, 2000, Garg et al., 2003). The functional groups, hydroxyl and carboxyl present on the cell wall of the algae usually confer an overall negative charge to the cell surface (Ho, 2005). Basic dyes release colored and positively charged dye ions in the solution which were electrostatically attracted towards the negatively charged algal surface.

Figure 1. Effect of pH on the removal efficiency of CV by *G. corticata* (dosage = 5 g/L; concentration = 100 mg/L; agitation speed = 150 rpm)

In the present study, the effect of pH on biosorption of CV by *G. corticata* was studied over a pH range of 2 - 9. The uptake of CV by *G. corticata* was severely affected by the equilibrium pH. The minimum (38%) and maximum (97%) dye removal efficiency were observed at pH 2 and 8, respectively (Figure 1). When pH was increased beyond pH 8, biosorption potential of *G. corticata* decreased. At strong acidic pH values, the negatively charged groups of *G. corticata* will be protonated which gives the biomass an overall positive charge. Under these conditions, the binding of positively charged CV molecules to cell surface of *G. corticata* was difficult; hence little uptake was observed (Figure 1). As the solution pH increased, the concentration of H⁺ ions decreased, which in turn makes the algal surface negative (Aksu, 2005). Thus, the binding of positively

The essential characteristics of the Langmuir isotherm can be expressed by a separation factor or equilibrium parameter ($R_L$), a dimensionless constant, which can be defined as (Aksu, 2003),

$$ R_L = \frac{1}{1 + K_L C_0} $$  (7)

$R_L$ indicates the nature of the adsorption process as given below (Kumar et al., 2006):

- $R_L > 1$: Unfavorable
- $R_L = 1$: Linear
- $0 < R_L < 1$: Favorable
- $R_L = 0$: Irreversible

where $Q_{\text{max}}$ is the maximum dye uptake (mg/g), $b$ is the Langmuir equilibrium constant (L/mg), $K_F$ is the Freundlich constant (mg/g) (L/mg)$^{1/n_F}$, $n_F$ is the Freundlich exponent, $K_R$ is the Redlich-Peterson isotherm constant (L/g), $a_R$ is the Redlich-Peterson isotherm constant (L/mg)$^{1/\beta_R}$, $\beta_R$ is the Redlich-Peterson model exponent, $b_T$ is the Toth model constant (L/mg), and $n_T$ is the Toth model exponent. $K_S$ is the Sips model isotherm constant (L/g), $a_S$ is the Sips model constant (L/mg) and $\beta_S$ is the Sips model exponent, $R_L$ is the separation factor, $K_L$ is the Langmuir equilibrium constant which is related to the affinity of binding sites and $K_L = Q_{\text{max}} b$ (Aksu, 2003).

The average percentage error between the experimental and the predicted values was calculated using,

$$ \% \text{Error} = \sum_{i=1}^{N} \left( \frac{Q_{\text{exp},i} - Q_{\text{cal},i}}{Q_{\text{exp},i}} \right) \times 100 $$  (8)

where $Q_{\text{exp}}$ and $Q_{\text{cal}}$ represent the experimental and calculated uptake values, respectively; and N is the number of measurements.
charged CV molecules increased as the pH of solution increased (Figure 1). Through the results, it is clear that pH above neutral conditions favor adsorption process. Hence, optimal pH was identified as pH 8 and used in further experiments.

### 3.2. Effect of dosage

In the present study, the effect of biosorbent dosage on the biosorption of CV by *G. corticata* was evaluated. The amount of biosorbent added into the biosorption medium were varied from 2 to 8 g/L at fixed initial dye concentration of 100 mg/L and pH 8. The results obtained are displayed in Figure 2. It was determined that increase in biosorbent dosage from 2 to 5 g/L, the percentage CV decolorization increased. A further increase in adsorbent dosage had no influence on CV removal efficiency as depicted in Figure 2. The increase in sorbent dosage generally increases the number of binding groups and thereby improves extent of sorption. However, at high sorbent dosages, the number of dye molecules was insufficient to cover all the exchangeable sites of the biosorbent and thereby decreases sorption (Chowdhury and Saha, 2012; Soni et al., 2012). Therefore optimum adsorbent dosage was found to be 5 g/L.

