Research Article

Removal of Methyl Violet 2B from Aqueous Solution Using Casuarina equisetifolia Needle

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One of the major contaminants of water bodies is dye pollutants that come from textile, paper, and leather industries. In this study, Casuarina equisetifolia needle (CEN) is used to remove methyl violet 2B (MV) from aqueous solutions. Batch experiments were done to investigate the contact time, effect of pH, initial dye concentrations, and temperature. Langmuir and Freundlich isotherm models were used to describe the interaction between the adsorbate and adsorbent. The sorption mechanism was described using Lagergren 1st order, pseudo 2nd order, and Weber-Morris intraparticle diffusion models. FTIR spectroscopy was used to analyze the functional groups of CEN before and after sorption with MV. Optimal conditions were found to be at room temperature with 2 h contact time and no pH adjustment was needed. Experimental data was best fitted onto Langmuir model with maximum adsorption capacity of 164.99 mg/g, while pseudo 2nd order best described the experimental data for the kinetics study. Thermodynamic parameters such as change in Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$), and entropy ($\Delta S^\circ$) were also investigated.

1. Introduction

Synthetic dyes are inexpensive and widely used in textile industry, food, and cosmetics as well as dyeing plastic, rubber, leather, and paper materials [1, 2]. Discharging industrial wastewater containing such dyes to aquatic environment can contaminate surface water bodies and groundwater. This can result in serious damage to the aquatic flora and fauna as dyes may be toxic and mutagenic [3, 4]. Damages can be extended to the soil through leachant and irrigated water.

Common methods used by the industry to treat the wastewater include adsorption, filtration, reverse osmosis, photodegradation, biodegradation, ion-exchange method, coagulation, and chemical treatments by reduction, oxidation, and neutralization [2, 5, 6]. Biosorption is a preferred method due to the usage of low-cost materials, low energy usage, and high efficiency [2]. Material that can be regenerated and reused is considered as an added advantage. In biosorption process, dye molecule is adsorbed onto the biomass through physical or chemical adsorption and thus avoids the formation of degraded dye products which may be more harmful than the dye itself. Biosorption via “renewable biomass” is a key advantage over nonrenewable adsorbents such as clay, peat, zeolite, lignite, and some forms of activated carbons [7].

Methyl violet 2B (MV), is a basic dye, with high brilliant and intensity and is highly used in the industry. Molecular structure of MV is shown in Figure 1. Reports have shown that MV could hinder the growth of bacteria and photosynthesis of aquatic plants [1, 5]. MV may be harmful by ingestion, inhalation and skin contact and long-term exposure can cause eye and skin damages [1]. Moreover, MV was reported by Vachálková et al. to be potentially carcinogenic [8]. Such harmful properties of MV dye create an urgency to be removed from industrial wastewater before being discharged into the environment.

Low-cost materials such as tarap core [9], dragon fruit skin [10], peat [11], pinewood [12], rice husk [13–16], corncobs [17], banana peel [18], orange peel [19], fly ash [20], sewage sludge [21], and waste newspaper [22] have been researched for their ability as biosorbents. The needle-like leaves of Casuarina equisetifolia (CEN) are renewable resource and can be
processed with ease into particles of desired size, and they are also abundant in nature making them an attractive potential as a biosorbent. Studies on the removal of chromium ion from aqueous solution had been done using activated carbon prepared from CEN seed husk \[23\] and leaves \[24\]. This study aims at exploring the potential use of CEN as a low-cost biosorbent in removing MV from aqueous solution under optimized conditions such as contact time, pH, initial dye concentration, and temperature. The adsorption kinetic models, isotherm models, and thermodynamic parameters were also investigated.

2. Experimental

2.1. Chemicals and Instrumentations. Methyl violet 2B (C.I 42535) was purchased from Sigma-Aldrich. pH was adjusted using NaOH (Univar) and HNO\(_3\) (AnalaR). Spectroscopy grade KBr was used for FTIR analysis. All reagents were used without further purification. Distilled water was used throughout this study.

