Mass transfer studies of Direct Orange 102 dye onto a non-conventional adsorbent

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Activated carbon with surface area of 896 m^2/g has been prepared from the wood of *Thevetia Neriifolia* Juss (TNJAC). The fitness of the prepared activated carbon is tested for its adsorption capability towards the textile dye direct orange 102 (DO102). On increasing the solution *p*H from 2 to 12, the percentage of DO102 adsorption increases from 41 to 75%. The adsorption kinetics is analyzed using pseudo-first order and pseudo-second order kinetic models. Pseudo-second order model is more appropriate to describe the adsorption kinetics with a correlation coefficient of $0.9311 < r^2 < 0.9871$. On analyzing the adsorption isotherm using Langmuir and Freundlich models, the adsorption of DO102 by TNJAC follows Langmuir type of isotherm with energetically homogeneous sorbent surface.

Increasing demand for industrial dyes and its processing led to great amount of effluent color-wastewater, which poses a serious impact on the environment. The dyes are the most important chemicals that pollute the environment. It was estimated in 1978 that the total production of dyes worldwide was 640,000 tons[1,2]. India has been considered the major source of dyes supplier to industries. Textile[3], paper[4] and pulp mills[5], tannery[6], electroplating factory[7], distillery[8], food processing unit[9] and other industries discharge a large quantity of coloured wastewater into the main local water bodies such as rivers, lakes and ponds[1,10]. In recent times, printing and dyeing industries handle coal tar based hydrocarbons such as Benzene, Naphthalene, Anthracene, Toluene, Xylene and so on to produce different kinds of dyes. Although some of the above are not totally innocuous, most dyes and pigments are considered to be inert or non-toxic[2,10]. In addition, the dyes affect the life and the food web. For example, several dyes are carcinogenic and mutagenic in nature[11]. An extreme condition that few dye stuffs in effluent water can withstand environmental conditions such as sun light, varying concentrations (*p*H) and microbial destruction. Thus these dye molecules need to be removed or processed before they are being released directly into the environment.

Disperse dyes seem to possess significant potential for bio-accumulation as they have high partition coefficient and solubility[2]. Biological treatment, coagulation, floatation, adsorption, oxidation and hyper filtration are the methods that are commonly used for colour removal from industrial wastewater. One of the most popular physico-chemical treatments for removing dissolved organics from wastewater is activated carbon adsorption which is important commercial perspective[2,10]. Requirement of less land area, flexibility in design and operation and superior removal of organic contaminants are the advantages of an activated carbon[1,2]. Nevertheless, the high cost of production coupled with problems associated with regeneration leads to the search for alternate adsorbents[12-17]. Conventionally, Coal based materials, Coconut shell and certain hard wood are used as raw materials for the manufacture of activated carbon in large scale industrial purpose. Whereas any raw material that is available in plenty with free of cost is a better alternate for the manufacture of activated carbon can be viewed as non-conventional sources of activated carbon. In the present study, we have employed *Thevetia neriifolia* Juss wood was used as precursor for the preparation of activated carbon.

Experimental Section

Plant wastes used for the present study are collected from the rural areas in and around Erode and Salem districts of Tamil Nadu province, India. The

dried material used for the preparation of the activated carbon is subjected to some procedures.

Preparation of TNJAC

In the present study, *Thevetia neriifolia* Juss wood was used as precursor for the preparation of the activated carbon. Initially, the wood was cleaned of its adhering dirt with water and then dried. It was cut into pieces of 2 to 3 cm and dried in sunlight for 10 days. Then it was soaked in a boiling solution of 40% of H_3PO_4 for 1 h and kept at room temperature for 24 h. Further, it was separated, air dried and carbonized in a muffle furnace at 400°C. It was powdered and activated in a muffle furnace at 800°C for 10 min. Then the material was dried at 110°C and sieved to a desired particle size and stored in a tight lid container for further adsorption studies. The material characteristics were studied based on the standard procedure.

