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Research Article

Removal of Direct Dye using Activated Carbon Prepared from *Prosopis juliflora* Bark: Isothermal, Thermodynamic and Kinetic Studies

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Abstract

Activated carbon of *Prosopis juliflora* Bark (PJBAC) is prepared using muffle furnace and employed for the removal of Direct Brown MR (DBMR) dye from aqueous solutions. Surface morphological studies carried out for unloaded and loaded carbons; indicate the surface changes in the porous nature of the dye loaded PJBAC. Batch equilibration experiments pertaining to the study of operating factors viz., varying initial dye concentrations, preset time intervals and different doses of PJBAC, variable pH and temperature environments are verified to assess the sorptive nature of PJBAC. Optimized conditions have been setup as 400 mg/L initial concentration; 60 min contact time; 100 mg dosage, pH 2 and 30^{0}C temperature for a maximum of 90.2% dye removal with a sorption capacity of 180.4 mg/g. The isothermal plots for Langmuir, Freundlich and Tempkin equations are tested, wherein the best fit of linearity is observed for both Langmuir and Freundlich adsorption isotherms, suggesting monolayer/multilayer sorption. Thermodynamic parameters are calculated to study the nature of sorption, observed as endothermic, irreversible and spontaneous for DBMR-PJBAC system. Kinetic studies reveal the applicability of second order kinetic model.

Keywords: Direct Brown MR dye, *Prosopis juliflora* bark activated carbon, adsorption, Isotherms, Kinetics.

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Introduction

Effluents discharged from textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries have been found to be the main sources of water pollution. Textile industries discharge a lot of wastewaters containing different dyes like direct, reactive, mordant, acid and basic dyes. The direct dyes are the second largest dye class in the color index, which are used for dyeing rayon, linen, cellulosic fibers, wool and silk. Generally, dyes 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 as a waste [1]. These dyes are recalcitrant molecules, which are difficult to degrade biologically [2]. They are carcinogenic, mutagenic and teratogenic affecting human beings, fish species and microorganisms. Hence, their removal from wastewaters has become environmentally important [3]. Thus, the removal of dyes from colored effluent of textile industries is of major concern. Various techniques like chemical coagulation [4], electrolysis, chemical oxidation [5], photochemical degradation [6], membrane filtration [7], biological treatment, adsorption by activated carbon [8] are known to be effective for the removal of dyes from polluted water.

Amongst, the numerous techniques available for dye removal, adsorption is the procedure of choice giving excellent results as it can be utilized for decolouration of dye effluents [9, 10]. Most commercial systems currently use activated carbon as a sorbent to remove dyes from effluents because of its excellent adsorption ability. However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, various attempts have been made to find inexpensive adsorbents. A sorbent can be considered low-cost if it requires little processing, being abundant in nature, a by-product or waste material generated from another industry [11]. Such alternatives include low cost activated carbons prepared from natural products like bagasse [12], nutshells [13], Jute fiber [14], rice husks [15], plum kernels [16] and coconut shells [17]. Activated carbons prepared from various products are widely used as adsorbents due to their high adsorption capacity, large surface area, microporous nature, chemical and thermal stability. In this article, an attempt has been made by employing phosphoric acid activated carbon prepared from *Prosopis juliflora* bark for the removal of Direct brown MR dye from aqueous solution, the first of its kind not reported elsewhere.

Materials and Methods

Preparation of Dye Solution

Direct brown MR was procured from Sigma Aldrich and was used without further purification. A stock solution of the dye (1000 mg/L) was prepared using doubly distilled water and the dilutions for the required concentrations were made. The characteristics and chemical structure of the dye is listed and depicted in **Table 1** and **Figure 1** respectively.

Table 1 Characteristics of Direct Brown MR.

