Dynamic and Equilibrium Studies on Adsorption of Direct Dye (Direct Red 28) by Lowcost Nanoporous Activated Carbon Derived From Ipomoea Carnea Stem Waste

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ABSTRACT *Nanoporous activated carbon materials were prepared from abundantly available Ipomoea Carnea stem waste. A series of Nanoporous carbon samples were prepared by subjecting the carbon material to various chemical processes. These materials accumulate superior properties and good adsorption behaviours. The adsorption capacity of selected derived carbon sample using Ipomoea Carnea stem waste prepared by Dolomite process was much greater than the capacities of the other carbons prepared by various processes. The adsorption of Direct Red 28 (Direct dye) on this dolomite treated activated carbon was investigated to assess the possible use of this adsorbent for the processing of dyeing industry wastewater. The influence of various factors such as initial dye concentration, agitation time, pH and temperature on the adsorption capacity has been studied. The percentage removal of dye is observed to decrease with the increase in initial dye concentration. With increase in temperature, the adsorption of dye also decreases, indicating exothermic nature of the reaction. Adsorption isothermal data could be interpreted by the Langmuir and Freundlich equations. Kinetic data have been studied using Elovich and Pseudo-first order and Pseudo-second order equations for understanding the reaction mechanism.*

INTRODUCTION

Activated carbon has been extensively used for the purpose of water purification. In particular, it has been commonly used for the removal of organic dyes from textile waste water. Discharge of organic pollutants like dyeing industry wastewater into water bodies contaminates the environment. Activated carbon is quite expensive and its regeneration produces additional effluent and results in considerable loss (10-15%) of the adsorbent. Many reports have appeared on the development of lowest activated carbon adsorbents developed from cheaper and readily available materials (Babel and Konawa 2003).Nanoporous carbon material with large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for removal of heavy dyes from industrial wastewater. The adsorptive properties of activated carbon for removal of pollutants are well documented (Macias et al. 1993).Adsorption of hazardous soluble chemicals from wastewater in to surface of a solid adsorbent has provided a new dimension to wastewater technology (Benfieldet al. 1982). One of the major challenges associated with adsorption by activated carbon is its cost effectiveness. This has led many workers to search for cheaper substitutes. Crab shell (Ann et al. 2001), peanut hull pellets (Brown et al. 2000), Petiolar felt-seath of palm (Iqbal et al. 2002), corn starch (Kweon et al. 2001), soyabean hull and sugar beat fibre (Jambulingam et al. 2005), rice husk (Low & Lee 1997), spent grain (Low et al. 2000), de-oiled soya (Gupta et al. 2005), Ipomoea carnea stem (Karthikeyan et al. 2007), Leuceana leucocephala shell waste (Karthikeyan et al. 2001), turmeric waste (Karthikeyan et al. 2008), Pome-granate peel (Jambulingam et al. 2007) and sawdust (Marshall & Johns 1996) are some new adsorbents, which have been tried with varying success.Moreover, the affinity of carbon surface towards solute molecules must be enhanced in order to increase the extent of solute adsorption. Comparison of size information available for commercial activated carbon pores and solute molecules in natural waters suggest that some fractions of solute will be able to access finer carbon pores (Namasivayam & Yamuna 1999). In the present work, we have prepared Nanoporous activated carbon from Ipomoea carnea stem waste which is used as an adsorbent for Direct Red 28 removal and the adsorption capacity of chosen adsorbent was

regulated by many influencing factors such as temperature, pH variations and initial dye concentrations. The kinetic and equilibrium adsorption data obtained were correlated to characterize the prepared carbon sample for the adsorption of Direct Red 28.

MATERIALS AND METHODS

Adsorbent

The study of Ipomoea carnea based carbon material is used as adsorbent which is expected to be economical, environmentally safe and it has practical importance. The raw stems of Ipomoea Carnea were collected from in and around Trichy district, TamilNadu, India. They were cut into small pieces and dried in sunlight until the moisture was evaporated. The dried materials were used for the preparation of activated carbons using physical and chemical activation methods. Ipomoea carnea stem waste material was treated with dolomite for a period of 24 hours. Then the material was placed in the muffle furnace carbonized at 400°C. The dried materials were powdered and activated in a muffle furnace kept at 800°C for a period of 60 minutes. After activation, the carbon obtained was washed sufficiently with plenty of water , dried and sieved then to desired particle size . The N_2 adsorption-desorption isotherms of activated carbons were measured at 77K using a gas sorption analyzer (NOVA 1000,Quanta Chrome corporation) in order to determine the surface areas and the total pore volumes. The surface areas were calculated using the BET equation.

