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# Kinetics and Equilibrium Studies on the Removal of Direct Blue Dye Using Activated Carbon from Phyllanthus Reticulatus (Black Honey)

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**Abstract:** ***The preparation of activated carbon from Phyllanthus Reticulatus plant steam by $H_2SO_4$ activation at 800ºC (PRAC) and its ability to remove direct blue 71 (DB71) from aqueous solution was reported in this study. The surface morphology of activated carbon was determined by using scanning electron microscope (SEM). The efficiency of the activated carbon was investigated by studying the effects of various experimental parameters such as contact time, initial dye concentration, adsorbent dosage, temperature and pH of dye solution. Adsorption followed pseudo-second order model. The equilibrium data were evaluated using Langmuir, Freundlich and Temkin isotherms and it was found that the Langmuir and Freundlich adsorption isotherm models were the best fit. The intra-particle diffusion studies indicate that the rate controlling step involves pore diffusion. This study indicates that the activated carbon prepared from Phyllanthus Reticulatus can be utilized as a better adsorbent for the removal of direct blue dye.***

**Keywords:** Phyllanthus Reticulatus, Direct blue dye, Adsorption, Kinetics, Langmuir isotherm

## 1. Introduction

Water pollution is one of the major environmental concerns of the globe. The waste water let out from textile industries contains various pollutants which include acidic or caustic dissolved solids and different dyes. The dyes are carcinogenic, mutagenic and tetragenic and toxic to human beings, aqua systems and microorganisms [1, 2]. Synthetic dyes in textile effluents resist their removal under aerobic and anaerobic conditions as they decompose into carcinogenic aromatic amines [3]. The different methods used to remove dyes such as coagulation, flocculation, ultra-filtration, nano-filtration, photo oxidation, electro chemical precipitation etc., are very expensive [4]. The adsorption technique was identified as one of the proficient method as it transfers pollutants from the solution to solid phase [5]. Due to their simplicity of design, low cost and ease of operation, this method was considered as superior process for the removal of dyes [6]. The most commonly used adsorbent materials include silica, alumina, metal hydroxides and activated carbon [7]. Activated carbon, the widely used adsorbent material, has a microporous structure and posses high surface area [8]. In recent years, activated carbon prepared from agricultural waste materials like coir pith, waste wood, fruit wastes, sunflower seed hull, pine-fruit shell, coconut husk [9-14] have been successfully used. The main objective of this study was to prepare an activated carbon from Phyllanthus Reticulatus (PRAC), evaluate its ability in removing direct blue 71 from aqueous solution and to make a kinetics and isotherm studies.

## 2. Materials and Methods

### 2.1 Preparation of Dye (Adsorbate)

Direct blue 71 dye (CI34140) obtained from Sigma Aldrich was used without any further purification. A stock solution of DB71 was prepared by dissolving 1g of dye in 1000 ml of distilled water and diluted to the required concentration.

### 2.2 Preparation of Activated Carbon (PRAC)

**Phyllanthus reticulatus stem** was collected from local areas situated in and around Odathurai village, Tamilnadu, India. The plant stems were cut in to pieces and washed several times with distilled water to remove the impurities and dried for 7 days in Sunlight. The dried **Phyllanthus reticulatus** stems were treated with concentrated sulphuric acid in the ratio 1:1 (w/v). When the reaction subsided, the material was left in a hot air oven at 110 -140ºC for a period of 24 hours. The dried mass was washed with large quantity of water to remove free acid and then dried at 110ºC. The powdered material was subjected for activation at 800ºC for a period of 10 minutes and used as adsorbent.

## 3. Results and Discussion

### 3.1. Batch adsorption experiments

Adsorption experiments were carried out in a 250 mL of Erlenmeyer flask containing known amount of adsorbent with DB71 dye solution. The flask was then shaken using mechanical rotating shaker at120 rpm. After that the solution was filtered and the residual dye concentration was measured at $\lambda_{max}$=580 nm using UV-Visible spectrophotometer (Systronics 166). Batch adsorption studies were performed to study the effects of contact time, pH, and adsorbent dose. All the experiments were carried out at natural pH (except for effect of pH). The effect of contact time was studied using 300 mg of the adsorbent per 100 mL of dye solution at various concentrations. The effect of adsorbent dosage was studied by taking different amount of the adsorbent per 50mL of the dye solution. The effect of pH was studied in the pH range of 2-11 taking 100 mg of adsorbent and 50mL of adsorbate. The effect of temperature

on the dye adsorption was investigated at four different temperatures, viz., 30°C, 40°C, 50°C and 60°C.

