Study of Adsorption Characteristics a Low-Cost Sawdust for the Removal of Direct Blue 85 Dye from Aqueous Solutions

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ABSTRACT

The performance sawdust as a low cost adsorbent to remove Direct Blue 85 (DB85) dye from aqueous solutions has been evaluated. The characteristic of sawdust analyzed by FTIR and XRD. The removal percentage of this dye was studied at different experimental conditions such as contact time, adsorbent dosage, particle size, temperature, and pH. The optimum removal percentage value was found at pH 2. Temperature also has a positive impact on adsorption, where the adsorption of this dye on the sawdust increased as the temperature increased. High values of correlation coefficient signified that the adsorption of (DB85) dye on the surface of sawdust obey Langmuir and Freundlich adsorption isotherms.

Keywords: Direct Blue 85 dye; adsorption isotherms; Langmuir; Freundlich

INTRODUCTION

The pollution of water by dyes is a worldwide problem especially in textile industries where large amounts of dyed wastewater from dyeing operations are unloaded to environment. These dyes are mostly used in large-scale industries like paper, rubber, cosmetic and plastic industries [1]. Most of the dyes may be toxic to living organisms and are not easily decomposed or removed from effluent by traditional wastewater treatment methods. This enhances the risk of pollution in an aquatic environment and makes need for the removal of dyes from wastewater [2]. Since most of these dyes are toxic in nature, their presence in industrial effluents poses major environmental concern [3]. Therefore, dyes removal become an important aspect of treatment of wastewater before being discharged. The removal of dyes from wastewater presents a great challenge because most dyes are quite soluble in aqueous solutions and they are not easily degradable. The presence of dyes in water can change its color prevent sunlight to cross and reach the deep water, consume oxygen and dyes are itself carcinogenic or can be degraded to carcinogenic intermediates compounds [4]. The removal of dyes from wastewaters is often more important than the removal of the colorless soluble organic substances, which commonly contribute to the main fraction of the biochemical oxygen demand (BOD) [5]. There are several treatment technologies used in the removal of dyes from industrial wastewater. The adsorption, oxidation, and biological methods [6].

Removal of dyes by adsorption has been extensively studied in the last years. Activated carbon has been successfully used in removing colored organic species while being the most widely used as adsorbent due to its high capacity of adsorption of organic materials [7-8]. However, due to its high cost,
an effective yet cheap adsorbent material is urgently required. Lately, many local inexpensive materials were studied as new adsorbents to remove pollutant and dyes from wastewater. It is preferable to use low cost adsorbents, such as natural ores, agricultural byproducts and an industrial waste. Thus the important task is to develop and improve adsorbents materials derived from solid wastes. These materials are no cost and can be used for contaminants treatment like dyes and these adsorbents can be the solution for treatment of colored effluents by dyes or pigments after increasing its performance [9].

Recently, many researchers were develop low-cost treatment technology, like using diatomite as alternative adsorbent for methylene blue dye removal [10]. Fly ash was used as an inexpensive adsorbent for Cr(III) removal from aqueous solutions [11]. Rice husk, spent tea leaves and orange peel were used for lead adsorption from aqueous solution. Like these adsorbents as reported are commercially viable, economical and eco-friendly [12].

The aim of this work is to evaluate the efficiency of sawdust as low-cost adsorbent to remove of the Direct Blue 85 (DB85) dye from aqueous solution. The effect of contact time, adsorbent dosage, particle size, temperature, and pH were studied to find the optimum condition of DB85 dye removal. The results are to evaluate to determine the possibility of sawdust as a potential alternative adsorbent replacing the more expensive adsorbent, such as activated carbon.

EXPERIMENTAL SECTION

Preparation of Adsorbent

Local wood sawdust is collected from carpentry workshops in Al-Hilla city. The powder was washed with large amount of distilled water several times to remove the soluble impurities and dust, then was dried at 50 °C overnight. The dried sawdust was grounded and sieved to a required particle size was (75) µm.

Characterization

Sawdust was characterized by FTIR and XRD analysis. Sawdust before and after adsorption process examined by Affinity FTIR instrument supplied by Shimadzu company, where about 10 mg of samples mixed with potassium bromide in an agitated mortar and pressed manually as a clear disc and tested in the range 400-4000 cm⁻¹. XRD analysis was accomplished by X-ray apparatus (DX-2700 SSC 40 kV/30mA, USA) using powder method in the range of 20 5–60°.