Adsorbate

The textile dye, Direct Red 28, was purchased from sigma- Aldrich (Germany) and all the chemicals used were obtained as research grade chemicals and were used without purification. A stock solution of Direct Red 28 was prepared by dissolving 1 g of dye in 100mL of double distilled water and used for further studies by diluting as concentrations required.

Batch adsorption studies

All reagents used were of AR –grade (E-merk). Different concentrations of dye solution of Direct Red 28 were prepared with distilled water. 50 ml of each this dye solution of known initial concentration (C_0) and initial pH was taken in a 100 ml

screw-cap conical flask with a required amount of adsorbent and was agitated at a speed of 200 rpm in a temperature controlled thermostatic shaker bath at 30^0 C for a specified period of time. Then the solution was filtered through a 0.45 μm membrane filter. The concentrations of dye in solutions were determined before and after adsorption using Elico UV-visible spectrophotometer. The amount of dye adsorbed and adsorption efficiency was calculated .

Determination of Direct Red 28
Direct Red 28 was estimated spectrophotometrically. The amount of Direct Red 28 adsorbed in mg/L at time ,t was computed by using the following equation.

$$q_t = \frac{\frac{C_0 - C_t}{}\times V}{m_s} \qquad (1)$$

where, C_0 and C_t are the Direct Red 28 concentration in mg/L initially and at given time t, respectively, V is the volume of the Direct Red 28 solution in ml and m_s is the weight of the activated nanoporous carbon.

The percentage of removed Direct Red 28 in solution was calculated using eqn.(2)

$$\% \, Removal = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

The initial concentration of Direct Red 28, pH and temperature were investigated by varying any one parameters and keeping the other parameters constant.

Adsorption dynamics
The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Direct Red 28 adsorption on the activated nanoporous carbon was analyzed using pseudo first order(Lagergren 1898), pseudo second order (Ho et al. 2000)kinetic models and Elovich equation (Chien and Clayton 1980). The conformity between experimental data and the model predicted values was expressed by the correlation coefficients. A relatively high R^2 value indicates that the model successfully describes the kinetics of Direct Red 2 adsorption.

The pseudo first – order equation
The pseudo first - order equation (Lagergren 1898) is generally expressed as follows.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g^{-1}), k_1 is the rate constant of pseudo first –order adsorption ($lmin^{-1}$). After integration and applying boundary conditions t =0 to t = t and q_t= 0 to q_t = q_t, the integration form of equation (3) becomes.

$$\log(q_e - q_t) = \frac{\log(q_e) - k_1}{2.303} \times t \qquad (4)$$

The value of log (q_e – q_t) were linearly correlated with t. The plot of log (q_e – q_t) Vs t should give a linear relation ship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

The pseudo second – order equation.
The pseudo second – order adsorption kinetic rate equation is expressed as (Ho et al. 2000)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

where, k_2 is the rate constant of pseudo second order adsorption (g. mg^{-1}. min^{-1}). For the boundary conditions t = 0 to t = t and q_t= 0 to q_t = q_t, the integrated form of equation (5) becomes.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_t \qquad (6)$$

Which is the integrated rate law for pseudo second – order reaction. Equation (6) can be rearranged to obtain equation(7), which has a linear form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \qquad (7)$$

If the initial adsorption rate h (mg g^{-1} min^{-1}) is

$$h = k_2 q_e^2 \qquad (8)$$

Then, Equations. (7) And (8) become:

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}(t) \qquad (9)$$

The plot of (t/qt) and t of equation (7) should give a linear relationship from which qe and k2 can be determined from the slope and intercept of the plot, respectively.

