Use of jackfruit peel carbon (JPC) for adsorption of rhodamine-B, a basic dye from aqueous solution

B Stephen Inbaraj* & N Sulochana
Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India
Email: sinbaraj@yahoo.com
Received 14 April 2005; revised received 18 October 2005; accepted 10 November 2005

A carbon sorbent derived from an agricultural waste, jackfruit peel was applied to study the removal of a basic dye, rhodamine-B from aqueous solution. Batch experiments were performed as a function of process parameters like agitation time, initial dye concentration, temperature, carbon dose and pH. Modified Ritchie second order equation better predicted the kinetic results compared to other rate equations (pseudo first order and pseudo second order) tested. Among the isotherm models applied to the equilibrium data Redlich-Peterson model better predicted the experimental values. The adsorption capacity was 121.47 mg g\(^{-1}\) at an initial pH of 6.0 and at 32 ± 0.5°C. The adsorption capacity increased with increase in temperature. The influence of pH on dye removal was not significant. An optimum carbon dose of 1.2 g L\(^{-1}\) was required for the maximum removal (96%) of dye from its 60 mg L\(^{-1}\) solution. A significant portion of the dye was recovered from the spent carbon using 50% acetic acid.

Keywords: Adsorption, Rhodamine-B, Jackfruit peel, Carbon, Kinetics, Isotherms
IPC Code: Int. Cl. 7 C09B61/00

Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of dyes\(^3\). However, owing to the high cost of commercial activated carbon, several researchers have been studying the use of various alternate inexpensive materials. Agricultural wastes/by-products form a promising group of raw materials that include quaternized rice husk\(^5\), tree fern\(^6\), rice bran\(^7\), coir pith\(^8\), soybean hull and sugar beet fiber\(^9\), banana pith\(^10\), coconut husk\(^11\), bagasse pith\(^12\), pine cones\(^13\), pearl millet husk\(^14\), date pits\(^15\) and orange and banana peels\(^16\), with little or no modification were applied for the removal of dyes from wastewater.

Jackfruit (Artocarpus heterophyllus) is one of the popular fruits in India and owing to its wide variety of applications, significant amount of peel (which constitutes ~59% of the ripe fruit) is discarded as waste\(^17\). The carbon prepared from jackfruit peel has earlier been used for the removal of malachite green dye\(^18\) and its efficiency in removing metal ions like Cd(II)\(^19\), Hg(II)\(^20\) and Cu(II)\(^21\) from aqueous solution has also been reported. This paper focuses on the use of jackfruit peel carbon for the removal of rhodamine-B dye from aqueous solution. Systematic batch-mode adsorption studies were carried out as a function of process parameters like agitation time,

---

*Present address: Department of Nutrition and Food Sciences, Fu Jen University, Taipei 24205, Taiwan, R.O.C.
initial dye concentration, temperature, carbon dose and pH.

**Experimental Procedure**

Jackfruit peel carbon (JPC) was prepared following the procedure reported earlier. The JPC was ground and the portion retained between 44 and 89 μm sieves was used for batch experiments. Physico-chemical characteristics and scanning electron micrographs of JPC were also reported in the previous article. Rhodamine-B dye was procured from Ciba-Geigy. Stock solution of the dye (1000 mg L$^{-1}$) was prepared by dissolving the requisite amount of dye in distilled water and making up to the desired volume. Different initial dye concentrations for batch experiments were prepared by making suitable dilutions. Batch experiments were carried out by agitating a known quantity of JPC with 100 mL of dye solution of desired concentration at pH 6.0 and at room temperature ($32 \pm 0.5^\circ$C) in an electronic orbital shaker (250 rpm) equipped with incubation hood. After equilibrium is achieved, samples were withdrawn from the shaker, centrifuged and the supernatant solution was analysed for residual dye concentration using a Jasco Double Beam Spectrophotometer (UV-DEC-430B) at a wavelength of 553.8 nm.