Effect of pH and Surface Chemistry

The point zero charge of sawdust as adsorbate according to reference [13]. In briefly, 1 g of sawdust was added to a solution of 50 mL of KNO₃ (0.01 N) and the initial pH was adjusted to be between 2 to 11 using KOH (0.01 N) and HNO₃ (0.01) solutions. The solutions were sealed and shaken vigorously for 48 h, then filtered and the final pH of the solutions were measured. The intersection point that obtained between the change in pH value against initial pH values is the point zero charge.

Boehm titration method was used for determination of the amount of acidity/basicity of functional groups [14]. A known amount of sawdust was added into 50 mL of the solutions of NaHCO₃ (0.1 N), Na₂CO₃ (0.1 N), NaOH (0.1 N) and HCl (0.1 N) separately. All solutions in the conical flasks were sealed and shaken at room temperature for 48 h. 10 mL of each filtrate was titrated with HCl (0.1 N) for the first three solutions and the sample treated with HCl titrated against NaOH (0.1 N).

Preparation of Adsorbate

The Direct Blue 85 (DB85) dye used in this study was obtained from Hilla textile factory, the chemical structure of this dye is shown in Fig. 1. To prepare a dye solution, 1 gm of dye powder was dissolved in 1 L of distilled water to obtain the concentration of a stock solution with 1000 mg L⁻¹. Stock solution diluted to obtain the required concentrations range (10–100) mg.L⁻¹ in the experiments. DB85 dye has a maximum absorbance at the wavelength (λ_max) equal to 576 nm was measured using optima UV-visible spectrophotometer.

![Fig 1. The chemical structure of DB85 dye](image-url)
**Adsorption Procedure**

For each experimental run, 0.25 g of sawdust powder with particle size was 75 μm added to 100 mL conical flask, then 25 mL of dye aqueous solution (10 mg/L) is added and the flask is tightly closed. These flasks were shaken at 200 rpm at room temperature for a predetermined contact time. After that, centrifuged at 3000 rpm for 10 min. The pH of solutions in all adsorption processes was (5–6). The dye concentration in the aqueous phase was determined spectrophotometrically by a UV spectrophotometer at ($\lambda_{\text{max}}$ 576 nm).

The removal percentage of dye was calculated by the following equation:

$$ R\% = \left( \frac{C_o - C_e}{C_o} \right) \times 100 $$

The adsorption capacity ($Q$) of dye by sawdust adsorbent (mg/g) was calculated using the following equation (15):

$$ Q = \frac{(C_o - C_e)V}{m} $$

where: $C_o$: the initial concentration of dye (mg/L); $C_e$: the equilibrium concentrations of dye in solution (mg/L); $V$: the volume of solution (L); $m$: the weight of sawdust (g).

**RESULT AND DISCUSSION**

The FTIR analysis (Fig. 2) showed the presence of intense bands of wood before adsorption which is mainly attributed to lignocellulose and hemicellulose OH stretching shows strong broadband in the range 3300–4000 cm$^{-1}$, and 1633 cm$^{-1}$ belongs to O-H bending [16]. C–H stretching (CH$_2$ and CH$_3$ asymmetric and symmetric stretching vibrations) 2800–3000 cm$^{-1}$ as alkyl groups that belong to lignin and cellulose and also intense bands attributed to lignocellulose components in the region 1000 to 1750 cm$^{-1}$. The aromatic skeletal vibrations bands appeared from 1508 and 1600 cm$^{-1}$ could belong to lignin, and the carbonyl group C=O stretch band (in non-conjugated ketones and esters) at 1735.9 cm$^{-1}$ is caused by hemicellulose [17-19].

The bands at 1608, 1510 and 1244 cm$^{-1}$ are assigned to C=C, C–O stretching or bending vibrations of different groups present in lignin [18]. The bands at 1460, 1429, 1328.9, 1244 and 1115 cm$^{-1}$ are characteristic of C–H, C–O deformation, bending or stretching vibrations of many groups in lignin and carbohydrates [18]. C–O stretching, O–H bending, C–O antisymmetric Stretching, stretching of the many C-OH and C-O-C bonds at 1244, 1155, 1045 and 1272 cm$^{-1}$ respectively, also C-H bending appeared at 835.67 and 897.87 cm$^{-1}$ [20].

The spectrum of DB85 adsorbed on sawdust surface exhibited a small shift in some bands like C–O deformation and O–H (stretching and bending) shifted to low and high frequency respectively. These changes in the spectrum as an indication of possible involvement of DB85 functional groups on the sawdust surface in the adsorption process.

The XRD pattern of wood sawdust appears in Fig. 3, the major diffraction peaks are 15.82°, 22.52°, and weak intensity 39.5° and this according to literature, the particle has some of the compositions of hemicelluloses, cellulose, and lignin [22]. The diffractogram after adsorption is slightly changed in diffraction angle but the intensity of peaks are increased due to dye adsorption on sawdust surface.

