Sawdust as a natural and low cost adsorbent for the removal of brilliant cresyl blue dye from water samples

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Abstract

Sawdust which is the main waste from wood industry has been used as a raw material for removal of Brilliant Cresyl Blue toxic dye. The effects of various parameters such as pH, electrolyte concentration, adsorbent dose, contact time and agitation rate were studied for the removal of the dye in a concentration of 50 mg L⁻¹. The optimum condition for the studied parameters was applied for various concentrations of the dye (20–200 mg L⁻¹) and in all the cases an efficiency of more than 96% is attainable. Adsorption isotherms were studied which were well in line with both Langmuir and Freundlich equations. The method was applied for the removal of dye from real samples of different waters such as industrial water, river water, tap water and sea water samples, in all of which dye removal was more than 94.

Keywords: Sawdust; Adsorption; Langmuire isotherm; Brilliant Cresyl Blue.

1. Introduction

Water pollution by dye through the discharge of industrial waste is a world-wide environmental problem. The effluents from dye manufacturing and consuming industries are highly colored coupled with high chemical and biochemical oxygen demands (COD and BOD). Therefore, the removal of dyes from wastewater is necessary. Adsorption is now recognized as an efficient and economic method to remove dyes from aqueous solution [1]. Recently, there has been an increasing emphasis on the adsorbents with low cost for dyes removal. Natural materials that are available in large quantities from agricultural operations may have the potential to be used as low cost sorbents, because they are widely available and environmentally friendly [2-6]. Sawdust is used as an adsorbent for the removal of many dyes [7-9].

The Brilliant Cresyl Blue (BCB) dye is a toxic dye, which has generally been removed from water samples through the use of magnetic multi-wall carbon nanotube [10], dimethyl terephthalate distillation residue [11], natural clay [12], peanut hull [13-14] and modified maghemite nanoparticles [15]. In this research, the BCB dye was removed through the use of sawdust. It is necessary to be mentioned that in this research no transformation was done in regard with this adsorbent. Sawdust is very appropriate and favorable, which makes the task very simple, easy and fast.

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2. Experimental

2.1. Apparatus and Materials

In this research the following apparatus were employed: A spectrophotometry uv–visable, manufactured by Varian, model: Carry 100; A pH meter, manufactured by Ohmeter, model: 750; A shaker, manufactured by Stuart-Scientific, Model: S-150.

Brilliant Cresyl Blue (BCB) was obtained from Merck. The chemical structure of the BCB dye is shown in Fig. 1.

![Chemical structure of BCB dye](image)

Fig. 1. The chemical structure of the BCB dye.

2.2. Preparation of the adsorbent

In order to prepare the adsorbent, sawdust was first washed well with distilled water. Next, that was kept in an oven with a temperature of 110 °C for 24 hours. and then that was sieved with mesh 0.50 mm.

2.3. Procedure of general removal

In the experiment, BCB dye with a concentration of 50 mg L\(^{-1}\) and intended pH was prepared in a 50 mL volumetric flask, and then it was added to a 250 mL erlenmeyer flask, containing 1.0 g of sawdust. The erlenmeyer flasks were placed on a shaker at 180 rpm, for 20 minutes. After filtration, the obtained solutions were analyzed, with a Varian spectrophotometer at \(\lambda_{\text{max}} = 624\) nm. The resulted adsorption was achieved through a calibration curve for BCB in concentration range of 0.1 to 10.0 mg L\(^{-1}\). It was then changed to concentration and the percentage of dye removal was calculated.

3. Results and Discussion

In order to achieve the best results, that is, the highest amount of dye removal, various factors were optimized. The approach for optimization in all cases was "one at the time" approach (i.e. changing a single variable while all other variables are kept constant). The equation number (1) was employed the calculate the amount of dye removal:

\[
\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100
\]

In this equation, \(C_0\) is the initial dye concentration, and \(C_e\) is the equilibrium concentration. The equilibrium concentration was achieved through a calibration curve for the BCB dye.

3.1. Effect of pH

In this study, 50 mL of dye solution of 50 mg/L initial concentration at different pH values (3.6–7.3) was agitated with 0.5 g of sawdust in a shaker at 200 rpm for 30 min. Fig. 2 shows that the adsorption of BCB was minimum at the initial pH 3.6 and increased with pH up to 4.3 and
then remained nearly constant over the initial pH ranges of 4.3–7.2. The observed low adsorption rate of BCB on sawdust at pH< 4 may be because the surface charge become positively charged, thus making (H⁺) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed A similar behavior was observed for methylene blue adsorption on jackfruit peel [5].

![Fig. 2. Effect of pH on BCB dye removal](image)

3.2. **Effect of Absorbent Dose**

In order to achieve the minimum amount of adsorbent for the removal of a maximum amount of BCB, the adsorbent dose was optimized. The results showed (fig. 3) that an adsorbent dose of 20 g L⁻¹ for a concentration of 50 mg L⁻¹ can remove more than 98 % of the dye. It is well to mention that an adsorbent dose of 2 g L⁻¹ can remove more than 74 %, which is better in comparison to sawdust with a dose of 25 g L⁻¹ for the removal of congo red up to 77% [16].