### 3.2 SEM analysis

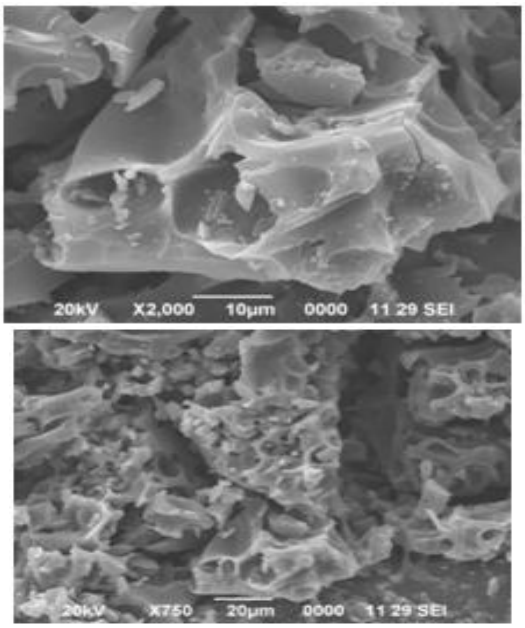


**Figure 1:** SEM images of PRAC

The surface morphology of PRAC was determined using scanning electron microscope (SEM). The SEM image (Fig.1) showed that PRAC has a heterogeneous and a partial honey comb like structure and provides more sites for adsorption**.**

### 3.3 Effect of Contact Time

Figure 2 shows the effect of various initial concentrations (40-60mg / L) with contact time on the adsorption of DB71 on PRAC. The amount of dye adsorbed increases with increase in initial dye concentration. The extent of dye removal was faster in initial stages, then showed a increasing pattern and finally became constant showing the attainment of equilibrium. The curves obtained are found to be single, smooth, continuous and leading to saturation, indicating the possibilities of monolayer coverage of DB71 on the surface of the adsorbent. More than 90% of DB71 was found to get adsorbed with initial concentrations ranging from 40-60 mg/L [15].

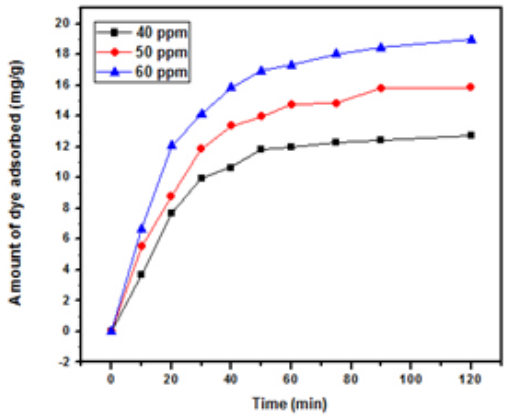


**Figure 2:** Effect of agitation time and initial dye concentration

### 3.4 Effect of adsorbent dosage

The adsorption of DB71 on PRAC was studied by varying the adsorbent doses (50 -500 mg/50mL). Figure 3 depicts that the percentage of dye removal increases with increase in adsorbent dose. This may be attributed to the increase in availability of larger surface active sites resulting from the increased carbon dose and conglomeration of the adsorbent [16].

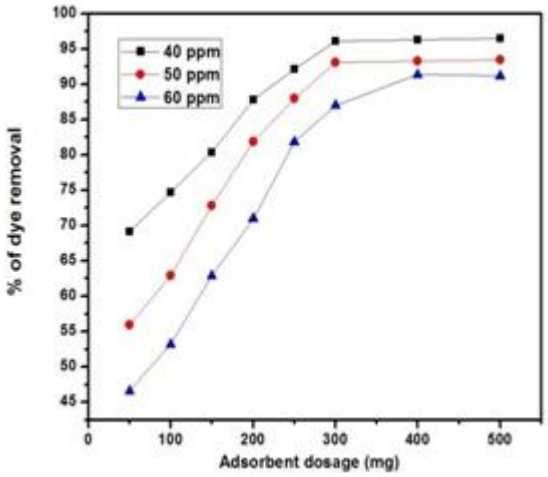


**Figure 3:** Effect of adsorbent dosage

### 3.5 Effect of pH

Figure 4 shows the effect of pH on the adsorption of DB71 onto PRAC. The effect of solution pH was studied between 2 to 11, controlling the initial pH by the addition of 0.1M HCl or 0.1M NaOH. The maximum uptake of DB71 by PRAC occurred at pH 2.0. However, when the pH of the solution was increased above pH 2, the uptake of DB71 gets decreased.