**Effect of Contact Time**

The effect of contact time on removal of dye was studied and shown in Fig. 4. This figure indicates that the dye concentration in aqueous solution decreases rapidly in the beginning and remains nearly constant after 60 min, this is attributed to the large surface area of the adsorbent is available in the starting of adsorption [23]. Also, the fast adsorption in the initial stage of adsorption was due to many sites available.

![Fig 2. FTIR analysis of sawdust (dark line) and sawdust after adsorption of DB85 dye (red line) ](image)
Thus, the progressive decrease of adsorption sites resulted in a slower adsorption reaction [24].

Effect of pH

The initial pH value of the solution is an important parameter in the adsorption study since it determines the surface charged of the adsorbent [23] and this value is resulted from the functional groups that distributed in sawdust surface. These functional groups can be determined by a simple titration method, where in the titration, the mmol of functional groups were estimated. These active groups are carboxylic acids, lactones and phenol and the no. of mmol were 0.103, 0.094, and 0.088 mmol/gm respectively, which are represent the acidic groups and the basicity was 0.086 mmol/gm. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of adsorption process [24]. Thus the effect of pH value was studied for sawdust and according to the change of initial pH values against the change in pH after agitation for 48 h in KNO₃ solution, we found the point zero charge at pH = 7.27 (Fig. 5) and this value is near to the previous study on sawdust [13]. According to Fig. 5 the surface charge determined by measuring the pH change against various constant initial pH, when we draw $\Delta$ pH against pH, the curve has an intercept with pH on x-axis, which is represent the point of zero charge (pzc) value.

When solution pH < pHzpc, the sawdust surface will be charged a positive, so enhance the attraction of anions. In this study, when pH is low (acidic medium), the adsorption is favorable for of the anionic dye (DB85) by the sawdust. Where, in acidic media (pH < pHzpc) the number of negatively charged adsorbent sites decreased and inverse situation is happened for the number of positively charged surface sites. As a result, adsorption is effected by pH and sawdust favors the negatively charged dye anions due to electrostatic attraction [14].

Fig. 6 shows the effect of initial pH of dye solution on removal percentage of dye. The results showed that the efficient removal of dye increase with decreasing pH value of the solution. The high percentage efficiency removal of the dye at acidic medium may be attributed to the electrostatic interactions between the positively charged adsorbent and the negatively charged dye anions. The surface charge of adsorbent
Fig 6. Effect of initial pH of dye solution on removal percentage of DB85 dye onto sawdust surface at 25 °C (± 2 °C)

Effect of Particle Size

Adsorption of DB85 dye on four particle sizes of adsorbent was studied. The results are shown in Fig. 8. It is observed from Fig. 6 that the percentage removal of dye decreases with increased the particle size of adsorbent. The decrease in particle size leads to an increase of available active sites on the surface of the adsorbent and consequently an increase in the adsorption process on the sawdust surface due to the high surface area. Furthermore, the diffusional resistance to mass transfer increases as the particle size increases [26].

Effect of Temperature

The effect of temperature on adsorption processes was examined at different temperatures ranging between 15 to 60 °C with a constant initial dye concentration of (10 mg/L). Temperature is an important controlling factor in the real applications of the dye removal process [27]. Thermodynamic parameters, such as the change in Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$), were calculated using Equations (3 and 4):

$$\Delta G = -RT\ln K_d$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where $K_d$ is the equilibrium partition constant calculated as the ratio between sorption capacity ($q_e$) and equilibrium concentration ($C_e$), $R$ is the gas constant (8.314 J/mol/K) and $T$ is the temperature in Kelvin (K). From Equation (4) a plot of log $K_d$ as a function of Kelvin (K) should give a linear relationship with a slope equal...
Fig 9. Arrhenius plot for DB85 dye sorption onto sawdust surface at different temperatures

$$y = -2.004x + 12.461$$

Fig 10. Adsorption capacity related to dye concentration onto sawdust surface at 25 °C (± 2 °C)

Table 1. Thermodynamics parameters for adsorption of (DB85) dye sorption onto sawdust surface

<table>
<thead>
<tr>
<th>T(K)</th>
<th>ΔH (KJ/mol)</th>
<th>ΔG° (KJ/mol)</th>
<th>ΔS (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>16.7</td>
<td>-13.6</td>
<td>103.6</td>
</tr>
</tbody>
</table>

Table 2. Freundlich and Langmuir parameters for the adsorption of DB85 dye onto sawdust surface