To study the kinetics of dye adsorption three different initial dye concentrations, 20, 40 and 60 mg L$^{-1}$ were agitated separately with 0.5 g L$^{-1}$ dose of JPC at a pH of 6.0 for predetermined intervals of time. For study of effect of initial dye concentration, dye solutions in a concentration range of 10-60 mg L$^{-1}$ were agitated with 0.5 g L$^{-1}$ of JPC dose at pH 6.0 for 12 h. The effect of adsorbent concentration was studied by agitating 60 mg L$^{-1}$ of dye solutions with a range of JPC dose, 0.2-2.0 g L$^{-1}$ at pH 6.0 for 12 h. The effect of pH on dye removal was established by adjusting 20 mg L$^{-1}$ of dye solutions to different pH values using dilute HCl or NaOH and agitating each with 0.5 g L$^{-1}$ of JPC dose for 12 h. The change in adsorption capacity on varying the temperature was studied by agitating 60 mg L$^{-1}$ of dye solutions with 0.5 g L$^{-1}$ dose of JPC at pH 6.0 for 12 h at 305, 313 and 323 K. Each batch experiment was carried out in triplicate and mean values were taken for calculation. Standard deviation and analytical errors were calculated and the maximum error was found to be ±5%.

The amount of dye adsorbed $q_t$ at time $t$, and at equilibrium, $q_e$ was calculated from the mass balance equation

$$q_t = \frac{(C_0 - C_t)V}{m} \quad \text{...(1)}$$

where, $q_t$ and $C_t$ are the amount of dye adsorbed (mg g$^{-1}$) and the concentration of dye in solution (mg L$^{-1}$), respectively, at time, $t$. $C_0$ is the initial dye concentration (mg L$^{-1}$), $V$ is the volume of dye solution (L) and $m$ is the mass of the adsorbent used (g). When $t$ = $t_e$, then the amount of dye adsorbed at equilibrium, $q_e$, is calculated using Eq. (1).

Desorption study was carried out by initially performing dye adsorption with 60 mg L$^{-1}$ and 1 g L$^{-1}$ of JPC. The carbon loaded with dye was carefully separated and gently washed with distilled water to remove any unadsorbed dye. The dye-laden carbons were then agitated with 100 mL of 1 M sulphuric acid, 1 M sodium hydroxide and 50% acetic acid ($v/v$) separately for 60 min and the concentration of dye desorbed from the spent JPC in each desorbing agent was determined.

**Results and Discussion**

**Adsorption kinetics**

Process performance and ultimate cost of an adsorption system depends upon the effectiveness of the process design and the efficiency of process operation. The efficiency of process operation requires an understanding of the kinetics of uptake or the time dependence of the concentration distribution of the solute in both bulk solution and solid adsorbent.

The agitation time experiments conducted with three different dye concentrations, 20, 40 and 60 mg L$^{-1}$, indicate that the uptake of dye increased progressively with time; removal being rapid in the initial stages of contact time and attains equilibrium in 60 min for 20 mg L$^{-1}$ and 100 min for 40 and 60 mg L$^{-1}$.

**Kinetic modeling**

Many models have been applied in batch reactors to describe the transport of solute species inside the adsorbent particles, however the mathematical complexity makes them inconvenient for practical use. Any kinetic or mass transfer representation needs to be global. From a system design viewpoint, a lumped analysis of kinetic data is, therefore, sufficient for practical operation. Hence identification of a simplified kinetic equation, which can represent the mass transfer precisely for the adsorption systems studied, assumes importance.
The kinetic results were initially fitted with Lagergren’s pseudo first order kinetic expression:

\[ q_t = q_e [1 - \exp(-k_1t)] \]  \hspace{1cm} \text{(2)}

where \( k_1 \) is the first order rate constant (min\(^{-1}\)). Fitting was done by a non-linear optimization method\(^\text{14,27}\) that involves Marquardt-Levenberg\(^\text{28,29}\) algorithm using GNUPLOT computer program. Similarly a pseudo second order\(^\text{30,31}\) and a modified Ritchie second order equations\(^\text{32,33}\), which are expressed as

\[ q_t = \frac{t}{(1/k_2q_e^2) + (t/q_e)} \]  \hspace{1cm} \text{(3)}

and

\[ q_t = q_e \left( 1 - \left[ \frac{1}{\beta_2 + k_2t} \right] \right) \]  \hspace{1cm} \text{(4)}

respectively, where \( k_2 \) is the second order rate constant and \( \beta_2 \) is the initial particle loading, were applied to the kinetic results. The fitted curves of these kinetic models along with the experimental data are illustrated in Fig. 1 and the fitted parameters of the models are presented in Tables 1 and 2. To measure the degree of fitness of the models with the experimental data correlation coefficient, \( r^2 \), and sum of the squares of errors, \( SSE \) (Eq. 5), were computed (Tables 1 and 2).