Molecular Formula	$C_{29}H_{19}N_5Na_2O_7S$
Molecular Weight	627.54
C.I Name	Direct Brown 2
C.I Number	22311
CAS Number	CAS 2429-82-5
λ_{max}	420nm

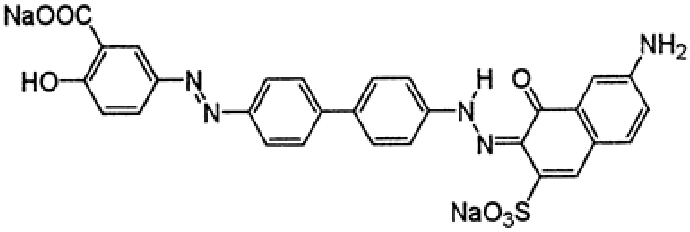

Figure 1 Structure of Direct brown MR.

Adsorbent Preparation/Characterization

The *prosopis juliflora* bark was collected from various localities in Coimbatore, washed well with distilled water and sun dried. The dried materials were soaked in boiling solution of 35% Phosphoric acid, subjected to charring and were separated, air dried and carbonized at 500^0C in muffle furnace for 1hr. Later, the material was powdered after cooling/activated at 800^0C for 10 min, washed well with distilled water. The pH was maintained at 7±0.2. The dried powder material was ground and stored in an airtight container and utilized for further experiments.

Results and Discussion

Morphological Studies

Scanning Electron Microscopy

Scanning electron microscopy is an important tool employed for characterizing the surface morphology of the adsorbent before and after the adsorption process. **Figure 2a** shows large number of unoccupied pores present on the surface of PJBAC and layered structures were also visible, whereas in Figure 2b, almost all the pores are covered with dye molecules and the layered structure had disappeared, these differences obviously being visualised in the images supporting the sorptive affinity of PJBAC for DBMR dye molecule.

Batch Adsorption Experiments

Varying PJBAC doses (50 mg-200 mg: 50 mg intervals) were added to 50 ml of aqueous DBMR dye solutions(at pH-7 intervals) taken in 100 ml Erlenmeyer flasks with varying concentrations (50 mg/L- 400 mg/L: 50 mg/L intervals) and subjected to agitation in a mechanical shaker at preset time interval(10 min-100 min:10 min interval). Residual concentrations of the filtered sample were estimated spectrophotometrically at a wavelength corresponding to maximum absorbance (λ_{max}=420 nm), using an UV/Vis spectrophotometer (LabIndia UV 3000^+ Model). The initial pH of the solution was adjusted by the addition of dilute aqueous solutions of HCl or NaOH (0.1N). Experiments pertaining to different sorption conditions ie., pH (2 -12 : 2) and temperature (30^0C-60^0C: 10^0C intervals) were performed and the amount of dye adsorbed onto activated carbon was calculated as follows. Duplicate experiments were conducted to ensure the reproducibility of values within ± 2%.

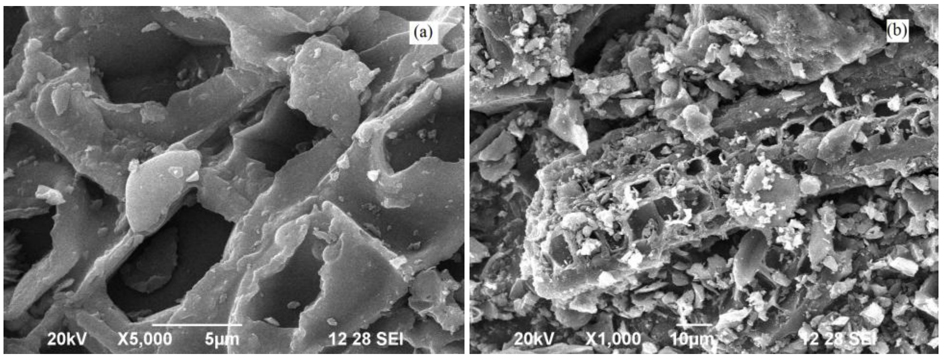

Figure 2 (a) SEM image of PJBAC Carbon (b) SEM images of dye loaded PJBAC Carbon

$$q_e = (C_0-C_e)\ V/W \qquad (1)$$

where, C0 and Ce are the initial and equilibrium concentrations (mg/L) of the dye respectively. V is the volume of the solution and W is the weight of the adsorbent used.