![Fig. 3. Effect of adsorbent dose on BCB dye removal](image)

3.3. **Effect of Electrolyte**

KCl was used as an electrolyte. Investigations of the effect of electrolyte on the BCB uptake have been done in the presence of KCl. The studies implied that an increase in electrolyte concentration up to 0.3 mol L⁻¹ does not have a considerable effect in the removal of BCB (removal decreases of about 2 percent was observed); while, in many adsorption methods, the presence of electrolyte results in a severe decrease of removal [4,17].

3.4. **Effect of Contact Time and Agitation Rate**
In this study, the necessary time interval was studied. The obtained results showed that even in a short interval of 2 minutes, more than 95% of the dye is removed (fig. 4). However, for a removal of about 98%, a time interval of 20 minutes (when the shaker is at 180 rpm) is needed. This method needs less time in comparison with many other methods [10-12]. That is probably due to the large surface area of sawdust for the adsorption of BCB ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [18]. Therefore, time of 20 min was considered in each sorption experiment.

Fig. 4. Effect of contact time on BCB dye removal

Furthermore, the effect of agitation rate was investigated. When samples of BCB dye with a concentration of 50 mg L$^{-1}$ and intended pH are shaken for 20 minutes at 180 rpm, there is a dye removal of 98% with 1.0 g of the adsorbent. Of course, there would be a removal of about 93% of dye at 80 rpm.

3.5. Effect of Initial Dye Concentration

In all the cases of optimization, the dye used had a concentration of 50 mg L$^{-1}$. In order to study the possibility of dye removal in other concentrations with the same optimization condition, other concentrations were studied, as well. The results showed that the optimization condition was applicable for concentrations 20-200 mg L$^{-1}$ and in all cases dye removal will be more than 96%.

3.6. Isotherms of Adsorption

In this study, Langmuire and Freundlich isotherms were employed for the study of the adsorption of BCB dye on sawdust. Such isotherms were achieved for an initial concentration of 40-200 mg L$^{-1}$ in the previous optimization condition and a temperature of 25±2 °C; and $q_e$ is achieved through Eq (2):

$$q_e = (C_s - C_e) \frac{V}{W}$$

(2)
In this equation, $q_e$ is the adsorption capacity in an equilibrium; $C_0$ is the initial concentration of dye; $C_e$ is the equilibrium concentration; $V$ is the volume of solution; and $W$ is the weight of the adsorbent.

The Freundlich model is known to characterize the adsorption on heterogeneous surfaces; its logarithmic form is given by Eq. (3):

$$\ln q_e = \ln K_F + \frac{1}{n} (\ln C_e) \quad (3)$$

Where $K_F$ is the Freundlich constant and $n$ is a constant related to the intensity of adsorption.

The Langmuir model which characterizes monolayer’s adsorptions is expressed in its linear form by Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} \frac{C_e}{Q_0} \quad (4)$$

Where $Q_m$ represents the maximum adsorption capacity, and $K_L$ the Langmuir constant. Both of the isotherms are well adapted with the adsorption of BCB on sawdust (Table 1). The coefficients of correlation were high ($R^2 = 0.991$ for Langmuir isotherm and $R^2 = 0.987$ for Freundlich isotherm) showing a good linearity. In fact, this means that the adsorption of BCB on sawdust is both monolayer and reversible, and it also practically shows that adsorption develops appropriately. The maximum adsorption capacity is better than what was reported for malachite green [2].

### Table 1
Isotherm parameters for removal of BCB on Sawdust.

<table>
<thead>
<tr>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
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<tbody>
<tr>
<td>$K_L$ (mg g$^{-1}$) = 7.31</td>
<td>$K_F$ (mg g$^{-1}$) = 0.36</td>
</tr>
<tr>
<td>$q_m$ (mg g$^{-1}$) = 20.41</td>
<td>$n$ = 0.82</td>
</tr>
<tr>
<td>$R^2 = 0.991$</td>
<td>$R^2 = 0.987$</td>
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### 3.7. Application

In order to test the reliability of the proposed removal methodology, it was applied to the removal of BCB from industrial, river, tap and sea water samples. For this purpose, 25 mL of each of the samples was treated under the general procedure. Spiking BCB dye to the samples performed the validity of the procedure. Dye removal in all the samples was more than 94%, which reveals the effectiveness of this method for all samples.

### 4. Conclusions

Recently, various low-cost adsorbents derived from agricultural wastes have been investigated intensively for dyes removal from contaminated wastewater. The present work shows that sawdust can be used as an adsorbent for the removal of Brilliant Crecyl Blue dye from aqueous solutions. The amount of dye adsorbed was found to vary with pH, an adsorbent dose and contact time. The presence of electrolyte exhibited only minor effects on the dye sorption, which
is important for potential applications of sawdust in real systems. The results showed that good extraction efficiencies are obtained for the removal of BCB spiked to river and industrial, tap and sea water samples. The isothermal data of adsorption followed both Langmuir and Freundlich models. The adsorption capacity of sawdust for the removal of BCB from aqueous solution was 20.41 mg/g at 25 °C.

References