

FILM AND PORE DIFFUSION MODELING FOR THE ADSORPTION OF DIRECT RED 81 ON ACTIVATED CARBON PREPARED FROM *BALSAMODENDRON CAUDATUM* WOOD WASTE

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The removal of Direct Red 81 from aqueous solution using low-cost adsorbent such as *Balsamodendron caudatum* wood waste (BAC) under different experimental conditions was investigated in this study. The influences of initial Direct Red 81 concentration (20-60 mg/L), and temperatures (30°, 45° and 60°C) and pH have been reported. Adsorption of Direct Red 81 is highly pH dependent and results indicate that the optimum pH 6.5 for the removal was found to be 98.2 %. A comparison of kinetic models applied to adsorption of Direct Red 81 on the adsorbent was evaluated for pseudo first-order, pseudo second-order and Elovich models, respectively. Results show that the pseudo second order kinetic model was found to correlate the experimental data well.

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1. Introduction

The earliest quality standards for drinking water almost reflect bacteriological aspects of water quality. The amount of waste water generated by textile industries alone works out to be 4,500 million kilo liters annually [1]. Direct Red 81 has been reported to be toxic to animals and humans and it is known to be carcinogenic. Many reports have appeared on the development of lowest activated carbon adsorbents developed from cheaper and readily available materials [2].

Activated carbon with large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for removal of heavy metals from industrial wastewater. The adsorptive properties of active carbon for removal of pollutants are well documented [3]. Adsorption of hazardous soluble chemicals from wastewater in to surface of a solid adsorbent has provided a new dimension to wastewater technology [4]. One of the major challenges associated with adsorption by activated carbon is its cost effectiveness. Hence research of recent past mainly focused on utilizing waste materials as alternatives to activated carbon. Rice husks [5,6], fruit stones [7-9], coconut shells [10,11], fertilizer waste [12,13], fly ash [14,15], peat moss [16,17], ferronia shell [18,19], are some of the waste materials which have been fruitfully tried for this purpose. In this study, the activated carbon prepared from *Balsamodendron caudatum* wood waste activated carbon (BAC) is used to remove Direct Red 81 from aqueous solution using temperature, concentration and pH as parameters.

2. Experimental

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2.1 Adsorbent

Balsamodendron caudatum wood waste material was obtained from various regions of Tirupur District, Tamil Nadu, and India. The study of *Balsamodendron caudatum* wood waste material is used as adsorbent is expected to be economical, environmentally safe and it has practical importance.

To develop adsorbents, the material was first ground and washed with doubly distilled water and then dried. The dried material thus obtained was treated with hydrogen peroxide (30%W/V) at room temperature for about 24 hrs to oxidize the adhering organic matter. The resulting material was thoroughly washed with doubly distilled water and then subjected to the temperature of 120°C for the moisture removal.

One portion of the above material was soaked well with 10% of H₃PO₄ solution for a period of 24 hours. At the end of 24 hrs the excess of H₃PO₄ solution were decanted off and air-dried. Then the materials were 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 of obtained were washed sufficiently with 4N Na₂CO₃ to remove cations. Then the obtained material was washed with plenty of water to remove excess of acid, dried then to desired particle size tight lid container. The material was sieved to desired particle size. A final product obtained was stored separately in a vacuum desiccator until used. The resulting carbon named as BAC.

The N₂ 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. The surface morphologies of activated carbon were observed with SEM (HITACHI S3000N model). The morphological study by SEM of the above adsorbent reveals that it is highly porous in nature.

2.2 Batch adsorption studies

Basic Direct Red 81 was estimated spectrophotometrically using PAR reagent 4-(2-pyridylazo) resorcinol. A suitable aliquot of the sample containing not more than 50 mg of Direct Red 81 was transferred into 25 ml volumetric flask. 10ml of ammonia–ammonium chloride buffer solution was added to provide a pH of 10.0 followed by 1ml of 0.01% solution of PAR reagent. The solution was diluted up to the mark with water. The absorbance was measured at 520 nm against a reagent blank. A calibration graph for 5-50mg of Direct Red 81 was prepared by the above procedure and concentration in the sample aliquot was established by referring to the calibration graph.

The amount of Direct Red 81 adsorbed in mg/L at time t was computed by using the following equation.

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

where, C₀ and C_t are the Direct Red 81 concentration in mg/L initially and a given time t, respectively, V is the volume of the Direct Red 81 solutions in ml and m_s is the weight of the activated carbon.

