



KINETICS OF ADSORPTION OF DIRECT YELLOW 12 DYE FROM AQUEOUS SOLUTION BY JACK FRUIT LEAF CARBON

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ABSTRACT

Wastewater containing pigment and/or dyes cause serious water pollution in the form of reduced light penetration, photosynthesis and the toxicity from heavy metals associated with pigments and/or dyes. The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from wastewater. Jack fruit leaves were collected from the local fields and converted into a low-cost adsorbent. The present study deals with the removal of dyes from textile effluent by activated carbons developed from Jack fruit tree leaves (JTC). Direct Yellow 12 (DY-12) was used as the model compound due to its wide range of applications and high stability in the environment¹. The experimental data fit perfectly with Freundlich & Langmuir isotherms. The adsorption of the DY-12 dye on JTC followed pseudo first order kinetics with interactions largely over within the first hour.

Key words: Jackfruit leaf powder carbon, Activated carbon, Textile dyes, Kinetics, Adsorption, Isotherm.

INTRODUCTION

Chemical contamination of air, water and soil with a wide range of pollutants is a serious environmental threat due to their potential organisms and human toxicity. Effluents of all sorts of industries contain different types of both organic and inorganic pollutants. For example, textile industry uses large volumes of water in wet processing operations and thereby, generates substantial quantities of dissolved dyestuffs and other products such as dispersing agents, dye bath carriers, salts, emulsifiers, levelling agents and heavy metals²⁻⁶.

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Now-a-days thousands of dyes are prepared for printing and dyeing industries from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. During the last 35 years India has become a major producer of dyes and pigments to cater to the needs of not only the textile industries but also of other industries such as paper, rubber, plastics, paints, printing inks, art and craft, leather, food, drug and cosmetics⁷. In particular, printing and dyeing unit wastewater contains several types of coloring agent, which are difficult to be treated by biological methods⁸. Dyes even in low concentrations affect aquatic life and the food web. Some dyes are carcinogenic and mutagenic. It is estimated that approximately 15% of the dyestuffs are lost in the industrial effluents during manufacturing and processing operations. Hence, ways and means are required to remove the dyes from wastewater.

Activated carbon adsorption is the most popular physico-chemical treatment for the removal of dissolved organics from wastewater. The various phenomena pertaining to decoloration and adsorptive efficiencies of carbon have been correlated and shown to be directly proportional to the 'activity' of carbon. A number of non-conventional, low cost adsorbents have been tried for dye removal⁹⁻¹⁴. Adsorption studies for dye removal have been carried out using activated carbon made from non-conventional sources as adsorbents¹⁵⁻¹⁶.

EXPERIMENTAL

Preparation of the adsorbent and the adsorbate

Direct Yellow dye (DY-12) (Microscopic grade, Sigma-Aldrich, India) was used without further purification. All solutions were made in doubly distilled water. Matured jackfruit leaves, collected from a number of Jack fruit trees, were mixed together and washed repeatedly with water to remove dust and other impurities. The leaves were dried first at room temperature in shade. The dried leaves were added in small portions to sulphuric acid (50%) to produce more effective adsorbent. The carbonization was completed at heating rate of $10^{\circ}\text{C min}^{-1}$ to the final carbonization temperature of 850°C for 30 min. The carbon residue was dried and immersed in 5% sodium bicarbonate to remove any remaining acid and then filtered. The carbon was then washed with distilled water until the pH of the activated carbon was 6. It was dried at 150°C for 3 h and sieved to the particle size of < 200 μm and kept in a glass bottle.

Adsorption experiments

The adsorption experiments were carried out in a batch process using aqueous solutions of DY-12 dye. The other variable parameters were adsorbent amount, agitation time and pH of the medium. In each experiment, an accurately weighed amount of JTC was added to 50 mL of the DY-12 dye solution in a 100 mL conical flask and the mixture was agitated in a thermostatic mechanical shaker for a given length of time at a constant temperature. If necessary, the pH was adjusted by addition of a few drops of dilute HNO₃ or NaOH. The mixture was centrifuged (Remi Centrifuge) and DY-12 dye remaining unadsorbed ($\lambda_{\text{max}} = 380\text{-}500\text{ nm}$) was determined spectrophotometrically (Hitachi 3210). Calibration curves were obtained with standard DY-12 dye solutions and the amount adsorbed was found by mass-balance procedure.