Effect of Initial Dye Concentration and Contact Time

The adsorption process is highly dependent on initial dye concentration [18]. The increase in dye concentrations from 50 mg/L to 400 mg/L decreased the percent removal from 91.8% to 83.6%, and the corresponding adsorption capacity calculated varying from 22.95 mg/g to 172.60 mg/g. It may be explained, at higher initial concentration, the ratio of initial number of dye molecules to the available surface area is high, hence fractional adsorption becomes dependent on initial concentration. For fixed adsorbent dose, the total available sites are limited, adsorbing almost same amount of sorbate, resulting in a decrease in the percentage removal [18]. The curves depicted in **Figure 3** are single, smooth, continuous leading to saturation implied by plateau formation suggesting the possibility of monolayer coverage of dye molecules. Similar results have been reported in the employment of modified Mango Bark / Neem Bark powder for the adsorption of Malachite Green and Babul Seed Carbon Powder in the Methylene Blue removal [19, 20].

The amounts of dye adsorbed in the initial stage of contact time, reached a maximum through steep rise upto a contact time of 60 minutes, later becoming almost constant denoting the attainment of equilibrium, which shall be due to the availability of large number of vacant surface active sites initially. After a lapse of time, when the adsorption of the dye molecules had occurred, the remaining unoccupied surface sites may be difficult to be filled in due to repulsive forces acting between the dye molecules and the carbon surface [21]. Thence, an initial concentration of 400 mg/L and 60 minutes contact time have been fixed as optimum conditions for further experiments.

Effect of Dosage

The influence of PJBAC dose furnished the information regarding sorption ability and an optimum requirement for the maximum % removal as illustrated in **Figure 4**, which reveals that 100 mg itself exhibited a maximum dye removal of 86.3% at pH 7. Further increase in adsorbent dose, did not register significant increase, this may be attributed to saturation of adsorption sites due to particulate interaction such as aggregation. Such aggregation would lead to a decline in total surface area and increase in diffusion path length [22]. The adsorbent dose was fixed as 100 mg.

Effect of pH

pH of the dye solution plays an important role in its degradation. Maximum adsorption of DBMR dye had occurred at pH 2, later a reduction in sorption was observed at increasing pH environments. This is observed obviously from the steep decline (**Figure 5**). Further reduction at basic pH values can be explained by the fact that when the pH of the dye solution is adjusted accordingly, the number of negatively charged sites will also increase, resulting in least adsorption of anionic dyes [23].

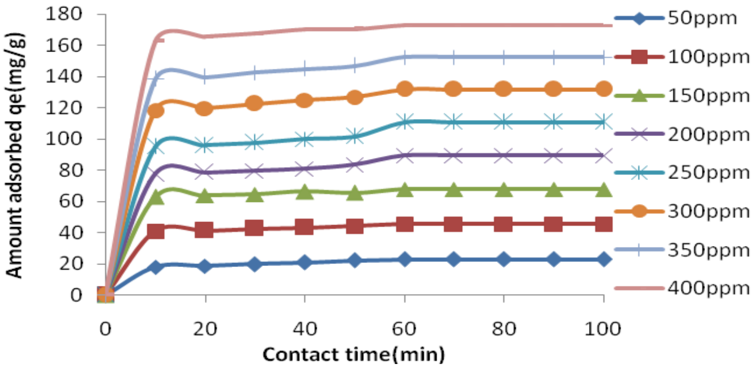

Figure 3 Effect of Initial Dye Concentration and Contact Time.

