Equilibrium uptake and sorption dynamics for the removal of reactive dyes from aqueous solution using activated carbon prepared from *Euphorbia tirucalli* L wood

P N Palanisamy¹, A Agalya²* & P Sivakumar³

¹ Department of Chemistry, Kongu Engineering College, Erode 638 052, India
² Department of Chemistry, Al-Ameen Engineering College, Erode 638 104, India
³ Department of Chemistry, Arignar Anna Government Arts College, Namakkal 637 002, India

Received 21 June 2011; accepted 5 May 2013

Activated carbon prepared from *Euphorbia tirucalli* L wood (ETAC) by chemical activation with phosphoric acid has been analysed for the removal of Reactive Red and Reactive Blue dyes from aqueous solutions through batch adsorption technique. Lower solution pH favours the adsorption of reactive dyes. The amount of dye adsorbed per unit mass of adsorbent increases with the increase in temperature and initial dye concentration. Freundlich and Langmuir models are used to analyze the equilibrium data at different temperatures. The equilibrium data for the adsorption of both dyes are better described by the Langmuir isotherm model. The adsorption of reactive dyes follows second order kinetics along with intra-particle diffusion model. Thermodynamic parameters such as free energy change, enthalpy change and entropy change for adsorption of reactive dyes show that the adsorption of Reactive Red and Reactive Blue onto ETAC are spontaneous, endothermic and physical adsorption. Activation energy and isosteric heat of adsorption suggests that adsorption of reactive dyes onto ETAC is a physical process.

**Keywords**: Activated carbon, Adsorption, *Euphorbia tirucalli* L, Kinetic study, Reactive dyes

The textile dyeing units release large quantities of dyes in their effluents. Reactive dyes are used for dyeing cellulosic fibres. Use of reactive dyes has been enhanced due to the increased consumption of cellulosic fibres, as in case of cellulosic other dyes suffer from technical and economical practical limitations in comparison with reactive dyes. They have a relatively low fixation degree on the textile substrate and hence 10-50% of the dye is unexhausted and remains in the dye bath waste. Reactive dye waste water has limited biodegradability in an aerobic environment. Many reactive azo dyes consisting of the largest dye groups decompose to potential carcinogenic aromatic amines under aerobic conditions.

Reactive azo dyes are more resistant to the usual water purification treatment. However, treatment methods based on adsorption, biological treatment, coagulation, electrochemical techniques, membrane process, or oxidation-ozonation are known to be effective for the removal of reactive azo dyes from polluted water. Conventional treatment methods are often disadvantageous to remove reactive dyes owing to their high solubility and low biodegradability.

Hence, adsorption is recommended as a viable means for reactive dye removal.

The aim of the present work is to investigate the removal of reactive azo dyes (Reactive Red and Reactive Blue) from aqueous solution by adsorption onto activated carbon. Effects of initial dye concentration, contact time, pH and temperature on dye removal have been studied. The adsorption data evaluated using Langmuir and Freundlich isotherm models and kinetic parameters for second order and intra-particle diffusion models are also evaluated.

**Experimental Procedure**

**Adsorbent**

Activated carbon was prepared from the precursor wood *Euphorbia tirucalli* L. The wood was cut into small pieces and dried under sunlight for 10 days. The dried material was soaked in a boiling solution of 35% H₃PO₄ for 1 hour and kept at room temperature for 24 hrs. The wood material was then separated, air dried and carbonized in muffle furnace at 550ºC for 1½ h. The carbonized material was powdered and activated at 800ºC for 10 min. The resulting carbon was washed with plenty of water until the residual acid was removed. The dried material was ground well to fine powder and sieved.

---

*Corresponding author.
E-mail: agalarun@rediffmail.com
Adsorbate

Both the dyes used, namely Reactive Blue 81 (RB) [Mol.wt 811.51, Mol. formula C_{25}H_{17}Cl_{2}N_{7}O_{10}S_{3}Na_{3}, λ 585 nm], Reactive Red 195 (RR) [Mol.wt 1136.31, Mol. formula C_{31}H_{19}ClN_{7}O_{19}S_{6}Na_{5}, λ 543 nm] are anionic in nature. The dyes were used as such without further purification. All other chemicals used were of analytical reagent grade.