Adsorbate

All the chemicals used here are of reagent grade. Direct Orange 102 (DO 102) which has molecular formula $C_{34}H_{21}N_6Na_3O_{11}S_2$ (Mol Wt: 822.66) (E. Merck, India) was chosen as the adsorbate. A stock solution containing 1000 mg of the dye per liter was prepared by dissolving the dye in double distilled water and it was used to prepare the adsorbate solutions by appropriate dilution as required; the percentage of purity was also taken into consideration while preparing the stock solution.

Adsorption studies

For the adsorption studies, 100 mg of adsorbent with 100 mL of dye solution at 180 rpm was agitated in a temperature controlled orbital shaker (REMI make). The solution was extracted at regular intervals and centrifuged (make: Universal centrifuge) at 5000 rpm for 10 min. Then the un-adsorbed supernatant liquid was analyzed of its level of residual dye concentration at 664 nm using Bio-UV visible spectrometer (BL-198). The entire process was repeated again and the mean of the two resultant values were taken.

Kinetics and isotherm studies of adsorption

Researchers[18-20] has advocated various kinetic models to evaluate adsorbents. The performance of an adsorbent depends upon many factors such as physical and chemicals properties of the adsorbent and the mass transfer process. The kinetic models are quite useful in the design and optimization of bulk effluent treatment in industries. To analyze the adsorption kinetics and isotherms, already proposed mathematical models are employed. The mathematical models used in this study are

Mathematical model	Equation	Plot	Reference
pseudo first-order	$\log(q_e - q_t) = \log q_e - \dfrac{k_1}{2.303}t$	log (q_e-q_t) vs t	21
pseudo second-order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^{\,2}} + \dfrac{1}{q_e}t$	t/q_t vs t	22
Langmuir isotherm	$\dfrac{C_e}{q_e} = \dfrac{1}{Q_0.b_L} + \dfrac{C_e}{Q_0}$	C_e/q_e vs C_e	23
Freundlich isotherm	$\log q_e = \log k_f + \dfrac{1}{n}\log C_e$	log q_e vs log C_e	24

where q_e is the amount of dye adsorbed at equilibrium (mg/g), q_t is the amount of dye adsorbed at time t (mg/g), k_1 is the first-order rate constant (min^{-1}), t is time (min), k_2 is the second-order rate constant, the constant Q_0 refers to the monolayer adsorption capacity and b_L is the Langmuir constant, n is a constant related to adsorption capacity and kf is the Freundlich constant.

Results and Discussion

Characteristics of TNJAC

TNJAC has been assessed for its physiochemical parameters such as ash content, bulk density, volatile matter, water soluble matter, acid-extractable content, moisture content, porosity, surface area, methylene blue number, iodine number and *p*H to check its effective employment for water and wastewater treatment (Table 1). Moisture content requires additional amount of carbon though it does not show differences in the adsorption capacity.

Surface morphology of TNJAC

Scanning electron microscopy (SEM) facilitates the observation of very fine details (high resolution) of

Table 1 — Physico-chemical properties of TNJAC

S.No	Properties	TNJAC
1	*p*H	6.90
2	Conductivity (mS/cm)	0.181
3	Moisture content in (%)	7.56
4	Ash (%)	13.4
5	Volatile matter (%)	21.1
6	Matter soluble in water (%)	0.40
7	Matter soluble in 0.25 M HCl (%)	1.22
8	Bulk density (g/mL)	0.42
9	Specific gravity	0.94
10	Porosity (%)	55.32
11	Surface area (m^2/g)	896
12	Methylene Blue value (mg/g)	375