Kinetics of adsorption

The kinetics of the adsorption processes was studied by carrying out a separate set of experiments with constant temperature, JTC amount and adsorbate concentration using the pseudo first order Lagergren equation¹⁷. The differential rate equation is of the form:

$$dq/dt = k_1 (q_e - q_t)$$

where q_e and q_t are the amount adsorbed per unit mass of the adsorbent (mg g^{-1}) at equilibrium and at time t , and k_1 is the pseudo first order rate constant (min^{-1}). Integrating the above equation for the boundary conditions $t = 0$ to $t = t$ gives:

$$\log (q_e - q_t) = \log q_e - k_1 t / (2.303) \quad \dots (1)$$

A linear plot of $\log (q_e - q_t)$ vs. t verifies the first order kinetics with the slope yielding the value of the rate constant.

Intra-particle diffusion

The variation in the extent of adsorption with time at different initial dye concentrations was processed for evaluating the role of diffusion in the adsorption system. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion into the interior of the pores. The intra-particle diffusion rate equation¹⁸.

$$q_t = k_i t^{0.5} \quad \dots (2)$$

where k_i is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$). The k_i values were calculated from the slopes of the linear plots of q_t vs. $t^{0.5}$.

Adsorption isotherms

The well-known Freundlich isotherm, (equation 3), is widely used to describe adsorption on a surface having heterogeneous energy distribution. The Langmuir isotherm, (equation 4) on the other hand is strictly applicable to monolayer chemisorption. The experimental data are tested with respect to both these isotherms:

$$\text{Freundlich isotherm: } q_e = K_f C_e^n \quad \dots(3)$$

$$\text{Langmuir isotherm: } C_e/q_e = (1/K_d C_1) + (1/C_1) C_e \quad \dots(4)$$

where q_e is the amount of dye adsorbed at equilibrium in unit mass of JTC, C_e is the concentration of the dye in aqueous phase at equilibrium, n and K_f are Freundlich coefficients, C_1 and K_d are Langmuir coefficients. The linear Freundlich and Langmuir plots were obtained by plotting (i) $\log q_e$ vs. $\log C_e$ (ii) C_e/q_e vs. C_e , and the adsorption coefficients were computed from the slopes and the intercepts. Another important parameter, R_L , known as the separation factor, could be obtained from the relation:

$$R_L = 1/(1 + K_d C_{\text{ref}}) \quad \dots(5)$$

where C_{ref} is any equilibrium liquid phase concentration of the solute. It has been established¹⁵ that (i) $0 < R_L < 1$ for favourable adsorption, (ii) $R_L > 1$ for unfavourable adsorption, (iii) $R_L = 1$ for linear adsorption, and (iv) $R_L = 0$ for irreversible adsorption.

RESULTS AND DISCUSSION

Kinetics of adsorption

The kinetics of DY-12 dye adsorption on Jackfruit tree leaves powder carbon (JTC) was studied with respect to different amounts of the adsorbent (Fig. 1).

The adsorption of dyes increased with the sorbent dosage and reached an equilibrium value after 0.9 g of sorbent dosage (Fig. 1). As one was expected that the percentage of dye removal increased with increasing amount of carbon, however, the ratio of dye sorbed to carbon (mg/g) decreased with the increasing amount of carbon (Fig. 2). The interactions appeared to attain equilibrium rapidly after about 1 h of agitation. Assuming pseudo first order kinetics for the adsorption process, $\log (q_e - q_t)$ was plotted against t and the linearity of the Lagergren plots (Fig. 2) confirmed the same (the correlation coefficients for the plots were in the range 0.996-0.998). The first order rate constants evaluated from these plots were between 2.82×10^{-3} and $4.97 \times 10^{-3} \text{ min}^{-1}$ for different amounts of the adsorbent.