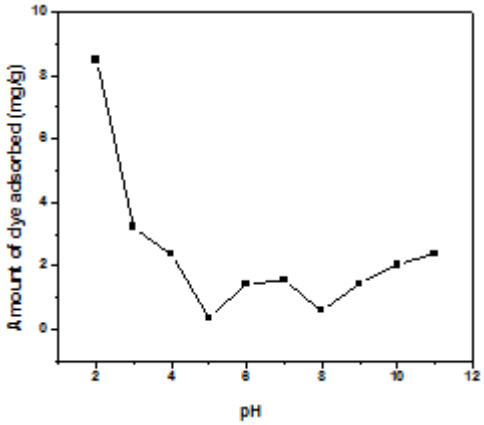


**Figure 4:** Effect of pH

### 3.6 Effect of Temperature

The effect of temperature on the adsorption of DB71 was studied at various temperatures viz., at 30°C, 40°C, 50°C and 60°C with constant initial dye concentration of 60 mg/L and the results are shown in Figure 5. The adsorption capacity of DB71 decreases with increasing temperature which may be attributed to the increase in Brownian movement of molecules in solution [17].

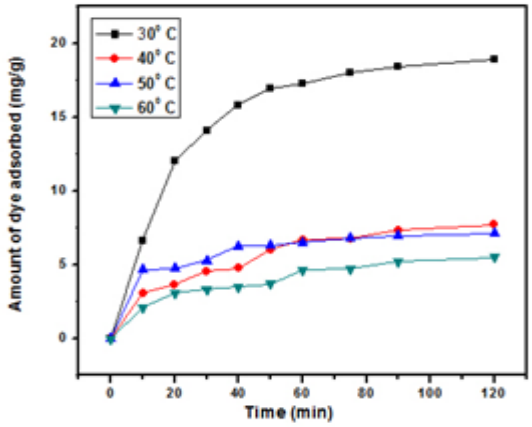


**Figure 5:** Effect of Temperature

## 4. Adsorption Kinetics

### 4.1 Pseudo-first order kinetic model

In order to examine the mechanism of adsorption of DB71 by PRAC, the following four kinetic models were considered. The pseudo first order kinetic equation proposed by Lagergren [18].

$$\log (q_e - q_t) = \log q_e - (k_1 / 2.303)\, t$$

where, $q_e$ is the amount of dye adsorbed at equilibrium (mg/g) , $q_t$ is the amount of dye adsorbed at time (mg /g) and $k_1$ is the pseudo first order rate constant ($min^{-1}$). The rate constant $k_1$ and $q_e$ (the) can be calculated from the slope and intercept of the graph. The $q_e$(the) and $q_e$(exp) values are shown in Table 1. The calculated $q_e$(the) values deviate largely from the $q_e$(exp) values indicating that the adsorption process does not follow first order kinetics.

### 4.2 Pseudo-second order kinetic model

The linear pseudo second order kinetic equation is given as [19].

$$t/q_t = 1/(k_2 q_e^2) + 1/q_e\, t$$

where $k_2$ is rate constant of second order adsorption (g $mg^{-1}min^{-1}$). As expected the plot of t/qt vs t (Figure 6) was linear. The values of $q_e$ and $k_2$ can be calculated from the slope and intercept. The $q_e$(the) and $q_e$(exp) values are shown in Table 1. The calculated $q_e$ (the) values are in consonance with $q_e$ (exp) with high correlation coefficient values. This shows that the adsorption of DB71 on PRAC followed pseudo-second order kinetics.

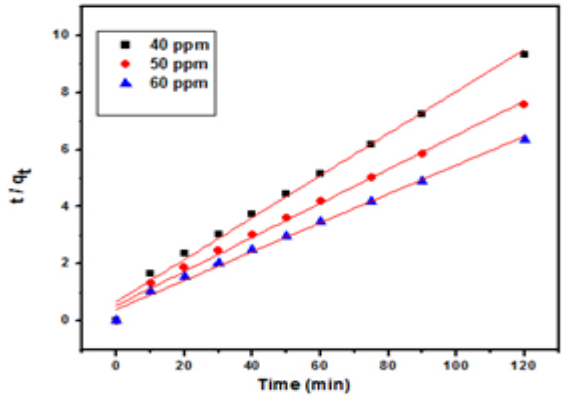


**Figure 6:** Pseudo-second order kinetics

### 4.3 Intraparticle diffusion

The most commonly used technique for identifying the mechanism involved in the adsorption process was fitting to the experimental data in an intraparticle diffusion plot. According to Weber and Morris, an intraparticle diffusion coefficient $K_{id}$ is defined by the equation,

$$q_t = k_{id}\, t^{1/2} + C$$

Where $K_{id}$ is the intraparticle diffusion rate constant ($mg/gmin^{1/2}$), C is the intercept (mg /g) can be calculated by plotting $q_t$ vs $t^{1/2}$ and the results are given in Figure 7 and Table 1. The linear portion of the plot does not pass through the origin. Such a deviation from the origin indicates that pore diffusion is the only controlling step and not the film diffusion [20].