\[ SSE = \Sigma (q_i - q_p)^2 \]  \hspace{1cm} \text{(5)}

where, \( q_i \) and \( q_p \) are the experimental and theoretical adsorption capacity data, respectively. The \( SSE \) (numerical value) represents the square of the distance between the experimental data points and the adsorption models.

The Lagergren’s pseudo first order equation does not fit well the whole range of adsorption period, as it is generally applicable for the initial stages of adsorption processes\(^\text{26,30}\). This is evident from the relatively lower \( r^2 \) and higher \( SSE \) values for pseudo first order model compared to the second order

![Fig. 1—Non-linear kinetic model fits with the experimental data](image)

Dye concentrations: (●) 20 mg L\(^{-1}\), (■) 40 mg L\(^{-1}\), (▲) 60 mg L\(^{-1}\). (-------) pseudo first order model, (−−−−) pseudo second order model and (-----) modified Ritchie second order model.
models tested. The pseudo first order model showed a good correlation (0.96-0.99) for initial stages of adsorption (a maximum of four experimental points) and thereafter deviates over the entire period of adsorption (Fig. 1). Among the second order models tested, modified Ritchie second order model provided a better fit compared to pseudo second order model. This is evident from the high \( r^2 \) and lower SSE values obtained for the former than the latter.

An increase in the degree of fit was observed with initial dye concentration for all the kinetic models, which is apparent from the decrease in \( r^2 \) and increase in SSE values with initial dye concentration. The Ritchie second order rate constant, \( k_2 \), decreased with increase in initial dye concentration (Table 2). This trend may be attributed to decrease in the readily available vacant sites as the dye concentration is increased. In other words, once the easily available sites are occupied the excess dye in solution find remote sites inside the pores of JPC with difficulty, which makes the rate of adsorption to decrease as the dye concentration is increased.

**Adsorption isotherms**

Adsorption isotherms are basic requirements for the design of adsorption systems. The isotherm expresses the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and the liquid phase dye concentration. Experiments conducted at a range of initial dye concentration (10-60 mg L\(^{-1}\)) showed an increase in adsorption capacity (17.60 to 78.00 mg g\(^{-1}\)) due to concentration gradient and reached a constant value after which there was no increase in adsorption capacity with increase in initial dye concentration.

**Isotherm modeling**

The distribution of dye between the liquid phase and the adsorbent is a measure of the position of equilibrium in the adsorption process and can be generally expressed by three of the most popular isotherm theories, 2-parameter Freundlich\(^{38}\) (Eq. 6) and Langmuir\(^{39}\) (Eq. 7) isotherms and a 3-parameter combination isotherm, Redlich-Peterson\(^{40}\) (Eq. 8), which is an intermediate isotherm that incorporates the features of both Freundlich and Langmuir isotherms.

\[
q_e = K_F C_e^{1/n} \quad \ldots(6)
\]

\[
q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad \ldots(7)
\]

where, \( K_F \) and \( n \) are Freundlich constants indicating the adsorption capacity (mg g\(^{-1}\)) and intensity of adsorption, respectively, \( Q_0 \) and \( b \) are Langmuir constants denoting the adsorption capacity (mg g\(^{-1}\)) and energy of adsorption (L mg\(^{-1}\)), respectively and \( \alpha, \beta \) and \( \gamma \) are Redlich-Peterson constants.

The equilibrium data obtained from the varying initial dye concentration study was modeled with the above three isotherm equations by non-linear curve fitting method in the similar way as done for kinetic modeling. The fitted models for rhodamine dye adsorption onto JPC along with the experimental data for comparison are shown in Fig. 2. The fitted isotherm parameters, \( K_F \) and \( n \) values obtained were found to be 22.87 mg g\(^{-1}\) and 2.30, respectively, \( Q_0 \) and \( b \) values were 104.17 mg g\(^{-1}\) and 0.18 L mg\(^{-1}\), respectively and the Redlich-Peterson constants, \( \alpha, \beta \) and \( \gamma \), were 18.22 L g\(^{-1}\), 0.15 (L mg\(^{-1}\))\(^{\gamma} \) and 0.99, respectively.