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
</tr>
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<tbody>
<tr>
<td>Freundlich</td>
<td>$K_f$ (mg/g)</td>
</tr>
<tr>
<td>Langmuir</td>
<td>$Q_o$ (mg/g)</td>
</tr>
</tbody>
</table>

for homogeneous surfaces is the Langmuir adsorption isotherm, where each the adsorbate molecules on the surface has similar sorption activation energy and independent of surface coverage [31]. The Langmuir isotherm equation is [32]:

$$q_e = \frac{Q_o K L C_e}{1 + Q_o K L C_e}$$  \hspace{1cm} (5)

The linear form of this equation is represented by the expression:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o K L C_e}$$  \hspace{1cm} (6)

where: $q_e$ (mg/g) is the equilibrium adsorption capacity, $C_e$ (mg/L) is the equilibrium concentration of adsorbate, $Q_o$ (mg/g) is the maximum capacity of monolayer adsorption and $K_L$ (L/mg) is Langmuir equilibrium constant. The values of $K_L$ and $Q_o$ can be calculated from the slope and intercept of the graph of $1/q_e$ versus $1/C_e$ and given in Table 2. The Linear relationship of Langmuir isotherm shows in Fig. 11. The favorability of the adsorption process can be determined by constant
called separation factor $R_L$ [33], which is calculated from the following equation:

$$ R_L = \frac{1}{1 + K_L C_0} $$  

(7)

The value of $R_L$ gives important information about adsorption, which is ($0 < R_L < 1$) for favorable adsorption, ($R_L = 0$) for irreversible adsorption, ($R_L = 1$) for linear adsorption and ($R_L > 1$) for unfavorable adsorption. The values of ($R_L$ is 0.709) and ($R^2$ is 0.948) appear that the adsorption process is favorable and fit quite for Langmuir isotherm.

Freundlich Isotherm Model

The Freundlich isotherm is applicable to multisite adsorption isotherm for heterogeneous surfaces as well as the adsorption capacity is dependent on the concentration of adsorbate at equilibrium and that the adsorption energy is diverse. The linear form of this isotherm is given by the equation [34-37]:

$$ \log Q_e = \log K_f + \frac{1}{n} \log C_e $$  

(8)

where $Q_e$ (mg g$^{-1}$) is the amount of dye adsorbed, $K_f$ and $n$ are constants for the Freundlich adsorption, an indicator of adsorption capacity and adsorption intensity respectively and $C_e$ (mg L$^{-1}$) is the equilibrium concentration of the adsorbate. The graph of $\log Q_e$ versus $\log C_e$ for the adsorption data of dye is shown in Fig. 12. The values of Freundlich constants ($K_f$) and ($n$) are calculated from the intercept and slope of this graph respectively and listed in Table 2. The value of ($n$) gives important information about adsorption, which is ($n < 1$) indicate that the adsorbate has a low affinity for the surface of adsorbent at low concentration. As well as, a value of ($n > 1$) signifies of a high affinity between the adsorbate and adsorbent surface that's lead to favorable adsorption [35-36]. The values of ($n$ is 0.831) and ($R^2$ is 0.922) indicate that the solute has a high affinity for the adsorbent at high concentrations and fit quite for Freundlich isotherm.

CONCLUSION

Dyes are an important group of pollutants for textile factories, therefore, must be treated before disposal it to the water resources. Adsorption technique had been carried out for the removal of (DB85) dye from aqueous solutions by use sawdust as a cheap and efficient adsorbent. The results showed the removal percentage of (DB85) dye increases by increasing the adsorbent dosage due to availability of more effective adsorption sites. The removal percentage of dye increased with decreasing of solution pH value. The removal percentage is increased by decreasing the particle size of absorbent. Data of isotherms indicate the adsorption of dye was fit quite for Langmuir and Freundlich isotherms, adsorption efficiency increase at high concentrations of dye. The removal of dye on the sawdust increased as the temperature increased. Thermodynamic results show that adsorption of (DB85) dye onto sawdust is spontaneous and endothermic, a positive value for the $\Delta S$ refers to that there is an increased randomly at the solid/liquid interface during adsorption of (DB85) dye onto sawdust surface. According to $\Delta H$, $\Delta S$, and $\Delta G$ values, we concluded that sawdust has a high efficiency as an adsorbent for the removal of (DB85) dye from aqueous solutions. Finally, the optimum conditions of using sawdust as adsorbent for DB85 adsorption are: contact time is 90 min, pH = 2.2, particle size is 75 $\mu$m and adsorbent dose is 0.25 gm.

REFERENCES