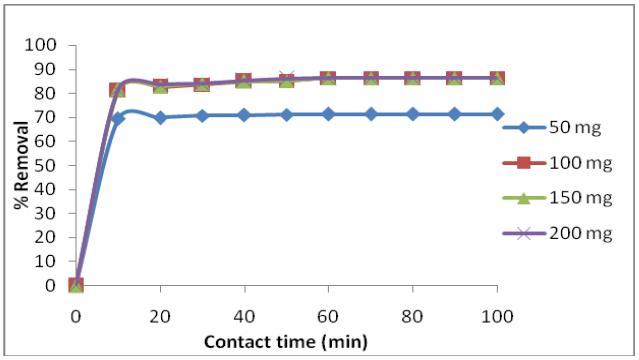

Figure 4 Effect of Dosage.

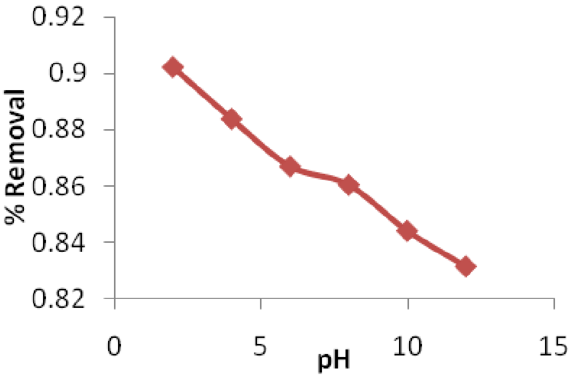

Figure 5 Effect of pH.

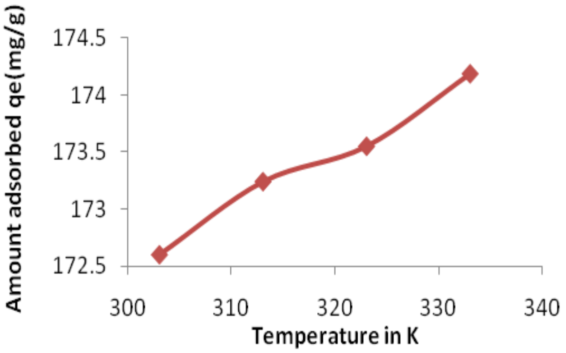

Figure 6 Effect of Temperature.

Effect of Temperature

Results pertaining to the influence of varying temperatures registered linear rise of q_e values (172.6 mg/g – 174.2 mg/g) with temperature (**Figure 6**). This trend reveals the increase in the mobility of dye molecules and the decline of retarding forces on the diffusing ions, thereby increasing the sorption capacity [18] of PJBAC.

Adsorption isotherm

The adsorption isotherm is fundamental in describing the interactive behaviour between adsorbent and adsorbate and is important in the design of adsorption system [24]. The most widely employed isotherms viz., Langmuir, Freundlich and Tempkin models were studied to predict the nature of the system at different initial dye concentrations with a dose of 100 mg.

Langmuir isotherm

In 1916, Langmuir developed a model that was based on the theory of adsorption of solute molecules on adsorbent at homogeneous sites with uniform energy levels [25]. The isotherm describes that no further adsorption takes place once the active sites are covered, that is only monolayer sorption occurs on the solid surface. The linearised form of the Langmuir equation is as follows

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \qquad (2)$$

where, C_e (mg/L) is the concentration of dye solution at equilibrium, q_e (mg/g) is the amount of dye adsorbed at equilibrium, Q_m is the binding capacity and ‘a’ is binding constant. The Q_m and ‘a’ values are calculated from the slope ($1/Q_m$) and intercept ($1/a\ Q_m$) respectively of the linear plot(C_e/q_e vs C_e). The linearity of the plot observed for C_e/q_e vs C_e (**Figure 7**) reveals the applicability of the Langmuir model.