The Elovich equation
The Elovich model equation is generally expressed (Chien and Clayton 1980) as

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \qquad (10)$$

where, a is the initial adsorption rate (mg.g-1 min-1), b is the adsorption constant (g. mg-1) during any one experiment. To simplify the Elovich equation, assumed abt >> t and by applying the boundary conditions qt = 0 at t = 0 and qt=qt at t = t Eq (10) becomes;

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \ldots \qquad (11)$$

If Direct Red 28 adsorption fits the Elovich model, a plot of q_t vs ln t should yield a linear relationship with slope of (1/β) and an intercept of (1/β) ln(αβ).

Isotherm models
Langmuir isotherm: The study of the Langmuir isotherm is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing conditions for effective adsorption. In this respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well recognized (Langmuir 1918).

The Langmuir and the rearranged Langmuir equations are given below.

$$\frac{1}{q_e} = \frac{1}{Q_o b} \cdot \frac{1}{C_e} + \frac{1}{Q_o} \qquad (12)$$

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \qquad (13)$$

where,

q_e = the amount of dye removed at equilibrium (mg/g)

C_e = the equilibrium concentration of dye (mg/L)

Q_0 = the Langmuir constant, related to the adsorption capacity (mg/g)

b = the Langmuir constant, related to the energy of adsorption(L/mg)

Freundlich Isotherm:
At equilibrium conditions, the adsorbed amount, q_e can also

be predicted by using the Freundlich equation (Freundlich, 1926).

$$q_e = k_f C_e^{1/n} \qquad (14)$$

where,

q_e = dye concentration in solid at equilibrium (mg/g)

C_e = dye concentration in solution at equilibrium (mg/L)

k_f = measure of adsorption capacity

n = adsorption intensity

A logarithmic form of the above equation is

$$\log q_e = \log k_f + (1/n) \log C_e \qquad (15)$$

The values of n and k_f were determined from the plot log C_e v_s log q_e.

where, k_f is the indication of the adsorbent capacity and 1/n is a measure of surface heterogeneity, ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero.

RESULTS AND DISCUSSION
Surface characters of activated carbon
The morphology of the surface of the prepared Nanoporous activated carbon sample was examined using Scanning Electron Micrographs. These micrographs provide positive reception of the porosity of adsorbents and consequently a qualitative evaluation of their ability to adsorb the dye molecules in solution. Ipomoea Carnea Activated Carbon (ICAC) has many pores, small cavities and rough areas with micro pores which were clearly found on the surface. This shows that dolomite treatment created welldeveloped pores with uniform distribution on the surface of the precursor, therefore leading to the activated carbon with large surface area and porous structure.The morphological study by SEM of the above adsorbent shown in the Fig. 1 revealed that it is highly porous in nature (Yoshida et al. 1993).
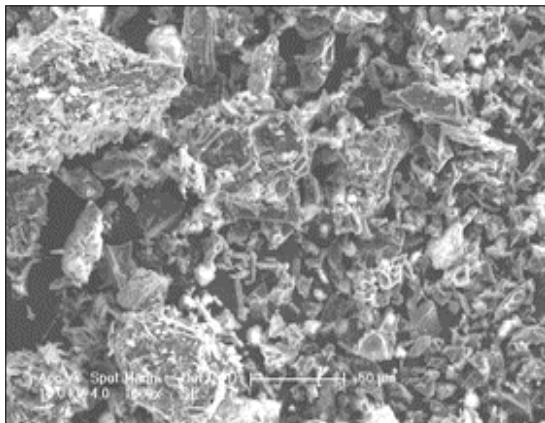

Figure. 1 SEM image of ipomea Carnea stem waste Activated carbon
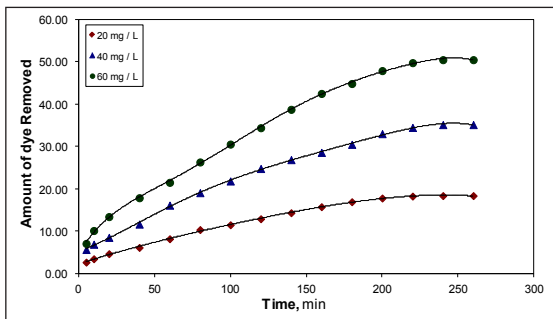