Panasonic MX-J210GN blender was used to blend the samples. The samples were dried in Gallenkamp Hotbox oven. Stuart orbital shaker was used for agitation of the solution and ThermoScientific Orion 2 Star pH Benchtop was used to measure the pH. Shimadzu UV-1601PC UV-Visible spectrophotometer (UV-Vis) at wavelength 584 nm was used for methyl violet 2B analysis. Shimadzu IR Prestige-21 spectrophotometer was used for FTIR analysis. Tescan Vega XMU scanning electron microscope (SEM) was used to observe the surface of the sample, which was gold-coated with SPI-MODULE sputter coater.

2.2. Sample and Stock Preparation. Casuarina equisetifolia needle (CEN) was collected from the campus ground and was submerged in distilled water inside ultrasonic bath to remove dirt. The sample was then oven-dried at \(\sim 80^\circ\text{C}\) before it was blended and sieved. Sample size of \(< 355\ \mu\text{m}\) was used for the experiment. 1000 mg/L stock solution of MV was prepared by dissolving 1 g of MV in 1 L of distilled water. Other concentrations of MV used in the experiment were done by diluting the stock solution.

2.3. Batch Experimental Procedure. Batch experiments were carried out by mixing 25 mL of known concentration of MV solution with 0.05 g of CEN in a 125 mL conical flask. The mixtures were then agitated on an orbital shaker at 250 rpm at room temperature. Various parameters such as effect of contact time (10–240 mins), effect of initial concentration (10, 50, and 100 mg/L), effect of medium pH (2–10), and effect of temperature (30, 40, 50, and 60°C) were done for optimizing the experimental conditions. The medium pH was adjusted using 1 M HNO\(_3\) and 1 M NaOH. The experiments were done under agitation time of 120 mins, determined from the effect of contact time experiment, after which the mixtures were filtered and the filtrates were analyzed for MV content using UV-Vis at wavelength of 584 nm.

The amount of MV adsorbed per gram of CEN, \(q_e\) (mg/g), was calculated using

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

where \(C_i\) is the initial dye concentration (mg/L), \(C_e\) is the equilibrium dye concentration (mg/L), \(V\) is the volume of MV solution used (L), and \(m\) is the mass of CEN used (g). The percentage removal of the dye is represented by

\[ \text{Percentage removal} = \frac{(C_i - C_e) \times 100}{C_i}. \]

Thermodynamic variables such as the Gibbs free energy (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)), and entropy (\(\Delta S^0\)) were investigated by studying the sorption process at different temperatures (20, 30, 40, 50, and 60°C). Van’t Hoff equation was used to calculate the following variables:

\[ \Delta G^0 = -RT \ln K, \]

\[ K = \frac{C_i}{C_e}, \]

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

\[ \ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \]

where \(K\) is the distribution coefficient for adsorption, \(C_s\) is the equilibrium dye concentration on the CEN (mg/L), \(C_e\) is the equilibrium dye concentration in solution (mg/L), \(R\) is the gas constant (J/K mol), and \(T\) is the temperature (K).

2.4. Isotherm Study. Adsorption isotherm experiment was done by mixing 25 mL of different initial MV concentrations (10–1000 mg/L) and 0.05 g of CEN under the predetermined conditions above.

Langmuir \[25\] and Freundlich \[26\] isotherm models are used to best describe the sorption process of removal of MV by CEN.
The Langmuir isotherm assumes a monolayer adsorption onto the surface with a definite number of identical sites. The nonlinear and linearized forms for Langmuir are given by (7) and (8), respectively, as follows:

\[ q_e = \frac{q_{\text{max}} b C_e}{(1 + b C_e)}, \]

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

where \( q_{\text{max}} \) is the monolayer biosorption capacity of the adsorbent (mg/g) and \( b \) is the Langmuir biosorption constant (L/mg) which is related to the free energy of biosorption.