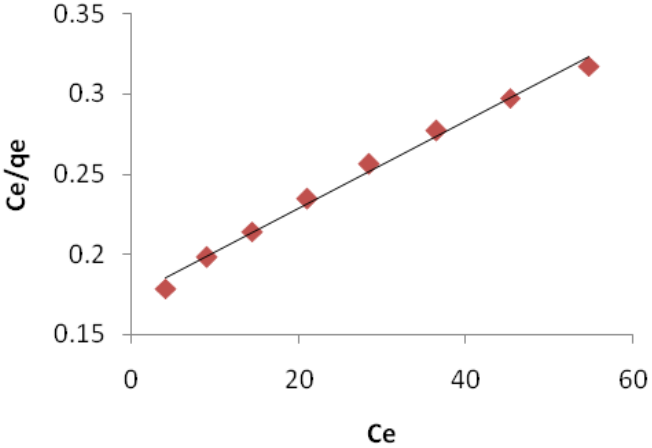

Figure 7 Langmuir isotherm.

Freundlich isotherm

Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of adsorption with increase in the fraction of occupied sites and the linearised form of equation:

$$\text{Log } q_e = \log K_F + 1/n \log C_e \qquad (3)$$

where, $C_{e,}$ is the equilibrium dye concentration in solution (mg/L); A plot of log q_e vs log C_e is depicted in **Figure 8**, from which the constants K_F and 1/n are calculated. K_F and 1/n are isothermal constants indicating the sorption capacity and sorption intensity respectively. The studied system follows Freundlich isotherm, as is evident from the graph with good correlation. The favourability of the adsorption isothermal process can also be supported through dimensionless factor (R_L),

$$R_L = 1/1+bC_0 \qquad (4)$$

where, C_0 is the initial concentration (mg/L).

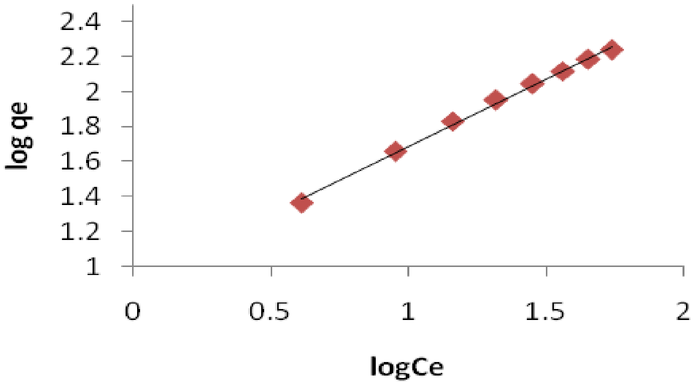

Figure 8 Freundlich isotherm.

The calculated R_L value for DBMR – PJBAC system was 0.17 indicating that the adsorption process to be favourable [26] as evidenced from **Table 2**.

Table 2 Equilibrium Parameter R_L.

R_L values	**Nature of adsorption**
$R_L > 1$	Unfavourable
$R_L = 0$	Irreversible
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable

Tempkin isotherm

Tempkin and Pyzhey (1940) assume that the heat of adsorption would decrease linearly with increase of coverage of adsorbent, which is due to some indirect adsorbate interactions on adsorption isotherm [27]. The linearised form of isotherm is

$$q_e = B_T \ln A_T + B_T \ln C_e \qquad (5)$$

where, $B_T = RT/b_T$, T absolute temperature in Kelvin and R is the universal gas constant. The constant b_T is related to the heat of adsorption (kJ/mol) and A_T is the equilibrium binding constant corresponding to the maximum binding energy. The Tempkin constants A_T and b_T were derived from the intercept and slope of the linear plots of q_e vs ln C_e shown in **Figure 9**. The consolidated parametric values of Langmuir, Freundlich and Tempkin constants are listed in **Table 3**. The values for the constants were observed to be higher than those reported by other researchers as evident from **Table 4**. This proves the better sorption capacity of PJBAC in trapping the anionic DBMR dye molecules.