![Figure 2. Effect of dosage on the removal efficiency of CV by *G. corticata* (pH=8; concentration=100 mg/L; agitation speed = 150 rpm)](image)

### 3.3. Effect of initial dye concentration

The dye removal efficiency of *G. corticata* decreased from 97.0 to 80.4% on increasing initial CV concentration from 50 to 1000 mg/L as presented in Figure 3. This is due to the fact that the available biosorption sites were relatively high when initial CV concentration was low and consequently the dye molecules could easily find accessible biosorption sites. Contradictorily at dye concentrations above 100 mg/L, a decreasing trend was noticed. This may due to the fact that at higher concentrations the available site for biosorption become fewer and consequently the dye uptake by biosorbent decreases (Nam and Renganathan, 2000; Verma and Mishra, 2005).

![Figure 3. Effect of initial dye concentration on the removal efficiency of CV by *G. corticata* (pH=8; dosage=5 g/L; agitation speed = 150 rpm)](image)

### 3.4. Biosorption isotherm and modeling

The quality of a biosorbent is usually judged by how much pollutant it can bind and retain in an immobilized form. Biosorption isotherm was evaluated by varying initial CV concentration in the range of 50 – 1000 mg/L at pH 8. Different adsorption isotherm models namely the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips have been examined for the present system (Garg et al., 2004). Figure 4 shows the experimental CV isotherm data along with predicted isotherms from the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips models. The model parameters along with the coefficient of determination ($R^2$) are presented in Table 1. It was evident from Figure 4 that the Langmuir isotherm described experimental CV isotherm well with $R^2$ value of 0.971. The Langmuir model constant, $Q_{max}$, corresponds to maximum dye uptake achievable for the present system; whereas b corresponds to affinity between dye molecules and seaweed particles. The maximum CV uptake was determined as 193 mg/g according to the Langmuir model. The separation factor, $R_L$, was found to be 0.143 and it reflects favorable condition for the adsorption (Soni et al., 2012).

The Freundlich model is an empirical equation
based on an exponential distribution of sorption sites and energies. The Freundlich isotherm exponent ($n_F$) values between 1 and 10 represents beneficial adsorption (Maurya et al., 2006). For the present system, $n_F$ value was determined as 2.89, which reflects favorable condition for adsorption. The Redlich-Peterson model is a combination of the Langmuir and Henry’s model. The model incorporates three parameters ($K_R$, $a_R$ and $\beta_R$) into an empirical isotherm, and thus can be applied to either homogenous or heterogeneous systems. When $\beta_R = 0$, the model reduces to the Langmuir model, while when $\beta_R = 1$, the model transforms to Henry’s law form. The constants $\beta_R$, $K_R$ and $a_R$ are shown in Table 1.

**Table 1. Isotherm model parameters for CV biosorption onto G. corticata**

<table>
<thead>
<tr>
<th>Model</th>
<th>$Q_{max}$</th>
<th>$b$</th>
<th>$R^2$</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>193</td>
<td>0.070</td>
<td>0.971</td>
<td>22.0</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>$n_F$</td>
<td>$R^2$</td>
<td>% Error</td>
</tr>
<tr>
<td></td>
<td>32.0</td>
<td>2.89</td>
<td>0.852</td>
<td>62.3</td>
</tr>
<tr>
<td>Redlich-Peterson</td>
<td>$K_R$</td>
<td>$a_R$</td>
<td>$\beta_R$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>14.4</td>
<td>0.089</td>
<td>0.972</td>
<td>0.965</td>
</tr>
<tr>
<td>Toth</td>
<td>$Q_{max}$</td>
<td>$b_T$</td>
<td>$n_T$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>167.6</td>
<td>0.0473</td>
<td>0.352</td>
<td>0.997</td>
</tr>
<tr>
<td>Sips</td>
<td>$K_S$</td>
<td>$\beta_S$</td>
<td>$a_S$</td>
<td>$R^2$</td>
</tr>
<tr>
<td></td>
<td>2.80</td>
<td>1.73</td>
<td>0.0164</td>
<td>0.997</td>
</tr>
</tbody>
</table>

**Figure 4.** Application of Langmuir, Freundlich, Redlich-Peterson, Toth and Sips models to experimental isotherm data obtained during CV Biosorption by G. corticata (pH = 8, biosorbent dosage = 5 g/L).