The stock solution was prepared by dissolving 1g of dye in water and up to 1000 mL using double distilled water. The concentration of the dye solution was determined by using UV-Vis spectrophotometer (Elico make BL-198) at their respective wavelengths.

Batch experiments

Dye adsorption experiments were carried out by taking 200 mL of dye solution with varying concentration (25, 50, 75 and 100 mg/L) and 100 mg of adsorbent. The variables studied were initial dye concentration, agitation time, pH and temperature. The flasks were kept in a shaker and agitated for a predetermined time interval at a constant speed. At the end of the predetermined time intervals, the concentration of the dye solution was determined using UV-Vis spectrophotometer (Elico make BL-198).

Results and Discussion

Effect of initial dye concentration and agitation time

The effects of initial dye concentration of reactive dyes on **Euphorbia tirucalli** L wood activated carbon (ETAC) are shown in Fig. 1. The percentage removal of dye is found to decrease with increase in initial dye concentration. The equilibrium is obtained in 110 min for both the dyes. But the actual amount of dye adsorbed per unit mass of ETAC increases with increase in initial dye concentration. This shows that the adsorption is highly dependent on initial concentration of dye\(^1\)\(^-\)\(^3\). The results show that the amount of dye adsorbed increases from 42.86 mg/g to 138.98 mg/g for RB dye and from 45.31 to 146.67 mg/g for RR dye when the dye concentration is increased from 25 mg/L to 100 mg/L respectively. Similar behaviour is also reported for the adsorption of Reactive Red 120 on activated oil palm ash\(^1\)\(^4\).

Effect of pH and temperature

It is observed that at lower pH, the adsorption of negatively charged dye anions is higher. As the pH of the solution increases the dye adsorbed decreases considerably. At pH 1, both the dyes show ∼82% dye adsorption which decreases to ∼45% for RB and ∼51% for RR when pH is increased to ∼8. The dye adsorption shows no change after further increasing the pH from 8. Similar results have also been observed for the adsorption of textile dyes onto agricultural residues and reactive dyes onto agricultural wastes\(^1\)\(^5\).

The effect of temperature on dye adsorption has been studied at 30, 35, 40 and 45 °C. It is observed that the amount of dye adsorbed at equilibrium increases with increasing temperature. The maximum adsorption capacity of ETAC increases from 78.38 mg/g to 89.19 mg/g for RB dye and from 83.72 mg/g to 90.70 mg/g for RR dye respectively when the temperature increases from 30 °C to 45 °C. The increase in equilibrium adsorption of dye with temperature indicates that the adsorption of reactive dyes onto ETAC is endothermic in nature. Similar endothermic nature is also reported for the adsorption of Remazol Black B cotton plant waste\(^1\)\(^6\).

![Fig. 1 — Effect of initial dye concentration on ETAC](image-url)
Kinetics of adsorption

The kinetics of adsorption describes the solute uptake rate, which in turn, governs the residence time of sorption reaction. It is one of the important characteristics in determining the efficiency of adsorption. The transient behaviour of the dye adsorption process is commonly analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion models.

Pseudo first order kinetics

The first order equation of Lagergren is generally expressed as follows:

\[
\frac{dq}{dt} = k(q_e - q_t)
\]

... (1)

The integrated form of equation is

\[
\log(q_e - q_t) = \log q_e - \frac{kt}{2.303}
\]

... (2)

where \(q_e\) and \(q_t\) are the amounts of dye adsorbed (mg/g) at equilibrium and at time \(t\) (min) respectively; and \(k_1\), the rate constant obtained from the slope of the plot \(\log(q_e - q_t)\) versus time. The results are shown in Table 1. The correlation coefficient shows that the experimental data is poorly fitted with pseudo-first order kinetic model.