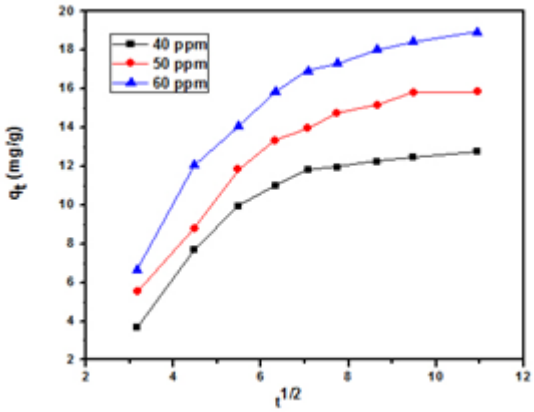


**Figure 7:** Intraparticle diffusion

**Table 1:** Results of kinetic plots for the adsorption of DB71 onto PRAC

| Concentration (mg/L) | 40 | 50 | 60 |
|---|---|---|---|
| **Pseudo first order model** | | | |
| $k_1$ ($min^{-1}$) | 0.0433 | 0.0566 | 0.03938 |
| $q_e$ exp (mg/g) | 12.74 | 15.84 | 18.95 |
| $q_e$ the (mg/g) | 11.68 | 22.02 | 16.65 |
| $R^2$ | 0.9784 | 0.8325 | 0.9917 |
| **Pseudo second order model** | | | |
| $k_2 \times 10^{-3}$(mg/g.min) | 8.0564 | 6.6544 | 6.3016 |
| $q_e$ exp (mg/g) | 12.74 | 15.84 | 18.95 |
| $q_e$ the (mg/g) | 13.59 | 16.75 | 19.80 |
| h (mg/g.min) | 999.96 | 1867.03 | 2470.96 |
| $R^2$ | 0.9897 | 0.9899 | 0.9920 |
| **Intra particle** | | | |
| $K_{id}$ (mg/g. $min^{1/2}$) | 1.1664 | 1.3339 | 1.7924 |
| $R^2$ | 0.9983 | 0.9184 | 0.9803 |

## 5. Adsorption Isotherms

Langmuir, Freundlich and Temkin isotherms were used to determine the amount of dye adsorbed and its equilibrium concentration.

### 5.1 Langmuir isotherm

Linear form of Langmuir model (Langmuir, 1918) is expressed by,

$$\frac{C_e}{q_e} = \frac{1}{b} Q_0 + \frac{C_e}{Q_o}$$

where $C_e$ is equilibrium concentration of dye (mg/L), $q_e$ is the amount of dye adsorbed at equilibrium (mg/g), $Q_0$ and b are the Langmuir constants correlated to adsorption capacity and rate of adsorption, respectively. A linear plot of $C_e/q_e$ vs $C_e$ is shown in Figure 8.The values of $Q_0$ and b were calculated from the slope and intercept of the plots and the values are given in Table 2. These values indicate that the maximum monolayer adsorption capacity of PRAC was 28.90 mg/g. The crucial features of the Langmuir isotherm was examined by the dimensionless constant separation term ($R_L$) to determine high affinity adsorption.

$R_L$ was calculated as follows:

$R_L = 1/ (1+bC_o)$, Where $C_o$ is initial DB71 concentration (mg /L).

The nature of adsorption if, $R_L > 1$= Unfavourable, $R_L = 1$ Linear, $R_L = 0$ Irreversible, $0 < R_L < 1$ Favourable. In the present study, the $R_L$ values were less than one in the concentration range studied, which shows that the adsorption process was favourable.