Thermodynamic Study

The feasibility and spontaneous nature of adsorption process is evaluated from the values of thermodynamic parameters (ΔG^0, ΔH^0& ΔS^0). These parameters were calculated using Van't Hoff equation [34].

$$\Delta G° = -RT \ln K_d \qquad (6)$$

$$\ln K_d = (\Delta S^0/R) - (\Delta H^0/RT) \qquad (7)$$

where, ΔG^o is the free energy change (kJ/mol) and K_d is the distribution coefficient. ΔH^0& ΔS^0 were calculated from the Van't Hoff Plot (**Figure 10**) and the corresponding values are listed in **Table 5**. The negative value of Gibbs free energy change (ΔG^0), positive values of enthalpy change (ΔH^0) and entropy change (ΔS^0) is indicative of the spontaneity, endothermicity and high disorderliness respectively.

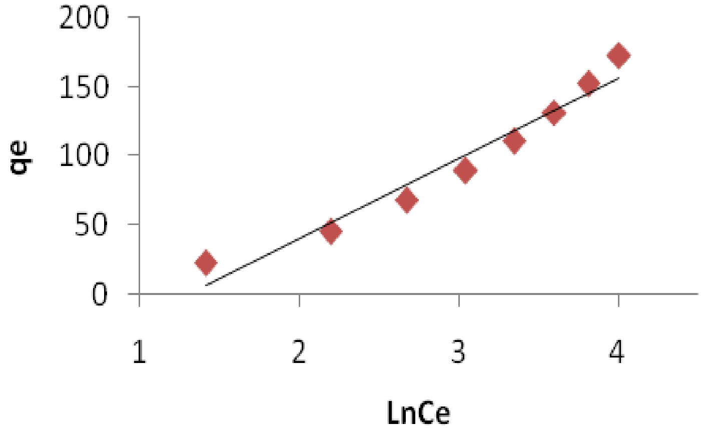

Figure 9 Tempkin isotherm.

Table 3 Isothermal Constants Data.

Isotherm models								
Langmuir			**Freundlich**			**Tempkin**		
q_m (mg/g)	b(L/mg)	R^2	1/n	K_F(mg/g)	R^2	b_T	A_T	R^2
500	0.012	0.992	0.774	8.128	0.996	43.44	5.686	0.950

Table 4 Comparison of PJBAC against studied Activated Carbons.

Adsorbent	**Dye**	**Adsorption capacity (mg/g)**	**K_F (mg/g)**	**Reference**
Poly aniline coated sawdust composite	Direct Green 6	217.4	4.47	[28]
Pine Cone	Acid Black 26	62.89	19.47	[29]
	Acid Green 25	43.29	7.25	
	Acid Blue 7	37.45	7.95	
Prosopis juliflora Seed	Direct red 23	90.9	12.4	[30]
Rice Husk	Direct Red 31	129.87	12.34	[31]
	Direct Orange 36	66.67	4.581	
Pomegranate Peel	Direct Blue 106	58.14	2.301	[32]
Macore fruit Shell	Methylene Blue	10.6	1.728	[33]
	Methyl Orange	3.4	1.225	
Prosopis juliflora Bark	Direct brown MR	500	8.128	Present study

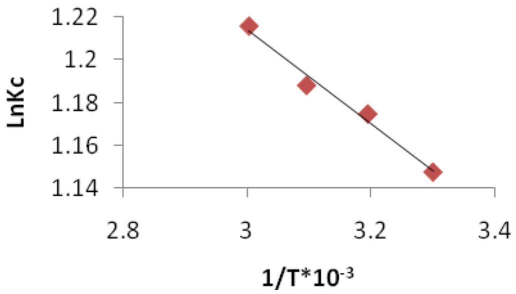

Figure 10 Van’t Hoff Plot.

Table 5 Thermodynamic parameters.