Pseudo-second order kinetics

Adsorption kinetics were explained by second order model, as shown below:

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

... (3)

where \(k_2\) is the second order rate constant (g/mg min). The value of \(k_2\) calculated from the slope of \(t/q_t\) versus \(t\) is shown in Fig. 2. The second order rate constant decreases from \(9.3827 \times 10^{-4}\) to \(1.3767 \times 10^{-4}\) (g/mg min) for RB and from \(12.0925 \times 10^{-4}\) to \(2.1777 \times 10^{-4}\) (g/mg min) for RR with increase in initial dye concentration. The correlation coefficients \(r^2\) ranges from 0.9926 to 0.9974 for Reactive Blue and from 0.9955 to 0.9984 for Reactive Red, suggesting the relationship between the parameters and also explains that the sorption of reactive dyes follows second order kinetics. The results are shown in Table 1. A similar result is also reported for the adsorption of Malachite Green onto chemically modified rice husk.

<table>
<thead>
<tr>
<th>Dye</th>
<th>First order kinetics</th>
<th>Second order kinetics</th>
<th>Intraparticle diffusion model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc., mg/L</td>
<td>(k_1), min(^{-1})</td>
<td>(q_e), cal mg/g</td>
</tr>
<tr>
<td>RB</td>
<td>25 0.0257 35.115 0.9593 9.3827 49.261 0.9926 3.5598 0.957</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 0.0287 66.649 0.9762 4.9857 91.743 0.998 6.7121 0.9507</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>75 0.0327 105.803 0.9905 2.749 135.135 0.9989 10.04 0.9536</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 0.0331 155.417 0.9634 1.3767 185.185 0.9974 13.279 0.9789</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RR</td>
<td>25 0.0271 33.783 0.9587 12.092 50.505 0.9955 3.571 0.9241</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50 0.0308 67.39 0.9794 5.9338 95.238 0.9991 6.941 0.9236</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>75 0.0336 92.875 0.982 4.3592 131.578 0.9988 9.624 0.8989</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 0.0335 141.742 0.9564 2.1777 178.571 0.9984 13.147 0.9468</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 — Results of kinetic plots for adsorption of reactive dyes onto ETAC

![Fig. 2 — Pseudo-second order plot for reactive dyes](image-url)
**Intra-particle diffusion model**

Adsorption is a multi-step process involving transport of solute molecules from the aqueous phase to the surface of the solid adsorbent followed by diffusion into the interior of the pores. In batch mode adsorption, this might be the rate controlling step:

\[ t^{1/2} = k_{ad} + C \]  \( \ldots (4) \)

The possibility of intra-particle diffusion was tested by plotting a graph between the amount of dye adsorbed and the time \( t^{1/2} \) at different time intervals (Fig. 3). All the plots have double nature, i.e. the initial curved portion is related to boundary layer diffusion effect and final linear portion is due to intra-particle diffusion effect. Further, the linear portions of the curves do not pass through the origin.

From the intra-particle plot obtained, the first region indicates surface adsorption (boundary layer diffusion through meso pores) followed by intra-particle diffusion (by micro pore diffusion) in the second region. The adsorptive removal of reactive dyes on ETAC involves initially the dye molecules adsorbed through boundary layer diffusion and then transformation to intra-particle diffusion gradually. The kinetic data indicates that the adsorption of Reactive Blue and Reactive Red on ETAC follows pseudo-second order rate with intra-particle diffusion as one of the rate determining steps.

**Equilibrium isotherm**

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems\(^21\). Langmuir and Freundlich models are used to describe the equilibrium characteristics of adsorption in the present study. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find out the suitable model that can be used for design purpose\(^22\). The applicability of isotherm equation is compared by judging the correlation coefficients \( r^2 \).