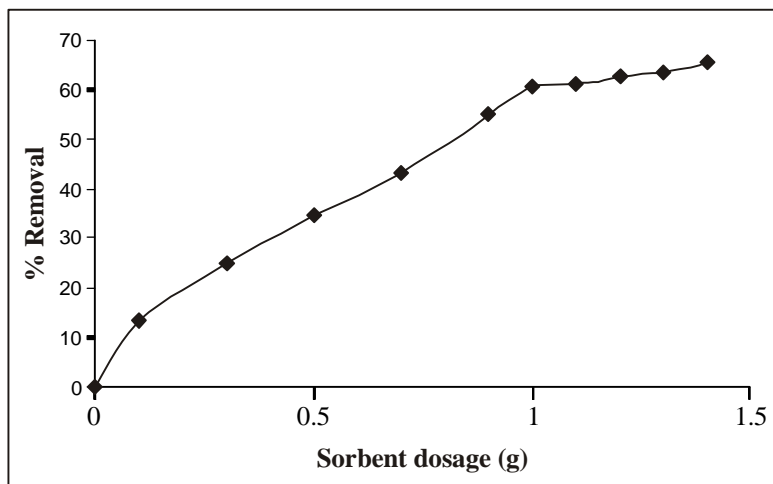


Fig.1: Adsorption % of the dye DY-12 on different amounts of the adsorbent, JTC at 300 K (dye conc. 100 mg/L)

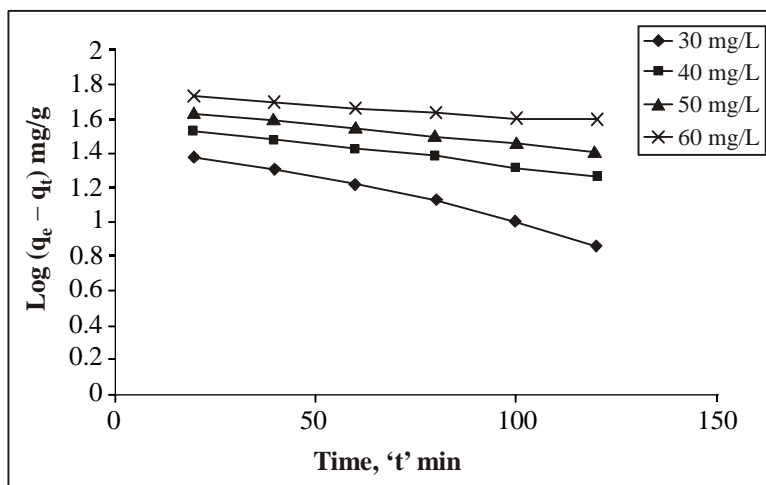


Fig. 2: Lagergren plots for adsorption of DY-12 on JTC at 300 K

The dye-JTC interactions could thus be predicted as reasonably fast. It may be noted that the pseudo first order reaction differs from a true first order reaction in two aspects: the expression $k_1(q_e - q_t)$ does not represent the number of available sites and the parameter $\log q_e$ is an adjustable parameter whose value is not equal to the intercept of the plot of $\log (q_e - q_t)$ vs. $t^{0.5}$. In the present work, the intercepts of the Langmuir plots were very close to the theoretical $\log q_e$ values, and therefore, the kinetics of DY-12 dye adsorption on Jackfruit leaf powder carbon (JTC) could be considered as almost true first order in nature. Further,

the difficulty usually associated with the application of the pseudo first order model to an adsorption system arising from the uncertainty of finding reliable q_e values within a reasonable time was not applicable in the present work as the system was very close to equilibrium even after 1 h of agitation time.

A number of authors (references are given in the Table 1) have reported pseudo first order kinetics for adsorption of dyes on various adsorbents prepared from biological sources similar to the JTC. The values of the rate constant, k_1 , obtained by these workers (Table 1) are compared with the values obtained in the present work also given in Table 1 (conditions vary). It is to be noted that the first order rate constant for the interaction of DY-12 with JTC, k_1 , in the present work were 10-100 times less when compared to the reported values in Table 1.

Table 1: Pseudo first order rate constant data for adsorption of dyes on various adsorbents

Adsorbent	Dyes	k (min ⁻¹)	Reference
JTC	DY-12	(2.82 - 4.97) x 10 ⁻³	Present works
Banana pith	Acid violet	(1.8-13.0) x 10 ⁻²	[27]
Banana peel	Methyl orange	3.9 x 10 ⁻¹	[20]
	Methylene blue	3.5 x 10 ⁻¹	[20]
	Rhodamine B	1.9 x 10 ⁻¹	[20]
Orange peel	Rhodamine B	(2.3-9.95) x 10 ⁻¹	[30]
	Congo red	(3.6-4.9) x 10 ⁻²	[30]
	Procion orange	(8.3-15.5) x 10 ⁻²	[30]
	Pith Basic red	22(1.0-1.1) x 10 ⁻²	[28]
	Methyl orange	4.0 x 10 ⁻¹	[20]
	Methylene blue	2.9 x 10 ⁻¹	[20]
Water hyacinth	Methylene blue	(4.2-6.9) x 10 ⁻²	[19]
Coir pith	Congo red	(2.1-3.9) x 10 ⁻¹	[26]
Neem leaf powder	Brilliant green	7.32 x 10 ⁻³	[24]
	Methylene blue	(2.9-5.1) x 10 ⁻³	[25]