Further, the Toth model was examined for its compatibility with the CV isotherm data. The model constants, $Q_{max}$ and $b_T$ were recorded as 167.6 mg/g and 0.0473 L/mg, respectively. The Toth model derived from potential theory has proven useful in describing the biosorption in heterogeneous systems. It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e. most sites have sorption energy less than the mean value (Padmesh et al. 2005a). The Sips isotherm is a combination of the Langmuir and Freundlich isotherms. The Sips isotherm has the benefit of reducing to the Freundlich isotherm at low concentrations and approaches the monolayer capacity at high concentrations similar to the Langmuir isotherm. The Sips model constants along with $R^2$ and % Error are presented in Table 1. Of the different isotherm models examine, the Toth model provided highest $R^2$ and lowest % Error values.

**Figure 5.** SEM micrographs of G. corticata. Sample before biosorption (top image) and sample after biosorption (bottom image).
3.5. Mechanism of biosorption

The SEM results of raw and dye-loaded G. corticata biomasses are presented in Figure 5. According to the images, raw G. corticata has surface protuberance and microstructures, which may be due to Ca and other salt crystalloid deposition. After biosorption, the surfaces of G. corticata were covered with dye molecules and hence appeared relatively smooth (Figure 5). Thus, SEM images confirmed the dye biosorption mechanism as electrostatic interaction between the negatively charged seaweed surface and positively charged CV cations (Nigam et al., 1996, Davis et al., 2003).

![Figure 6. FTIR spectra of G. corticata. (a) sample before biosorption and (b) sample after biosorption](image)

To confirm the role of functional groups during removal of CV by G. corticata, the FTIR study was carried out on raw and dye-loaded G. corticata biomasses. As shown in Figure 6, the FTIR spectrum of raw G. corticata displayed a number of absorption peaks, indicating the complex nature of the biomass. The raw seaweed displayed peaks at 3269 cm\(^{-1}\) (–OH, –NH stretching), 1633 cm\(^{-1}\) (asymmetric C=O stretch of COOH), 1413 cm\(^{-1}\) (symmetric C=O), 1235 cm\(^{-1}\) (C-O (COOH) stretch), 1146 cm\(^{-1}\) (symmetric –OSO\(_3\)), and 1021 cm\(^{-1}\) (C-O (alcohol) band). After exposure to CV significant changes in G. corticata functionalities were observed (Figure 6). This is basically due to the participation of binding sites during interaction with dye and thus causing the changes in the observed wave numbers. In particular, major shifts were observed with asymmetric and symmetric C=O and C–O stretches in dye-loaded samples of G. corticata on comparison with raw G. corticata. Similarly, involvement of sulphonate groups was also confirmed as significant shifts were identified with symmetric -OSO\(_3\) bands in comparison with raw G. corticata. These results confirm the involvement of negative binding groups on the surface of G. corticata during biosorption of dye molecules (Bajpai and Jain, 2012).

4. CONCLUSIONS

The main results obtained in the present study can be summarized as below:
- G. corticata exhibited maximum biosorption performance towards CV molecules at optimized conditions of pH (8) and biosorbent dosage (5 g/L).
- Biosorption isotherms were modeled using the Langmuir, Freundlich, Redlich-Peterson, Toth and Sips models. G. corticata exhibited maximum CV uptake of 193 mg/g, according to the Langmuir model.
- Through SEM analysis, biosorbent surface was identified as smooth and flat after CV biosorption which confirmed CV biosorption onto G. corticata.
- On the other hand, FTIR spectroscopy provided the information on the role of negative functional groups during biosorption of CV.
- The results of present study clearly showed that G. corticata can be used as an effective low cost biosorbent for the removal of CV from aqueous solution.

REFERENCES