To measure the degree of fitness of each isotherm model with the experimental data, \( r^2 \) and SSE (Eq. 5) values were computed and are 0.92 and 234.26, 0.98 and 53.41 and 0.99 and 48.87, respectively, for Freundlich, Langmuir and Redlich-Peterson isotherm models. The 3-parameter combination isotherm, Redlich-Peterson isotherm followed by the Langmuir...
isotherm defined the experimental data more closely than the Freundlich isotherm, as evidenced from the $r^2$ and $SSE$ values obtained. As the equilibrium data is well defined by the Langmuir and Langmuir-incorporated Redlich-Peterson isotherm models, the basic assumptions of the Langmuir theory\(^3^9\) that maximum adsorption corresponds to a saturated monolayer (one molecule in thickness) of adsorbate molecules on the adsorbent surface, the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface hold good also for the adsorption of rhodamine-B dye on JPC.

Using the best-fit isotherm model (Redlich-Peterson) along with the adsorption parameters obtained specific for the system, the volume of wastewater that could be treated was determined. If wastewater contains rhodamine-B dye concentration of 10 mg L\(^{-1}\), 1 g of JPC can treat about 6.7 L of wastewater.

The Freundlich constant, $n$ value obtained between 1 and 10 (2.30) indicate favourable adsorption\(^4^1\) of rhodamine-B on JPC. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant separation factor called equilibrium parameter\(^3^9\), $R_L$, which is defined as $R_L = 1/(1+bC_0)$, where $b$ is the Langmuir constant and $C_0$ is the initial dye concentration. The value of $R_L$ indicates the shape of isotherm to be either unfavourable ($R_L > 1$) or linear ($R_L = 1$) or favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The $R_L$ values obtained were in the range of 0.0870-0.3638, which indicate that the adsorption of rhodamine-B dye on JPC is favourable ($0 < R_L < 1$) for the concentration range studied.

**Effect of temperature and thermodynamic parameters**

It is likely that many effluents are discharged above ambient temperature. With this intention, experiments were conducted at 305, 313 and 323 K which showed an increase in dye adsorption from 75.20 to 111.30 mg g\(^{-1}\) with increase in temperature from 305 to 323 K.

From this study, thermodynamic parameters like $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ were determined using the following relations\(^1^8,3^7\):

$$K_c = \frac{C_{Ac}}{C_c}$$  \(\ldots(9)\)

$$\Delta G = -RT\ln K_c$$  \(\ldots(10)\)

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}$$  \(\ldots(11)\)

where $K_c$ is the equilibrium constant, $C_{Ac}$ is the solid phase concentration at equilibrium (mg g\(^{-1}\)), $T$ is the temperature in Kelvin and $R$ is the gas constant. The $\Delta H^\circ$ and $\Delta S^\circ$ were obtained from the slope and intercept of the van’t Hoff plot of $\log K_c$ versus $1/T$ (Fig. 3) and are presented in Table 3. The positive value of $\Delta H^\circ$ confirms the endothermic adsorption of rhodamine-B onto JPC. The negative values of $\Delta G^\circ$ (Table 3) indicate the feasibility of dye adsorption and the process is spontaneous. The positive value of $\Delta S^\circ$ reflects the affinity of JPC for rhodamine-B dye and suggested some structural changes in dye and JPC\(^6,4^3\). Also, the positive value of $\Delta S^\circ$ shows the increased randomness at the solid-solution interface. Apparently, the adsorbed water molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system\(^1^8,3^7\).