Intra-particle diffusion

The plots of q_t vs. $t^{0.5}$ (Fig. 3) were found to be linear with regression coefficients of 0.90-0.99. The intra-particle diffusion rate constant, k_i , was in the range of $(1.21-14.17) \times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$. The linearity of the plots demonstrated that intra-particle diffusion played a significant role²⁰ in the uptake of the dye by JTC. This also confirms that adsorption of the dye on the adsorbent was a multi-step process, involving adsorption on the external surface and diffusion into the interior. All the steps slow down as the system approaches equilibrium. If the steps are independent of one another, the plot of q_t vs. $t^{0.5}$ usually shows two or more intersecting lines depending on the exact mechanism, the first one of this representing surface adsorption and the second one intra-particle diffusion. The absence of such features in the plots of the present work indicated that the steps were indistinguishable from one another and that the intra-particle diffusion was a prominent process right from the beginning of dye-solid interaction. Weber and Morris²¹ have proposed that if the uptake of the adsorbate varies with the square root of time, intra-particle diffusion can be taken as the rate-limiting step. Ho²² has shown that it is essential for the q_t vs. $t^{0.5}$ plots to go through the origin if the intra-particle diffusion is the sole rate limiting step. Since this was also not the case in the present work (the q_t vs. $t^{0.5}$ plots have intercepts in the range $2.72 - 3.19 \text{ mg g}^{-1}$), it may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the DY-12 dye - JTC interactions.

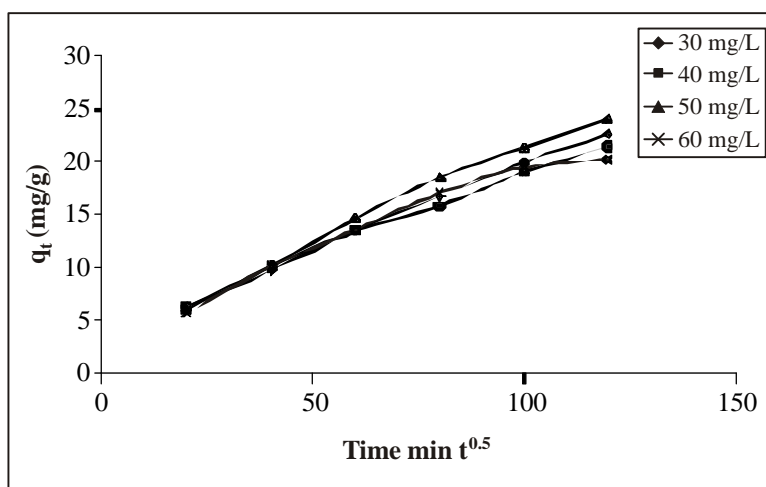


Fig. 3: Plots of q_t (mg g^{-1}) vs. $t^{0.5}$ for evaluating intra-particle diffusion rate constant (DY-12 dye, temperature 300 K)

Effect of the amount of adsorbent and the initial concentration of the adsorbate

To investigate the effect of adsorbent mass on amount of adsorption, a series of experiments were carried out keeping the agitation time constant and varying both the amount of adsorbent and the adsorbate concentration at constant temperature. For a JTC leaf powder carbon of 50 mg/L, the amount adsorbed 3.26 mg g⁻¹. The DY-12 dye concentration was increased from 50 to 250 mg/L (Table 2). The results as a whole indicate two distinct trends: the amount adsorbed q_t (mg g⁻¹), increased with an increase in the dye concentration and decreased with an increase in the amount of the adsorbent. The latter trend may be due to the effect of adsorbent mass on porosity of the adsorbent suspension. In general, the trends might have been influenced by changes in a number of physical properties of the solid-liquid suspensions including their viscosity.