The percentage of removed Direct Red 81 (R %) in solution was calculated using eqn. (2)

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

The initial concentration of Direct Red 81, pH and temperature was investigated by varying any one parameters and keeping the other parameters constant.

2.3 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 81 adsorption on the activated carbon were analyzed using pseudo first order [20], pseudo second order [21], Elovich [22] and intra particle diffusion [23], kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (r^2 values closer or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of Direct Red 81 adsorption.

2.4 The pseudo first – order equation

The pseudo first - order equation [20] is generally expressed as follows.

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

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 (l min^{-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.

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

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.

2.4.1 The pseudo second – order equation.

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

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

Where, k_2 is the rate constant of pseudo second order adsorption ($\text{g. mg}^{-1}. \text{min}^{-1}$). 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.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (6)$$

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.

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

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

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

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

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

The plot of (t/q_t) and t of equation (7) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

2.4.2 The Elovich equation

The Elovich model equation is generally expressed [22] as

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (10)$$

Where, α is the initial adsorption rate ($\text{mg.g}^{-1} \text{min}^{-1}$), β is the adsorption constant (g. mg^{-1}) during any one experiment.

To simplify the Elovich equation, assumed $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq (10) becomes;

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\ln t} \quad (11)$$

If Direct Red 81 adsorption fits the Elovich model a plot of q_t vs $\ln t$ should yield a linear relationship with slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha \beta)$

2.4.3 The intra particle diffusion model

The intra particle diffusion model is expressed [23] as

$$R = K_{id}(t)^a \quad (12)$$

A linear form of equation is followed by

$$\log R = \log k_{id} + a \log(t) \quad (13)$$

Where, R is the percent Direct Red 81 adsorbed, a is the gradient of linear plots, t is the contact time (h), k_{id} is the intraparticle diffusion rate constant (h^{-1}), a depicts the adsorption mechanism, k_{id} may be taken as rate factor, i.e., percent Direct Red 81 adsorbed per unit time.

The values of k_{id} were calculated from the slope of such plots (plots not shown here) and the r^2 values led to the conclusion that the intraparticle diffusion process is the rate-limiting step. Higher values of k_{id} illustrate a better adsorption mechanism which is related to an improved bonding between Direct Red 81 and adsorbent particles table (2).

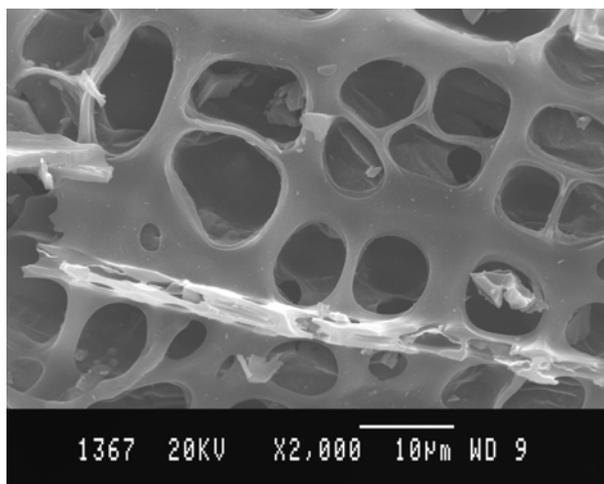
3. Results and discussion

3.1. Characterization of adsorbent

From the SEM results, it was found that there are holes and cave type openings on the surface of the specimen that would definitely have increased the surface that are available for the adsorption [24]. Shifts in adsorption position may be caused by factors such as intramolecular and

intermolecular hydrogen bonding, steric effect and degree of conjugation. For instance, within its given range, the position of C=O stretching band (common to carbonyls, carboxylic acids and lactones) is determined by many factors, such as:

1. The physical state
2. Electronic and mass effects of neighboring substituents
3. Conjugation
4. Hydrogen bonding and
5. Ring strain [25].



Scanning Electron Microscopic image of Balsamodendron caudatum wood waste activated carbon (BAC)

The FT-IR absorption bands of oxygen groups on the surface of activated carbon prepared using by various processes are likely to be affected by some or all of the factors listed above.