materials and good focus over a wide range of specimen surface (large depth of field). It also produces clear image of specimen ranging from object visible to the naked eye to a structure spanning few nanometers. Besides its use in studying soils, sedimentary particles, rock materials, synthesized compounds, and biological materials, it also helps to elucidate the architecture and evolution of microfossils. The SEM image of TNJAC before and after adsorption is given in Fig. 1a. The SEM image reveals its surface morphology. It is clear that the surface of TNJAC is more fractured and fragmented than the other carbons. In addition, these carbons show relatively smooth regions, cavities, cracked and pitted morphology. TNJAC has a structure similar to honey comb with large number of pores indicating higher surface area. The SEM recorded after the adsorption (Fig. 1b) shows that, the entire surface trough and cre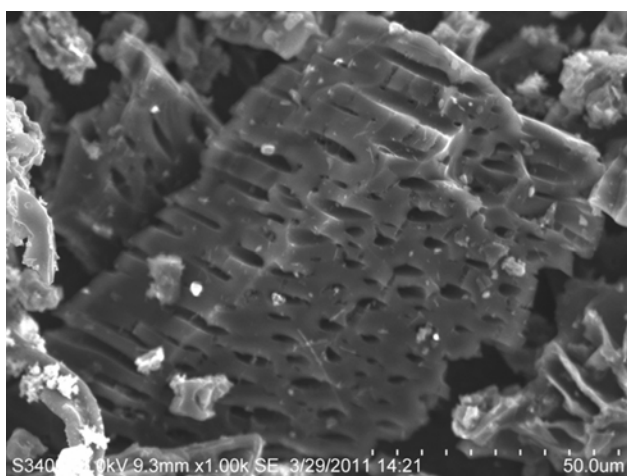sts were completely filled with organic dye molecules. Figure 2 shows the X-ray Diffraction (XRD) pattern of the activated carbon. The broad diffraction peaks indicates that the prepared materials exhibit amorphous nature. As is necessary for wastewater treatment with any activated carbon, TNJAC has many porous networks with varying particle dimensions.

Effect concentration and temperature

Figure 3a shows the adsorption of DO102 onto TNJAC at various initial dye concentrations. The percentage of dye uptake increased from 37.93 to 68.38 mg/g with an increase in the initial dye concentration from 50 to 100 mg/L. At the initial dye concentration of 100 mg/L, the dye is rapidly adsorbed during the first 20 min at 1.74 mg/g/min, whereas the initial sorption rate for 50 mg/L has gone at 5.35 mg/g/min. The adsorption reaches equilibrium at 90 minutes. The slow rate of the adsorption of DO102 might occur due to the electrostatic hindrance of repulsion between the adsorbed negatively charged sorbate species onto the surface of TNJAC in addition to the available anionic sorbate species in solution.
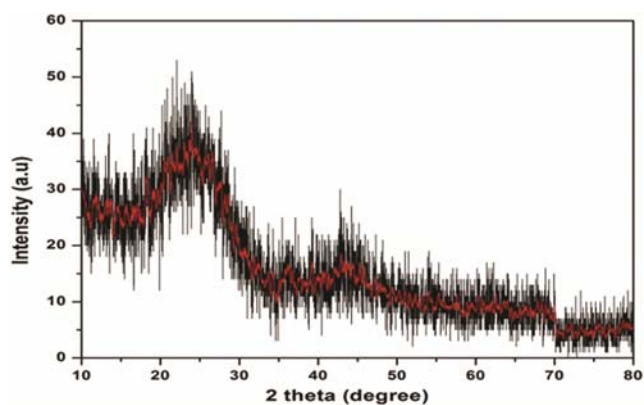

Fig. 1A — SEM image of TNJAC before adsorption

Fig. 2 — XRD pattern of TNJAC

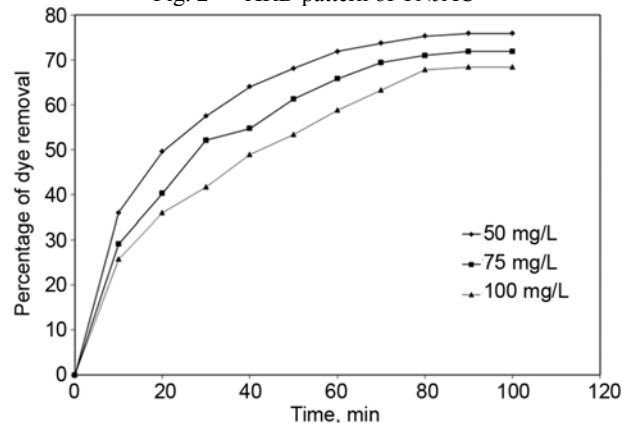
Fig. 1B — SEM image of TNJAC after adsorption