**Effect of adsorbent concentration**

The amount of dye adsorption increased with increase in JPC dose (0.2 to 2.0 g L\(^{-1}\)) and reached a maximum value after a particular dose (Fig. 4). This was due to the availability of more binding sites for

![Fig. 3—van’t Hoff plot](image)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$q_e$ (mg g(^{-1}))</th>
<th>$K_c$ (kJ mol(^{-1}))</th>
<th>$\Delta G^\circ$ (kJ mol(^{-1}))</th>
<th>$\Delta H^\circ$ (kJ mol(^{-1}))</th>
<th>$\Delta S^\circ$ (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>75.20</td>
<td>3.46</td>
<td>-3.15</td>
<td>83.98</td>
<td>285.82</td>
</tr>
<tr>
<td>313</td>
<td>99.00</td>
<td>8.52</td>
<td>-5.58</td>
<td>285.82</td>
<td>285.82</td>
</tr>
<tr>
<td>323</td>
<td>111.30</td>
<td>21.99</td>
<td>-8.30</td>
<td>285.82</td>
<td>285.82</td>
</tr>
</tbody>
</table>
adsorption as the JPC dose was increased. From the study it was found that a maximum removal of 96% from 60 mg L\(^{-1}\) of dye solution was achieved at an optimum JPC dose of 1.2 g L\(^{-1}\). While increasing the JPC dose from 0.2 to 2.0 g L\(^{-1}\) the percentage removal increased from 35.8 to 95.8% whereas the adsorption capacity decreased from 107.40 to 28.74 mg g\(^{-1}\). There are many factors that can contribute to this adsorbent concentration effect. The first and most important factor is that adsorption sites remain unsaturated during the adsorption reaction. This is due to the fact that as the dose of JPC is increased, there is less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of JPC. The second cause may be the aggregation/agglomeration of carbon particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusion path length. The particle interaction at higher carbon concentration may also help to desorb some of the loosely bound dye from the adsorbent surface.

The results of this experiment can be used to develop a mathematical relationship between percentage removal (R) and adsorbent dose (m, g L\(^{-1}\)). The relationship developed is as follows:

\[
R = \frac{m}{3.78 \times 10^{-3} + 7.76 \times 10^{-3} m}
\]  

(12)

This equation can be used to predict the percentage dye removal for any JPC dose within the experimental conditions studied. The correlation coefficient, \(r^2\), obtained between the experimental and calculated percentage removal values was 0.98.

**Effect of pH**

The experiments carried out at different pH show that there was no significant change in the per cent removal of dye over the entire pH range. This indicates the strong affinity of the dye onto JPC that either H\(^+\) or OH\(^-\) ions could not influence the dye adsorption. Similar negligible pH influence was reported for sorption of basic blue 9 by a carbon sorbent prepared from Indian Rosewood saw dust by sulphuric acid treatment.

**Desorption**

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. Sodium hydroxide (1 M) did not show any desorption of dye and 1 M sulphuric acid showed a desorption of only 2%. But 50% (v/v) acetic acid solubilized about 88% of dye from the spent carbon. Less desorption of dye in acid or base again confirms the strong affinity of dye on the carbon. Another plausible explanation is the agglomeration or association of dye molecules on the surface which prevents desorption of dye. On the other hand the organic solvent (acetic acid) solubilized the dye molecules by breaking the agglomeration/association and diffusing into the pores. Thus, the strong forces holding the rhodamine-B dye on JPC may predominantly be strong coulombic interaction, as irreversible coulombic attraction and ion-exchange are the possible mechanism involved in basic dye sorption by sorbents derived from high cellulosic materials.

**Conclusion**

From the foregoing experimental results, it can be concluded, that, the use of jackfruit peel carbon for the removal of rhodamine-B dye was effective. The kinetic and equilibrium data gained from this study conformed well with the modified Ritchie second order kinetic model and the Redlich-Peterson isotherm model, respectively. The equilibrium adsorption capacity, according to Redlich-Peterson isotherm, was 121.47 mg g\(^{-1}\) under the experimental conditions studied. There was no significant effect in adsorption capacity while changing the pH of the dye solution. The adsorption capacity increased with increase in temperature and the adsorption is endothermic and spontaneous with increased...
randomness at the solid-solution interface. Significant portion of the dye was recovered from the spent carbon using 50% acetic acid.

As jackfruit peel is a discarded waste material and available relatively in abundance, the treatment is expected to be economical. In addition, it can also provide solution for solid waste management.

Acknowledgement

B Stephen Inbaraj thanks the CSIR, New Delhi, India for the award of Research Associateship.

References