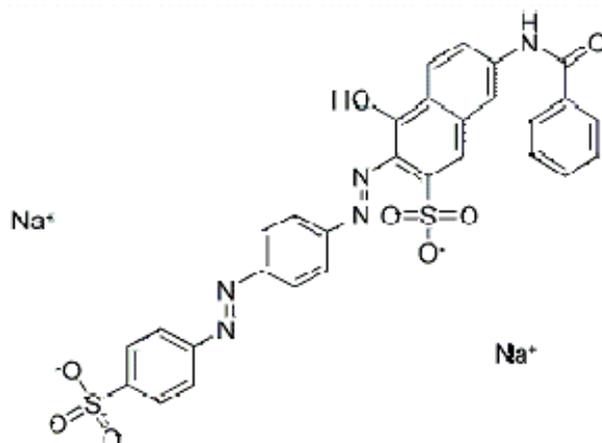
Most of the carbons exhibit similar IR spectroscopic features, that is a very intense / sharp H-bonded –OH stretching of carboxyl, phenol chelated and alcohols vibration from 3600 – 3000 cm^{-1} and aliphatic C-H stretching absorption from 2750 to 3000 cm^{-1} .

Saturated aliphatic ethers show a strong band in the region 1070 to 1150 cm^{-1} for asymmetric C-O-C stretching. Esters, aldehydes, ketones, lactones, quinonoid carbonyl groups, chromene structure etc., shows a broad band in the region 1650 to 1900 cm^{-1} due to C=O stretching. The group of bands appeared in the region 1420 to 1460 cm^{-1} corresponding to C-H def is characteristic of alkyl group provided, it is not under some electrical influence. The broad band observed in the spectrum of OH derivatives between 1000 to 1250 cm^{-1} was assigned due to a characteristic absorption of -C-OH group. These results are in good agreement with the findings of many investigators [26, 27]. Characteristics of the carbon were presented in Table 1.

Table 1. Characteristics of the Activated Carbon BAC.

Parameter	BAC
Bulk density (g/ml)	0.45
Ash content (%)	2.06
pH	6.5
Moisture content (%)	6.17
Surface area (m^2/g)	458
Solubility in water (%)	0.80
Solubility in 0.25M HCl (%)	1.16
Decolorizing power (mg/g)	40.3
Iodine number (mg/g)	212

Structure of Direct Red 81



3.2 Adsorption studies

Effect of pH

The adsorption behavior of the Direct Red 81 on the adsorbent was studied over a wide pH range of 2.0 -10.0 Fig.1 depicts that the pH significantly affects the extent of adsorption of Direct Red 81 over the adsorbent and a reduction the amount adsorbed with increasing pH was observed. Fig.1 also specifies that maximum up take of the Direct Red 81 (20 mg/L) is observed at pH 6.5 on BAC. The percentage of amount of dye adsorbed then increases up to pH 6.5 for BAC. After this pH it remains almost constant in cases. Thus, all further studies were carried out at pH 6.5 in (BAC) adsorbent.

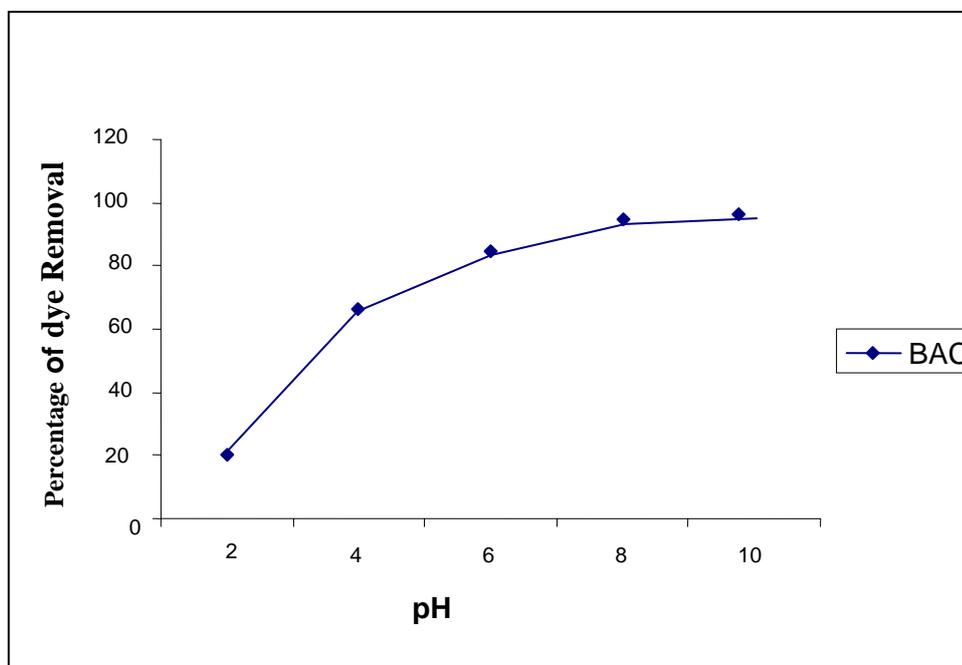


Fig .1. Effect of of pH on percentage of removal of Direct Red 81 by BAC.