Fig. 3A — Percentage of the removal of DO102 by TNJAC concentration variation

Also slow pore diffusion of the solute ions into the bulk of the adsorbent might causes such phenomena. The adsorption curves are single, smooth and continuous until the saturation of the dye as the carbon surface suggests the visible monolayer coverage of DO102 molecules on the surface of the adsorbents. The adsorption of DO102 onto TNJAC at 30, 40 and 50°C for a fixed initial dye concentration of 50 mg/L is shown in Fig. 3b. On increasing the temperature from 30 to 50°C, the equilibrium adsorption capacity of DO102 onto TNJAC gets increased from 53.1 mg/g to 44.53 mg/g. This decrement indicates that TNJAC is exothermic. The decrease in the thickness of the boundary layer surrounding the sorbent with temperature is the reason for the decreased adsorption, which lead to the decrease in the mass transfer of the adsorbate in the boundary layer.

Effect of *p*H

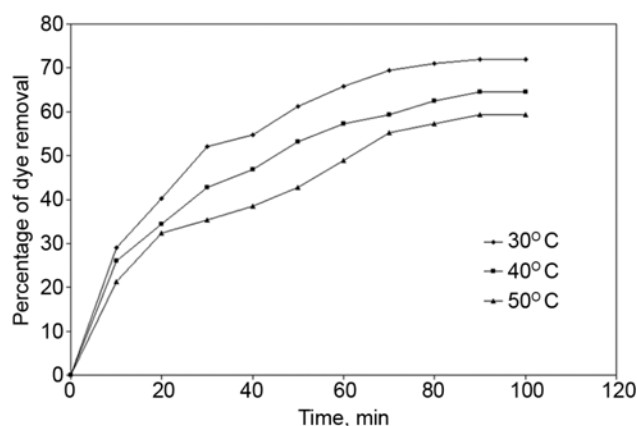The *p*H is one of the most significant factors that control the adsorption process. When the *p*H of the dye solution is increased, the rate of dye adsorption also increases. A *p*H 2.0, the surface of TNJAC becomes positive, that leads to a strong electrostatic repulsion between the adsorbent and the adsorbate. As the *p*H of the solution is increased progressively from 2.0 to 7.0, there is a marginal increase in the dye uptake. When the *p*H exceeds 7.0, the surface of TNJAC becomes negative, that favors the more adsorption of cationic dye molecules (Fig. 4). The adsorption of DO102 was 40.0 % at a *p*H of 2.0 and it rose to 75.0 % at a *p*H of 10.0.

Kinetics of adsorption

Various initial dye concentration and temperature are used to plot the first order kinetic and the results are presented in Table 2. It is observed that the experimental q_e values do not agree with the calculated values at various initial dye concentrations and temperatures. As can be seen from Table 2, the correlation coefficient r^2 is relatively low with for most of the adsorptions. Deviation from the straight line is obtained for the adsorption data achieved for all the levels of temperatures. It is clear that the rapid adsorption occurs well only at initial stages, but it is
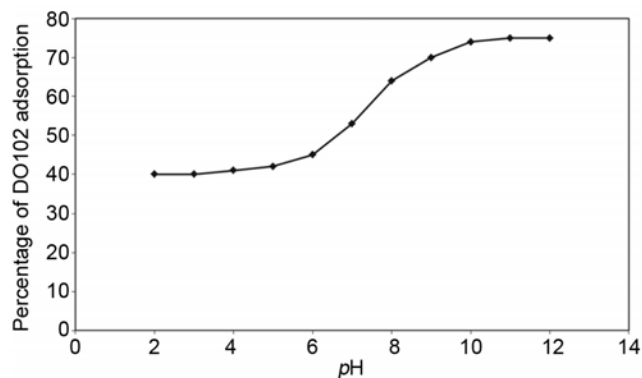