The Freundlich isotherm model, on the other hand, takes into account multilayer coverages where the dye can still be adsorbed onto the dye saturated biosorbent surface. The nonlinear and linearized forms for the Freundlich are given by

\[ q_e = K_f q_{\text{max}}^{1/n}, \]

\[ \ln q_e = \frac{1}{n} \ln C_e + \ln K_f, \]

where \( K_f \) [mg/(L/mg)^{1/n}] is the adsorption capacity of the adsorbent while \( n \), the Freundlich constant, gives indication of how favourable the adsorption process (adsorption intensity) is or surface heterogeneity.

The separation factor \( (R_L) \) is a dimensionless constant which is an essential characteristic of the Langmuir model. It is given by the following equation:

\[ R_L = \frac{1}{(1 + b C_0)^n}, \]

where \( C_0 \) (mg/L) is the highest initial dye concentration and \( b \) (L/mg) is the Langmuir constant. \( R_L \) indicates whether the isotherm is either unfavorable \( (R_L > 1) \), linear \( (R_L = 1) \), favorable \( (0 < R_L < 1) \), or irreversible \( (R_L = 0) \).

2.5. Kinetics Study. Kinetic study was done by mixing 1 g of CEN with 500 mL of 100 ppm MV solution. The mixture was agitated at 250 rpm and room temperature. 1 mL aliquot was taken at specific time interval between 1 and 120 minutes.

Lagergren 1st order [27], pseudo 2nd order [28], and Weber-Morris intraparticle diffusion [29] models were used to describe the mechanism of the sorption process.

(i) Lagergren 1st model,

\[ \log(q_e - q_t) = \log q_e - \frac{t}{2.303 K_1}, \]

(ii) pseudo 2nd model,

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

(iii) Weber and Morris intraparticle diffusion model

\[ q_t = K_3 t^{1/2} + C, \]

where \( q_e \) is the amount of dye adsorbed per unit of adsorbent (mg/g) at time \( t \), \( K_1 \) is the pseudo-first-order rate constant (min^{-1}), \( t \) is the time shaken (min), \( K_2 \) is pseudo second-order rate constant (g/mg min), \( K_3 \) is the intraparticle diffusion rate constant (mg/g min^{1/2}), and \( C \) is the slope that represents the thickness of the boundary layer.

2.6. Characterization of CEN

2.6.1. Fourier Transform Infrared (FTIR) Spectroscopy. 2 mg of the biosorbent was mixed with 200 mg of KBr and the mixture was grounded to powder. The powder was then compressed into a KBr translucent disk under a pressure of 10 ton using bench press for 5 min. The IR spectra were then analysed and recorded at spectral range from 4500 to 400 cm^{-1}. This step was repeated for the biosorbent after treatment with MV.

2.6.2. Scanning Electron Microscope (SEM). Morphological analysis of CEN’s surface was done using scanning electron microscope. Dried CEN was mounted on a conducting adhesive tape and sputter coated with gold for 2 minutes. SEM images were taken at ×2000 magnification.

2.7. Statistical Analysis. The best isotherm model and kinetic model were chosen based on the correlation coefficient \( (R^2) \) value, fitting of the non-linear regression, the residual root mean square error (RMSE), and the chi-square test \( (\chi^2) \):

\[ \text{RMSE} = \sqrt{\frac{1}{m-2} \sum_{i=1}^{m} (Q_i - q_i)^2}, \]

\[ \chi^2 = \sum_{i=1}^{m} \frac{(Q_i - q_i)^2}{q_i}, \]

where \( Q_i \) is the experimental value while \( q_i \) is the calculated value and \( m \) is the number of observations in the experiment. The smaller the RMSE and \( \chi^2 \) values, the better curve fitting [30].

3. Results and Discussion

3.1. Effect of Initial Concentration and Contact Time. Figure 2 shows the effect of contact time and initial concentration on the adsorption of MV at room temperature. The dye uptakes are very fast for the first 10 mins in the case of 10 mg/L and 50 mg/L and 50 mins for 100 mg/L. It then slows down as the surface of CEN becomes saturated with MV and eventually reaches equilibrium after 120 mins. Therefore, in this study, the agitation time was set to 120 mins as the optimal contact time.