Temp°C	ΔG^0 KJ/mol	ΔH^0 KJ/mol	(ΔS^0) KJ/mol
30	-0.2890	0.2221	1.878
40	-0.3057		
50	-0.3190		
60	-0.3366		

Kinetic Studies

Pseudo-first-order and pseudo-second-order kinetic models have been investigated to assess the sorption dynamics of the current system. Pseudo-first-order equation employed to explain the solid/liquid adsorption is as follows

$$\log(q_e - q_t) = \log q_e - k_{ad}\, t/2.303 \qquad (8)$$

where, q_e and q_t corresponds the amounts of DBMR adsorbed at equilibrium and time t respectively (mg/g), k_{ad} is the rate constant of pseudo-first-order adsorption (min^{-1}). A plot of $\ln(q_e - q_t)$ versus t is a straight line, where q_e and k_1 are calculated from intercept and gradient of the line, respectively [35].

Pseudo second order kinetic model is given by the following equation:

$$t/q_t = 1/k^2 q_e^{\,2} + t/q_e \qquad (9)$$

where k_2 (g/mg /min) is second order rate constant. A plot of t/qt versus t (**Figure 11**) gives a straight line, and q_e and k_2 are calculated from gradient and intercept of the line, respectively [36].Constants calculated from pseudo first order, pseudo second order kinetic models are given in **Table 6**. When the calculated q_e values and experimentally verified q_e values calculated for pseudo first order are significantly different from each other, they are comparable in the case of pseudo second order kinetic model. On the other hand, when correlation coefficients of both models are compared, it is apparent that coefficients of pseudo second order model is higher and much closer to unity. Hence, it is obvious that DBMR adsorption on PJBAC is better described by pseudo second order model [37]. Similar trend was observed for the adsorption of direct dyes onto activated carbon prepared from saw dust [38], palm ash [39].

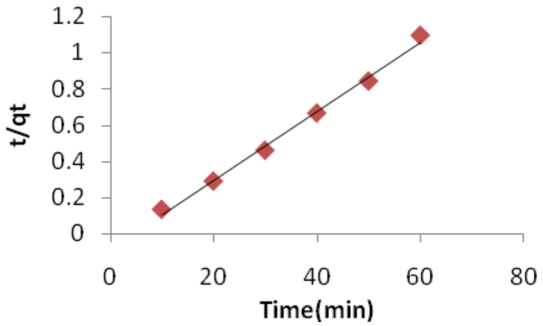

Figure 11 Pseudo second order plot.

Table 6 First-order and second-order kinetic constants.

		First order kinetic model			**Second order kinetic model**		
C_0 (mg/L)	$q_{e\ exp}$ (mg/ g)	$q_{e\ cal}$ (mg/g)	k_1(min^{-1})	R^2	$q_{e\ cal}$ (mg/g)	k_2(min^{-1})	R^2
400	172.6	55.63	0.002	0.966	194.0	0.044	0.994

Conclusion

Phosphoric acid activated carbon was prepared from *Prosopis juliflora* bark, an ecofriendly tree waste. This carbon was characterized using SEM, which registered significant morphological changes on the surface of both dye loaded and unloaded carbons. Its efficient role play as an adsorbent for removal of Direct Brown MR from aqueous solutions was experimentally verified by employing batch equilibration method. The maximum amount of dye adsorbed was optimized under different operating factors, initial dye concentration, contact time, PJBAC dosage, pH and temperature of the solutions. Verification of the isothermal studies viz., Langmuir, Freundlich and Tempkin revealed that both Langmuir and Freundlich isotherms had better linear fit compared to Tempkin model. Variations in free energy, enthalpy and entropy registered favourable nature of adsorption. The calculated rate of adsorption for the sorptive system follows second order kinetic model. Comparison of the efficiency of PJBAC with other prepared activated carbons exhibited better chelating property in the removal of anionic DBMR dye, justified by the isothermal constants. Thus, it is concluded that PJBAC possesses good sorption ability in the removal of dyes.

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