Fig. 3B — Percentage of the removal of DO102 temperature variation

Fig. 4 — Effect of *p*H on the amount of DO102 removed by TNJAC

Table 2 — Calculated kinetic parameters for the adsorption of DO102 onto TNJAC

Parameters	Initial dye concentration (mg/L)			Temperature (°C)		
	50	75	100	30	40	50
$q_e$exp. (mg/g)	37.93	53.91	68.38	53.91	48.44	44.53
Pseudo first order kinetics						
$k_1 \times 10^{-2}$ (min^{-1})	0.0483	0.0437	0.0474	0.0502	0.0386	0.0370
$q_e$cal (mg/g)	36.74	56.91	93.38	66.09	50.78	50.78
r^2	0.9912	0.9665	0.8294	0.9465	0.9697	0.9101
Pseudo second order kinetics						
$k_2 \times 10^{-4}$ (g/mg/min)	24.982	11.745	6.811	11.740	11.380	9.559
h	4.301	4.366	4.290	4.366	3.435	2.539
$q_e$cal (mg/g)	41.49	60.97	79.36	60.97	54.94	51.54
r^2	0.9871	0.9726	0.9500	0.9726	0.9638	0.9311

unsuitable for the entire adsorption process which implies that, the adsorption of DO102 onto TNJAC is unfavorable. Moreover, the reaction does not belong to first-order reaction mechanism. The equilibrium adsorption capacity decreases with temperature, which is just opposite to the experimental q_e which increases with the increase in temperature. This proves that the first order equation does not fit the adsorption process. Hence pseudo-second order kinetic model is best suited at various concentrations and temperatures for the adsorption of DO102 onto TNJAC.

The initial sorption rate (h) exhibits non-linear relationship with the increase in the concentration and the temperature. It is noted that the pseudo second order rate constant (k_2) gets decreased with the increase in concentration: k_2 is found to increase initially, but it gets decreased with the increase in temperature. Both the adsorption capacity q_e and the experimental q_e are similar to each other with the use of pseudo-second order model. It is clear that the high adsorption DO102 by TNJAC is obtained by pseudo-second order kinetics with a high correlation coefficient (r^2). There is a fall in the value of pseudo-second order rate constant (k_2) from 24.982×10^{-4} to 6.811×10^{4} g/mg/min on decreasing the concentration. The value also increased from 11.740×10^{-4} to 9.599×10^{-4} g/mg/min for the range of temperatures considered.

Isotherm studies

Adsorption isotherms are obtained at 30, 40 and 50°C. The results Langmuir plot at different temperatures (Figure not shown) are given in table 3. The Langmuir adsorption capacity increases from 9.442 to 33.00 mg/g on increasing the temperature from 30 to 50°. The Langmuir monolayer adsorption capacity TNJAC is found to be equivalent to that of the other exciting adsorbents. It is evident that

TNJAC is quite effective in the adsorption of DO102 from the effluent

Freundlich plot results are given in Table 3. On increasing temperature from 30 to 40°C, the Freundlich constant (k_f) gets increased from 7.70 to 11.22 mg$^{1-1/n}$ L$^{1/n}$ g^{-1}, but it gets decreased to 1.171 mg$^{1-1/n}$ L$^{1/n}$ g^{-1} at 50°C. The adsorption capacity of the sorbent also gets increased as revealed from the high valve of k_f. The slope 1/n calculates the surface heterogeneity and it becomes more prevalent as 1/n gets closer to zero. For n=1, the partition between the two phases not involve, the concentration. Value for 1/n below 1 reveals a common level of adsorption; moreover, the surface is much heterogeneous with many functional groups to good adsorption. Both Langmuir and Freundlich model demonstrate the effective adsorption of DO102 onto TNJAC. In order to decide which type of isotherm fits the experimental data better, the model is established from the regression co-efficient (r^2). Langmuir model is more appropriate to explain the nature of adsorption with r^2 of 0.9899 to 0.9976 while Freundlich model shows poor fit with $r^2 = 0.6724$ to 0.9625.