Figure. 2 Effect of Agitation time and Initial dye Concentration on Direct Red 28 Adsorption
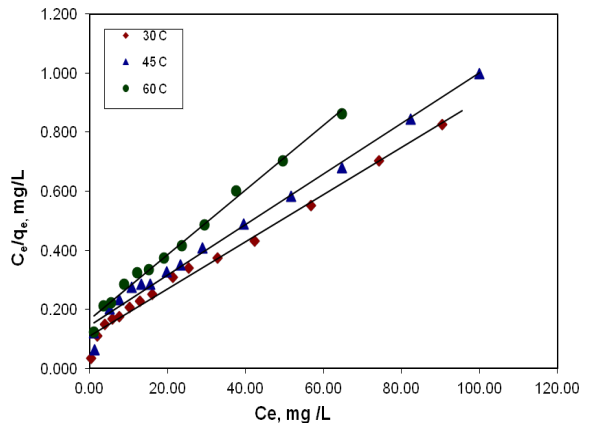

Figure 3 Effect of Temperature Variation on Langmuir Plot for Direct Red28 Adsorption
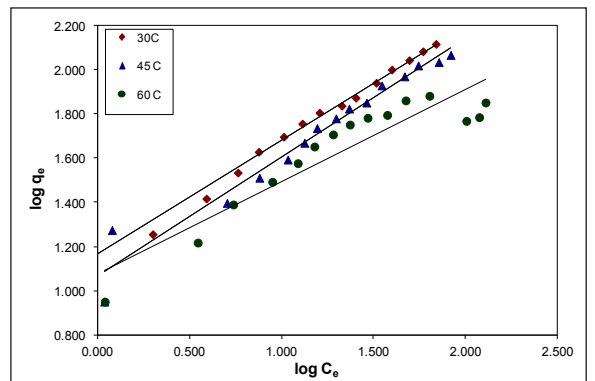

Figure 4 Effect of Temperature Variation on Freundlich Plot for Direct Red 28 Adsorption
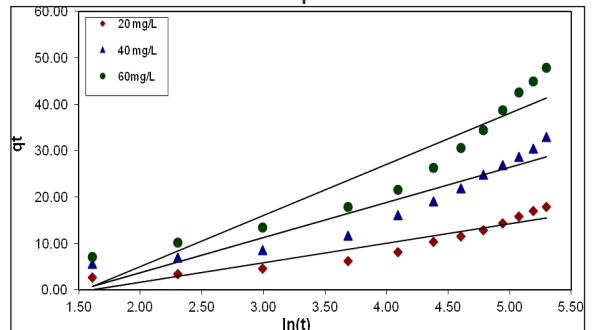

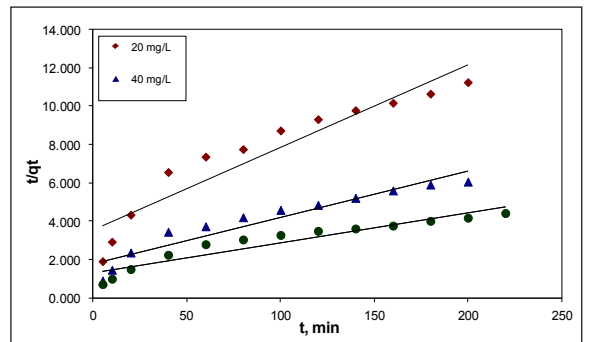Figure 5 Effect of Initial Dye Concentration on Elovich Plot for Direct Red 28 Adsorption

Figure 6 Effect of Initial Dye Concentration on Pseudo Second Order Plot for Direct Red 28 Adsorption

Characterization of adsorbent
Physico-chemical characterizations of the adsorbent were

presented in Table 1.

Table 1 . Characteristics of the Nanoporous Activated Carbon prepared from Ipomoea Carnea Stem Waste (ICAC)

Parameter	ICAC
Bulk density (g/ml)	0.39
Ash content (%)	18.81
pH	7.8
Moisture content (%)	9.6
Surface area (m²/g)	746
Iodine number(mg/g)	728
pH_{zpc}	5.9
porosity (%)	58.06

Effect of pH

The pH value of the solution being an important controlling parameter in adsorption is mainly influenced by two factors: (i) Distribution of the dye ionized species in the solution phase and (ii) Overall charge of the adsorbent. Therefore the interaction between dye molecule and the adsorbent is basically a combined result of charges on the dye molecules and the surface of the adsorbent. The adsorption behavior of the dye on the adsorbent was studied over a wide pH range of 2 -10. It is Observed that the pH significantly affects the extent of adsorption of dye over the adsorbent and a reduction in the amount adsorbed dye with increasing pH was observed . The maximum uptake of the Direct Red 28 is observed at pH 5.0 as well as a large decrease in adsorption capacity was observed as the pH is increased above its pKa(4.1) value.