Table 2: Amount of DY-12 (mg g⁻¹) adsorbed on JTC at 300 K Contact time 5h

Dye conc. (mg/L)	Weight of carbon (mg)	Amount of adsorbed carbon (mg g ⁻¹)	% amount of dye adsorbed
15	50	3.20	10.22
30	100	4.20	24.10
50	150	5.27	42.12
70	200	6.17	61.79
90	250	7.00	83.00

Effect of pH

An important influencing factor for dye biosorption on agricultural by-products has been referred to pH as in most studies published in the literature. The variation of equilibrium dye uptake with initial pH is given in Fig. 4 for an initial dye concentration of 100 mg/L⁻¹ at 300 K for a contact time of 4 h. As seen from the Fig. 4, the biosorption with pH of the medium varying from 2.0 to 9.0, the adsorption of the dye oscillated between 60 and 70%. Ho *et al.* (2001)²⁸ have shown that the extent of removal of a basic dye (Basic Red 18) by activated clay decreased rapidly as pH increased from 3.0 to 5.0 and from 8.0 to 10.0. However, the adsorption remained constant within the range of pH 5.0-8.0. It was suggested that the increase in sorption depended on the properties of the adsorbent surface and the dye structure. At a lower pH, the adsorbent surface might have become negatively charged attracting more of the basic dye molecules. It is likely that positive charge develops on the surface of an adsorbent in acidic medium, resulting in a higher adsorption of anionic dyes

than in a basic solution. If this is the case, the sorption of the cationic dye should decrease at a lower pH. In addition, the effect of pH may also be explained on the basis of surface hydroxylation, acid-base dissociation and surface complex formation.

The adsorption of DY-12 dye was increased with the increase of pH of the solution. The variation in the amount of adsorbed dye with respect to pH of the medium has been shown in Fig. 4. The maximum removal was noted at pH 6.5 -7.5. With an increase of pH from 4.2 to 7.02, the uptake of DY-12 dye increases from 58 to 66 % which is close to the satisfactory level by JTC at a temperature 300 K.

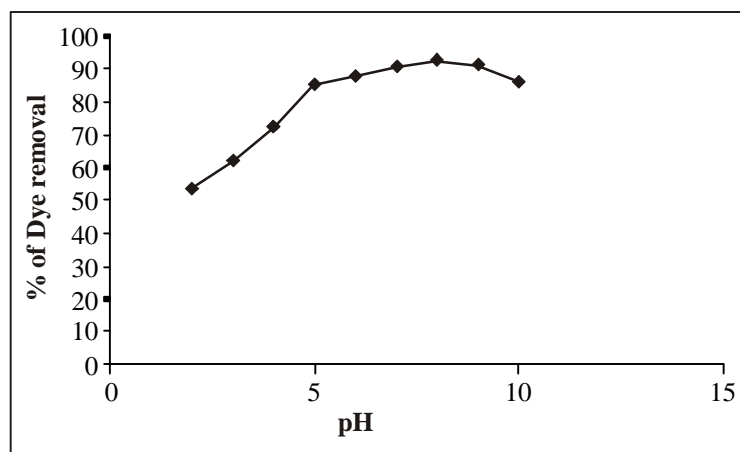


Fig. 4: Effect of pH on the removal of DY-12 dye by JTC (concentration 40 mg/L), temperature 300 K

Adsorption isotherms

The experimental data yielded good linear plots with both Freundlich isotherm (Fig. 5, Regression coefficient $R = 0.99$) and Langmuir isotherm (Fig. 6, $R = 0.96-0.99$). The Freundlich coefficient, n , which should have values in the range of $0 < n < 1$ for favourable adsorption, remained in a narrow range of 0.51 - 0.66 for different amounts of the adsorbent. The Freundlich adsorption capacity, K_f , was in the range of 2.42-9.47 lg^{-1} .

The Langmuir monolayer adsorption capacity, C_1 was large with values between 4.12 and 11.21 mg g^{-1} . The Langmuir adsorption intensity, K_d had values of 0.182-0.722 lmg^{-1} . The dimensionless separation factor, R_L , had an average value of 0.96 in the range of 0.91-0.98 in concurrence with the suggested values for favourable adsorption. This value being very close to 1.0, the adsorption of the dye on JTC could be described as linear in nature, i.e., there was an almost linear increase in adsorption with increase in JTC amount. The isotherm

constants indicated that the JTC had very good potential as an adsorbent for the dye, DY – 12 and JTC, and it might have similar potential for other dyes, as had already been demonstrated for Brilliant Green (Bhattacharya)²⁴.