It can be observed that the adsorption capacity, \( q_e \), increases as the initial concentration increases. The \( q_e \) for 10, 50 and 100 mg/L are 1.66, 12.44, and 38.11 mg/g, respectively. This is because as the initial concentration increases, the resistances against the mass transfer of the dye molecule from solution to the solid phase are overcome by the mass transfer.
driving force and hence more sorption occurs. Also, an increase in concentration results in an increase in the interaction between the dye molecule and CEN, therefore, increases the sorption process [31].

3.2. Effect of pH. Effect of pH on the removal of MV from aqueous solution by CEN is shown in Figure 3. Data for pH 2 was omitted as colour change was observed when the MV solution’s pH was adjusted to pH 2. Removal of MV decreased slightly when the pH increased from pH 4 to pH 10. Hence, it can be said that pH has no significant effect on the adsorption of MV onto CEN. This case is unusual as most other studies [31–35] showed an increase in removal of adsorbate with increasing pH. The ambient medium (no pH adjustment) was pH 6.70 and has the highest percentage removal of 69%. Therefore, in this study, no pH adjustment was made.

3.3. Effect of Temperature and Thermodynamic Parameters. As shown in Figure 4, the $q_e$ increases as the temperature increases albeit a small increase from 16 to 18 mg/g. As a result of temperature increases, the rate of diffusion of the dye molecule increases as the viscosity of the solution decreases. This leads to an increase in sorption process as the movement of molecule increases from the bulk solution to the surface of the solid at higher temperature [36].

Plotting the linear plot of ln $K$ against $1/T$ from (6), the thermodynamic variables $\Delta H^0$ and $\Delta S^0$ can be calculated from the slope and intercept, respectively. Table 1 shows the thermodynamic variables at different temperatures. Negative value of $\Delta G^0$ signifies the feasibility of the process and as shown in Table 1, the $\Delta G^0$ becomes more negative as the temperature increases, suggesting that the process is more spontaneous at higher temperature. The $\Delta H^0$ value (8.05 kJ/mol) with the sorption process being positive indicates that the process is endothermic. Adsorption process is usually considered as physical sorption if the $\Delta H^0 < 84$ kJ/mol and as chemisorption when the value lies between 84 and 420 kJ/mol [32]. The $\Delta S^0$ value of this study is $-35$ J/(mol K), where a positive value indicates the increase of disorder of solid-liquid interface during the sorption process, while a negative value indicates less disorder, and no significant changes occur in the adsorbent’s internal structure by the sorption process [33].

3.4. Isotherm Studies. Adsorption isotherm is important for the optimization of adsorbent used and also to describe the interaction between the adsorbate and adsorbent. Therefore, the correlation of equilibrium data using either empirical or theoretical equation is important for data interpretation and prediction [37]. For this purpose, two widely used isotherm models, Langmuir and Freundlich, were employed to interpret the experimental data. Plotting $C_e/q_e$ versus $C_e$ from (8)
Table 2: Parameters of Langmuir and Freundlich models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_{max}$</td>
<td>164.99</td>
</tr>
<tr>
<td></td>
<td>$b$</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>42.64</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>141.39</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$</td>
<td>[mg/g(L/mg)^1/2]</td>
</tr>
<tr>
<td></td>
<td>$n$</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>67.62</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>201.69</td>
</tr>
</tbody>
</table>

Table 3: Comparison of $q_{max}$ for MV adsorption by various biosorbents.

<table>
<thead>
<tr>
<th>Biosorbent</th>
<th>$Q_{max}$ (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yunnan Pu-ehr tea</td>
<td>285.71</td>
<td>[35]</td>
</tr>
<tr>
<td>Peanut straw char</td>
<td>101.01</td>
<td>[3]</td>
</tr>
<tr>
<td>Rice hull char</td>
<td>48.65</td>
<td>[3]</td>
</tr>
<tr>
<td>Soybean straw char</td>
<td>70.36</td>
<td>[3]</td>
</tr>
<tr>
<td>Sunflower (Helianthus annuus L.) seed hull</td>
<td>92.59</td>
<td>[1]</td>
</tr>
<tr>
<td>Acid modified activated carbon</td>
<td>83.30</td>
<td>[39]</td>
</tr>
</tbody>
</table>

Figure 5: Comparison of Langmuir and Freundlich non-linear regression plots with experimental data.

should give a straight line, where $q_{max}$ and $K_F$ can be calculated from the slope and intercept, respectively. Similarly, for Freundlich variables, $K_F$ and $n$ can be obtained by plotting $\ln q_e$ versus $\ln C_e$. Both isotherm models’ parameters are shown in Table 2.