Effect of Agitation time and Initial dye Concentration

The uptake of Direct Red 28 from water by activated Ipomoea carnea stem waste carbon increases when the agitation time was varied from 10 to 260 minutes and attains equilibrium at 30°C and at pH 6.5, when the initial concentration of the direct dye solution used was 20 mg/L and the adsorbent dosage of 50mg. The increase in adsorption of Direct dye with increase in agitation time may be attributed to the increased intra particle diffusion occurring at long shaking time (Fig. 2). A similar result was observed by Rao & Bhole (2001) in the removal of chromium using fly ash and bagasse.

Effect of Temperature on kinetic rate constant and rate parameters

For this adsorption process, adsorption experiments were carried out with fixed initial dye concentration (20mg/L) and pH 6.5 at different temperatures viz. 30 °C. 45 °C and 60 °C. The analysis of the data in Table 2 reveals that the influence of temperature on the dye adsorption has comparatively little effect on the pseudo second order and Elovich(Fig.5) rate constants. The table 2 also reveals that the influence of the temperature of dye on pseudo-first order(Fig.6) rate constant is appreciable. It is obvious that the adsorption of dye onto the adsorbent is best described by pseudo first order rate equation with greater regression coefficient values.

Isothermal modelling

The Langmuir adsorption isotherm (Fig. 3) and the values of high correlation coefficients (R²), obtained in this study indicates the applicability of Langmuir adsorption isotherm. Fig. 4 shows that the values of adsorption intensity reveal that the applicability of Freundlich adsorption is not good when compared to Langmuir adsorption isotherm. The values of n and R² are given in Table 3 . The study of temperature effects on the Freundlich parameter reveals increasing trend in the adsorption capacity(Q_0) with increase in temperature. These data are useful for practical design purposes.

Table 2. The adsorption kinetic model rate constants for ICAC at different Temperatures

Adsorbent	Initial Temperature oC	Pseudo first order		Pseudo Second order			Elovich Model		
		k 1 lmin-1	R2	k 2 g mg-1 min-1	H mg g-1 min-1	R2	b g min-1	a mg g-1 min-1	R2
ICAC	300	0.0092	0.9792	3.122	4.8992	0.9274	0.1754	0.4466	0.9615
	450	0.0142	0.9206	8.590	2.5497	0.9505	0.2036	0.8709	0.9372
	600	0.0122	0.9617	8.779	2.9975	0.9236	0.2150	0.7413	0.9114

Table 3: Parameters of Langmuir and Freundlich adsorption isotherms for the adsorption of Direct Red 28.

Temperature, °C	Langmuir Isotherm			Freundlich Isotherm	
	R²	Q₀		n	R²
30	0.9866	90.91		1.072	0.9097
45	0.9863	116.3		1.671	0.9458
60	0.9900	125.0		3.005	0.8638

CONCLUSION

In the present study adsorption of Direct Red 28 on activated Ipomoea carnea stem waste carbon has been investigated. The data obtained through this work support that the Ipomoea carnea carbon is an effective low cost adsorbent for the removal of Direct Red 28 from aqueous solution. The adsorption of Direct Red 28 is dependent on the initial concentration and agitation time. Equilibrium of Direct Red 28 adsorption reaches at 150 min. The values of correlation coefficients obtained in this study indicates the applicability of Langmuir adsorption isotherm. The study of temperature effects on the Freundlich parameters reveals that increasing trend in the adsorption capacity with increase in temperature. These data are useful for practical design purposes.

The Elovich and pseudo-second order equations provided a best fit description for the sorption of Direct Red 28 onto Ipomoea carnea stem waste carbon, but the pseudo-second order equation had better correlation coefficient value than Elovich equation. Therefore, pseudo-first order was considered the most appropriate due to high correlation coefficient when compared to Elovich equation and pseudo second order equation. The adsorption of Direct Red 28 onto activated Ipomoea carnea stem waste carbon gave better results.

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