Thermodynamics of adsorption

The adsorption of DO102 onto TNJAC is represented with Van't Hoff plot as given in Fig. 5 and the resultant values are presented in Table 4. Based on enthalpy, the physisorption and chemisorption of the adsorbent can be identified to a certain extent. The
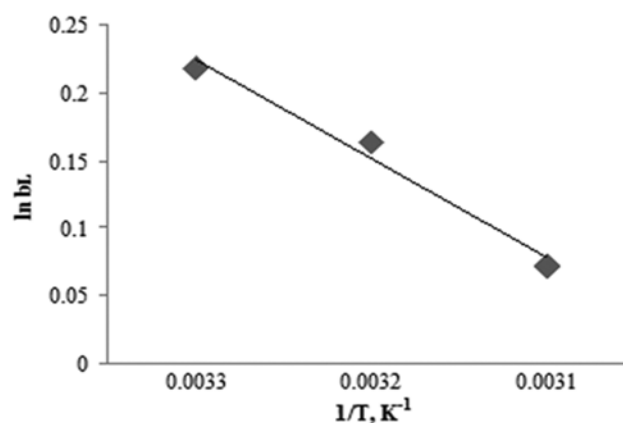

Fig. 5 — Van't Hoff plot for the adsorption of DO102 by TNJAC

Table 3 — Results of isotherm models for the adsorption of DO102 by TNJAC

Parameters	Temperature in (°C)		
	30	40	50
Langmuir isotherm			
Q_0 (mg/g)	9.442	17.54	33.00
$b_L \times 10^{-3}$ (L/mg)	0.2176	3.434	0.0723
r^2	0.9899	0.9976	0.9951
Freundlich isotherm			
n	17.06	10.35	4.24
k_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	7.70	11.22	1.17
r^2	0.9509	0.6724	0.9625

Table 4 — Thermodynamical parameters for the adsorption of DO102 by TNJAC

Temperature (°C)	ΔH° (kJ/mol)	ΔS° (J/mol-K)	ΔG° (kJ/mol)
30			-548.16
40	- 0.599	2.461	-425.21
50			-194.15

enthalpy of adsorption is -0.599 kJ/mol for the DO102 adsorption onto TNJAC. The adsorption DO102 by TNJAC is found to be exothermic as the adsorption rate decreases with increase in temperature. The positive values of $\Delta S°$ indicate that the adsorption is spontaneous in nature and that the degree of random also increases at the solid surface for the adsorption of DO102 onto TNJAC.

The $\Delta G°$ values are found to be negative for the temperatures ranging from 30°C to 50°C revealing that the adsorption of DO102 onto TNJAC is spontaneous and thermodynamically favorable. In other words, the lesser negative $\Delta G°$ implies that the lesser driving force is involved during the adsorption[25,26]. Generally, $\Delta G°$ for chemisorption is greater than that of physisorption; the former is between 0.0 and -20.0 kJ/mol and the latter is between -80.0 and -400 kJ/mol[27]. The values of $\Delta G°$ and $\Delta H°$ suggest that the adsorption of DO102 onto TNJAC is driven by physisorption process.

Desorption studies

The rate of desorption of DO102 gets decreased with the increase in pH from 2 to 8 and there is no considerable change in the desorption which is above pH 8.0 (figure not shown) though all the thermodynamical studies support the physisorption nature. The maximum percentage of desorption observed at pH 2.0 is 45.02% for DO102 from adsorbed TNJAC surface. The bulky dye molecules could have been trapped inside the pores leading to a poor adsorption which substantiates that the pore diffusion mechanism.

Conclusion

The present study proves that the activated carbon from *Thevetia Neriifolia Juss* wood is a suitable adsorbent for the removal of DO102 from aqueous solution. The SEM analysis proves the highly porous and branched carbon network with good amorphous nature. In batch studies, the rate adsorption gets increased with the increase in initial dye concentration and decreased with increases in temperature. The decrease of adsorption with temperature substantiated the exothermic nature of DO102 adsorption on TNJAC surface. The removal of DO102 dye is higher at the basic pH range. The pseudo-second order kinetic model and Langmuir adsorption are found perform better with high correlation coefficient (r^2).

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