**Langmuir isotherm**

The Langmuir equation has been applied for monolayer sorption onto a surface of a finite number of identical sites with negligible interaction between adsorbed molecules\(^23\). The linearised form of Langmuir isotherm is presented by the following equation:

\[ \frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0} \]  \( \ldots (5) \)

where \( C_e \) is the equilibrium concentration (mg/L); \( q_e \), the amount of dye adsorbed at equilibrium (mg/g); and \( Q_0 \) (mg/g) and \( b_L \) (L/mg), the Langmuir constants related to adsorption capacity and energy of adsorption respectively. The values of \( Q_0 \) and \( b_L \) are determined from the slopes and intercepts of the linear plots of \( C_e/q_e \) vs \( C_e \) (Fig. 4). The Langmuir isotherm fits with the experimental data very well, may be due to the homogeneous distribution of active sites onto the surface, since the Langmuir model assumes that the surface is homogeneous. The maximum sorption capacity \( Q_0 \) varies from 181.81 mg/g to 200 mg/g for Reactive Blue and from 204.08 mg/g to 217.39 mg/g for Reactive Red while increasing the temperature from 30ºC to 45ºC.

![Fig. 3 — Intra particle diffusion plot for reactive dyes](image-url)
The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter $R_L$ that is defined by the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad \cdots \quad (6)$$

where $C_0$ is the highest initial solute concentration. $R_L$ value indicates the type of adsorption isotherm to be either unfavourable ($R_L > 1$), favourable ($R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). Langmuir model is more appropriate to explain the nature of adsorption with correlation coefficient of $0.9922 - 0.9973$ for Reactive Blue and $0.9911 - 0.9949$ for Reactive Red.

**Freundlich adsorption isotherm**

The Freundlich equation is an empirical one employed to describe heterogeneous systems, in which it is characterized by heterogeneity factor $1/n$. The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \cdots \quad (7)$$

where $K_f$ and $1/n$ are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent respectively; $q_e$, the amount of dye adsorbed per unit mass of adsorbent (mg/g); $C_e$, the equilibrium concentration of adsorbate (mg/L). The values of $K_f$ and $1/n$ are calculated from intercept and slopes of linear plot of $\log q_e$ versus $\log C_e$. The value of $1/n$ is found to be below one for both dyes, indicating that the adsorption of reactive dyes on ETAC is favourable. But it poorly fits with the experimental data with correlation coefficient $0.9327 - 0.9317$ for Reactive Blue and $0.978 - 0.97938$ for Reactive Red. The results of isotherms are shown in Table 2.

**Thermodynamics of adsorption**

The thermodynamic parameters such as change in standard free energy ($\Delta G^0$), enalphy ($\Delta H^0$) and entropy ($\Delta S^0$) can be determined by using Vant Hoff equation. By plotting a graph of $\ln K_L$ vs $1/T$, the values of $\Delta S^0$ and $\Delta H^0$ can be estimated from the slopes and intercepts (Table 3).

Gibbs free energy values are found to be negative, indicating the feasibility and spontaneous nature of
adsorption for both dyes with the range of temperature studied. The values of $\Delta G^o$ obtained in this study are within the range of -20 and 0 kJ/mol, indicating that the physisorption is the dominating mechanism. The similar results have also been reported earlier. Positive value of $\Delta H^o$ indicates that the adsorption is endothermic and it governs the possibility of physical adsorption. Since in the case of physisorption, while increasing the temperature of the system the extent of dye adsorption increases and rules out the possibility of chemisorption. The low $\Delta H^o$ values (< 40 kJ/mole) suggest that the reactive dyes are physisorbed onto ETAC. The heat of physisorption involves only relatively electrostatic interactions. The positive value of $\Delta S^o$ suggests good affinity of the dyes towards the adsorbent and the increased disorder and randomness.