Both isotherm models gave good linearity with Langmuir having better $R^2$ value than that of Freundlich. Also, the RMSE and $\chi^2$ values for Langmuir are smaller than Freundlich suggesting that Langmuir isotherm model is a better fit for the experimental data. Figure 5 shows the comparison of non-linear regression for both models and experimental data. Langmuir can be seen as the better fit between the two models with the experimental data. Therefore, from these three factors, it can be said that Langmuir can describe the experimental data the best. Sorption of MV by CEN yields an $R_L$ value of 0.1, indicating that the process is favourable. The parameter $n$ (1.55) from the Freundlich model also indicates that the process is favourable as $1 < n < 10$ [38]. The maximum adsorption capacity, $q_{max}$ is 164.99 mg/g which is better than many of the reported biosorbents (Table 3). Therefore, CEN can be a potential material for the removal of MV.

3.5. Kinetic Studies. Chemical interaction between the adsorbent surface’s functional groups and adsorbates is often included in the mechanism of adsorption. Other mechanisms such as mass transport process, bulk transport, diffusion across the liquid film around the surface, and diffusion into micropores and macropores are also involved. Availability of the adsorbent’s surface, physicochemical nature, surface area, physical size and form of the adsorbent particles is an important characteristic that determines equilibrium capacity and rate [40].

In this study, almost 70% removal of MV by CEN was achieved within 1 minute (data not shown). This shows that the kinetics of the system was very fast and this is useful as fast kinetics is highly desired for application purposes. As shown in Table 4, the trend of $R^2$ value was pseudo 2nd order > Weber-Morris > Lagergren 1st order, indicating that pseudo 2nd order is the best fit model for the experimental data. This is supported by the RMSE and $\chi^2$ tests, where pseudo 2nd order has the lowest values for these tests. Also, pseudo 2nd order $q_e$ calculated value is closer to the $q_e$ experimental; hence, pseudo 2nd-order model is the best fit for the experimental data. Pseudo 2nd-order model indicates that the overall process is dependent on the amount of adsorbate and the available sites on the adsorbent’s surface [41]. It also
3.6. Characterization of CEN. FTIR spectra of CEN before and after treatment with MV are shown in Figure 6. Broad band around 3342 cm\(^{-1}\) represents the O–H and/or N–H stretching vibrations. The two bands observed at 2922 and 2852 cm\(^{-1}\) indicate the presence of C–H bond from aldehyde group. This is confirmed by the band stretching at 1732 cm\(^{-1}\) which usually indicates the presence of carbonyl group (C=O). Alkene (C=C) stretching band is observed at 1620 cm\(^{-1}\). From FTIR spectrum (i), shifts can be observed in these functional groups’ stretching bands. This suggests that adsorption of MV onto CEN’s surface involves these functional groups. The SEM image in Figure 7 showed that CEN surface has no large pores or cavities and has a rather homogeneous surface. Treatment of CEN with MV shows that the surface has changed and MV is clearly seen to be adsorbed onto the surface.

4. Conclusion

The result of this study showed that CEN has the potential to be used as a low-cost adsorbent for the removal of MV from wastewater. The optimal conditions were found to be ambient pH (6.70), at room temperature, as no significant increase
of adsorption capacities was observed at higher temperatures and 2 h contact time is sufficient to bring the system to equilibrium. The kinetics follows the pseudo 2nd-order model and Langmuir isotherm model best fit onto the experimental data with the maximum adsorption capacity, $q_{\text{max}}$, of 164.99 mg/g. Thermodynamic study showed that the sorption process was endothermic, spontaneous, and physical in nature.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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