The Langmuir monolayer capacity of the JTC (4.12-12.01 g kg⁻¹), may be compared with a number of adsorbents derived from biological sources like the Derris leaf powder. Some of the large adsorption capacities recorded were: 160 g kg⁻¹ for Atrazon Blue on Maize cob²⁵, 94.5 g kg⁻¹ for Maxilon Red also on Maize cob²⁵ and 133.7 g kg⁻¹ for Brilliant Green on Neem leaf powder²⁴.

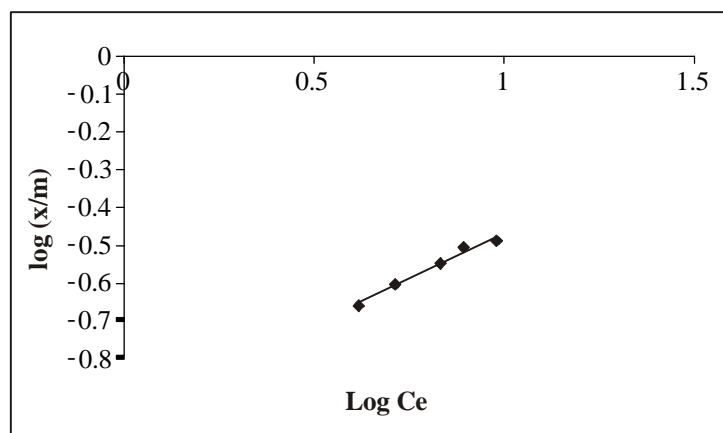


Fig. 5: Freundlich isotherm for adsorption of DY-12 dye on JTC at 300 K with dye conc. of 50 mg/L and agitation time 5 h.

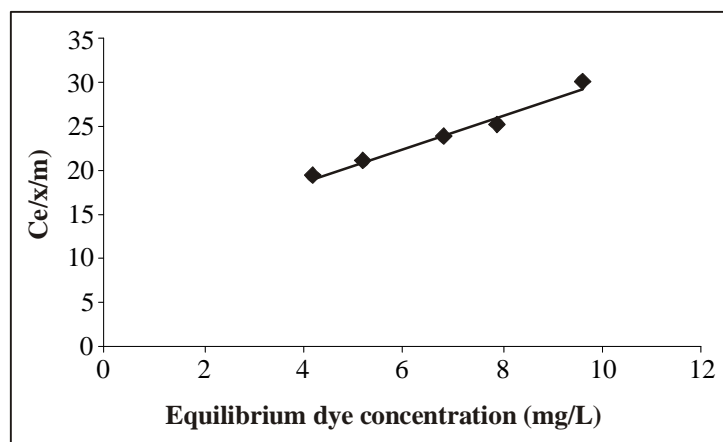


Fig. 6: Langmuir isotherm for adsorption of DY-12 dye on JTC at 300 K with dye conc. of 50 mg/L and agitation time 5h.

The Jack fruit tree leaf powder carbon thus has good potential to be used as an adsorbent for the removal of DY-12 from effluent water.

CONCLUSION

The results of this work can be summarized as follows:

- (i) Jackfruit leaf powder carbon is a promising adsorbent for removal of the dye DY-12 dye from water. A small amount (2 g/L) of the adsorbent could almost completely decolorize an aqueous solution of DY-12 (40 mg/L) if agitated for 5 h.
- (ii) The experimental data produced perfectly fit with the Freundlich isotherm showing that the surface of the JTC particles was heterogeneous, non-specific and non-uniform in nature. The mechanism of the dye-JTC interactions is thus likely to be very complicated involving a wide range of sites differing in a number of aspects including energy considerations.
- (iii) The data were in good agreement with the Langmuir isotherm.
- (iv) The adsorption of the DY-12 dye on JTC followed pseudo first order kinetics with the interactions largely over within the first hour.

The Jackfruit tree regularly sheds its leaves during January-February, which become waste. These leaves can be put to good use as an adsorbent for removal of colour from industrial and other effluents. However, as with all other bio-resources, the processes are likely to be very complicated and a detailed characterization of the surface will be necessary to develop more insight into the mode of action.

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