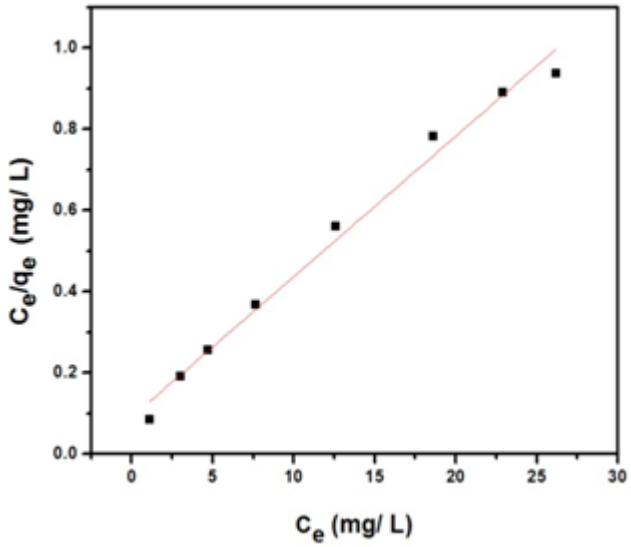


**Figure 8:** Langmuir adsorption isotherm

### 5.2 Freundlich isotherm

The Freundlich isotherm was represented by the following equation,

$$\log q_e = \log K_f + 1/n \log C_e$$

Where $K_f$ and n are Freundlich constants represent adsorption capacity and intensity of the adsorbent respectively. The plot of $\log q_e$ vs $\log C_e$ shown in Figure 9 indicates that the adsorption of DB71 fit into the Freundlich isotherm to some extent. The Freundlich constants ($K_f$ and 1/n) are given in Table 2. The value of 1/n was less than one which indicates a favorable adsorption isotherm [21].

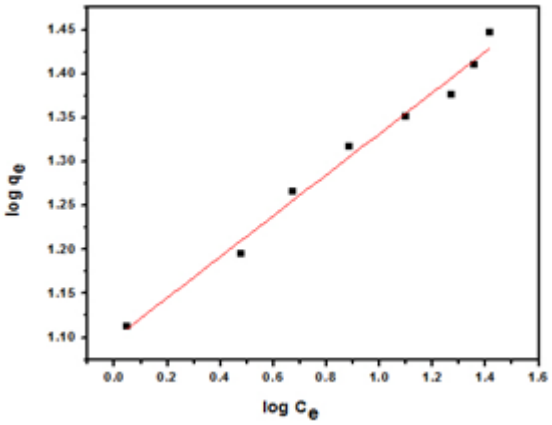


**Figure 9:** Freundlich adsorption isotherm

### 5.3 Temkin isotherm

The Temkin equation was also employed for the adsorption process under study. The linear form of Temkin isotherm is expressed as,

$$q_e = B \ln A + B \ln C_e$$

Where B is a constant related to the heat of adsorption (J/mol) and A is the Temkin isotherm constant, corresponding to the maximum binding energy (L/mg). A plot of $q_e$ vs $\ln C_e$ is shown in Figure 10.The values of A and B calculated from the slope and intercept of the graph are given in Table 2.

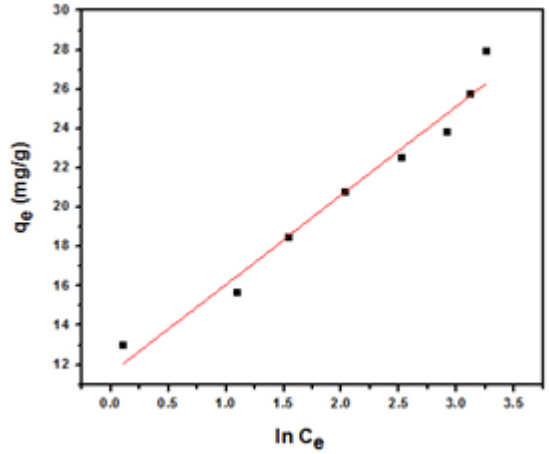


**Figure 10:** Temkin adsorption isotherm

**Table 2:** Results of isotherm plots for the adsorption of DB71 onto PRAC

| Langmuir isotherm Parameters | | | | Freundlich isotherm parameters | | | Temkin isotherm parameters | | |
|---|---|---|---|---|---|---|---|---|---|
| $Q_0$ (mg/g) | b (L/mg) | $R_L$ | $R^2$ | $K_f$ (mg/g) | 1/n | $R^2$ | A (L/mg) | B (J/mol) | $R^2$ |
| 28.90 | 0.3823 | 0.0238 – 0.0614 | 0.9863 | 12.549 | 0.2332 | 0.9843 | 12.95 | 4.516 | 0.9645 |

## 6. Conclusion

***Phyllanthus reticulatus*** plant stem can be effectively utilized as a low cost adsorbent for the removal of DB71 from aqueous solution. The amount of dye adsorbed varied with initial dye concentration, pH, temperature and adsorbent dosage. Adsorption was found to increase with increasing adsorbent dosage. From the three isotherm models, it was observed that the adsorption data fitted well with Langmuir and Freundlich isotherm models. The

adsorption of DB71 onto **PRAC** followed pseudo second order kinetics. Intra particle diffusion studies indicate pore diffusion as the rate limiting step.

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