**Activation energy**

The rate constant $k_2$ at different temperatures is used to estimate the activation energy of sorption of reactive dyes onto ETAC using the following Arrhenius equation:

$$\ln k_2 = \ln A - \frac{E_a}{RT}$$ ... (8)

where $E_a$ and $A$ refer to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting $\ln k_2$ versus $1/T$ (Fig. 5). The activation energies are found to be 20.1406 kJ/mole and 16.5199 kJ/mole for Reactive Blue and Reactive Red respectively. The minimum value of $E_a$ for sorption of RR onto ETAC indicates the higher adsorption. The magnitude of activation energy gives an idea about the type of adsorption. The physisorption usually have energies in the range 5-40 kJ/mole, while higher activation energies of 40-800 kJ/mole suggest chemisorption. The activation energy < 40 kJ/mole for both the dyes indicates the diffusion controlled physisorption. Similar results are also reported for the adsorption of Lanaset Grey G on activated carbon.

**Isosteric heat of adsorption**

It is the basic requirements for the characterization and optimization of an adsorption process and also very important for equipment and process design.

The isosteric heat of adsorption at constant coverage is calculated using following Clausius-Clapeyron equation:

$$\ln Ce = \frac{\Delta H_x}{RT} + K$$ ... (9)

where $Ce$ is the equilibrium dye concentration in solution (mg/L); and $\Delta H_x$ the isosteric heat of adsorption (kJ/mole). The isosteric heat of adsorption is calculated from the slope of the plot $\ln Ce$ versus $1/T$. The magnitude of $\Delta H_x$ provides an information about the nature and mechanism of the process. For physical adsorption $\Delta H_x$ should be below 80 kJ/mole and for chemical adsorption it ranges between 80 kJ/mole and 400 kJ/mole. The values of $\Delta H_x$ for the adsorption of reactive dyes onto ETAC are 36.2673 kJ/mole and 29.7709 kJ/mole, which is within the range of physisorption, suggesting that the adsorption process is physisorption.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Temp., °C</th>
<th>$\Delta G^o$, kJ/mol</th>
<th>$\Delta H^o$, kJ/mol</th>
<th>$\Delta S^o$, kJ/K/mol</th>
<th>$E_a$, kJ/mole</th>
<th>$\Delta H_x$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>RB81</td>
<td>30</td>
<td>-6.8988</td>
<td>35.9946</td>
<td>0.1415</td>
<td>20.1406</td>
<td>36.2673</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-7.6066</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-8.3144</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-9.0222</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RR195</td>
<td>30</td>
<td>-7.5861</td>
<td>27.8128</td>
<td>0.1168</td>
<td>16.5199</td>
<td>29.7709</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>-8.1703</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>-8.7544</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>-9.3385</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5 — Plot for Arrhenius activation energy

---

Table 3 — Thermodynamic parameters at various temperatures
Desorption studies

Desorption studies help to elucidate the mechanism of adsorption and recovery of the adsorbate and adsorbent. Regeneration of adsorbent may make the treatment process economical. Percentage of adsorbent. Regeneration of adsorbent may make the of adsorption and recovery of the adsorbate and observed in the solution.

In this work, activated carbon prepared from Euphorbia tirucalli L wood (ETAC) has been used as a potential adsorbent for the removal of reactive azo dyes from aqueous solution. Removal of reactive azo dyes is found to be pH dependent and the maximum removal occurs at pH 2-3. The kinetic data reveal that sorption of reactive azo dyes follows second order kinetics with intraparticle diffusion as the rate controlling step. The equilibrium data is best fitted with Langmuir isotherm model. Adsorption of reactive dyes is found to increase with the increase in initial dye concentration, agitation time and T. However, it also decreases with increase in pH. ETAC is highly selective to Reactive Red as compared to Reactive Blue. Increase in maximum adsorption capacity of ETAC indicates that the adsorption process is endothermic in nature. Thermodynamic analysis using Arrhenius equation shows that the removal of reactive azo dyes is endothermic, favourable and spontaneous in nature. The lower activation energy indicates that adsorption of reactive azo dyes onto ETAC is physiosorption in nature.

References

17. Langedroen S & Svenska B K, Handlingar, 24 (1898) 39.
29. Renim Gong, Ying Zhi Sun, Jian Chen Huijun & Chao Yang, Dyes, 67 (2005) 179.