The variation in the removal of Direct Red 81 with respect to pH can be elucidated by considering the surface change of the adsorbent materials. The higher adsorption of the dye on

each adsorbent at low pH may result due to the neutralization of the negative charge at the surface of the adsorbents, there by increasing the protonation. This facilitates diffusion and provides more of the active surface of adsorbents resulting there by enhanced adsorption at their surface. A constant fall in the amount adsorbed with increasing pH may be due to deprotonation, which hinders the diffusion.

Effect of concentration

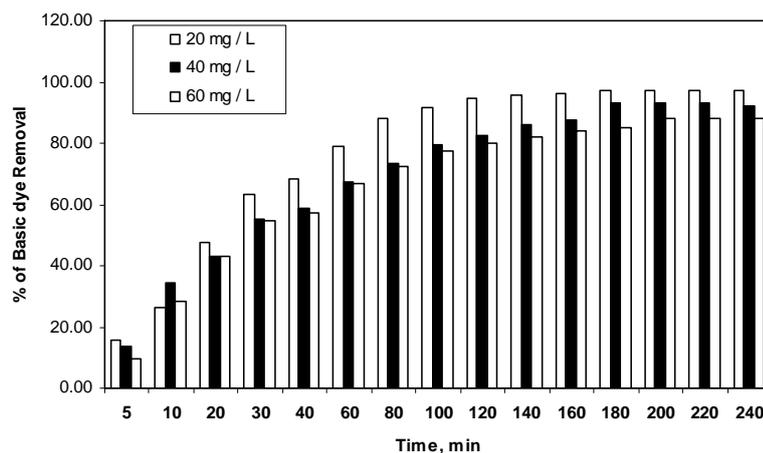


Fig .2. Effect of concentration on adsorption of Direct Red 81 over BAC at different temperatures (pH6.5), adsorbent dosage.0.2g

The adsorption process for the Direct Red 81 – BAC system was investigated at concentrations ranging from 20 to 60 mg/L was selected at a fixed pH and at different temperature (30, 45 and 60 °C)

Figure 2 clearly reveals the extend of adsorption of dye on adsorbent increases linearly with decrease in concentration of the Direct Red 81 – BAC system. The adsorption also increases with in increase the temperature.

Effect of temperature

An analysis of the data in (Table 2) reveals that the influence of temperature of the Direct Red 81- BAC (20mg/L) has very little influence on the Lagergren and first order reversible rate constants. The table 2 also reveals that the influence of the temperature of on Elovich and pseudo-second order rate constant is neither appreciable nor little.

Table 2. The adsorption kinetic model rate constants for BAC at different Temperature

Adsorbent	Initial Temperature	Pseudo first order		Pseudo Second order			Elorich Model			Intra particle diffusion		
		k_1 $l\ min^{-1}$	r^2	k_2 $g\ mg^{-1}\ min^{-1}$	h $mg\ g^{-1}\ min^{-1}$	r^2	$\beta\ g\ min^{-1}$	α $mg\ g^{-1}\ min^{-1}$	r^2	k_{id} $mg / g\ min^{-0.5}$	a	r^2
BAC	30 ⁰	0.213	0.996	0.0051	10.540	0.999	31.801	0.117	0.967	27.611	0.421	0.981
	45 ⁰	0.114	0.963	5.401	5.811	0.998	13.964	0.136	0.974	16.933	0.451	0.983
	60 ⁰	9.131	0.811	1.57	1.445	0.991	2.52	0.231	0.963	4.23	0.563	0.987

It is obvious that the adsorption of Direct Red 81 on the *Balsamodendron caudatum* wood waste activated carbon is best described by Pseudo second -order order rate equation .Results also show that the adsorption reaction can be approximated with Pseudo second –order model. The smallest value of correlation coefficient was > 0.991 (Table 2).The rate constants are represented in (Table 2).

4. Conclusions

Removal of Direct Red 81 from aqueous solution was possible using several abundantly available low cost adsorbents. The adsorption of Direct Red 81 was found to be dependent on pH, temperature, adsorbent dose and concentration for the adsorbent. Thermodynamic parameters obtained for the adsorbent accounts for feasibility of the process at each concentration. Further the kinetic studies apparently reveal that the removal takes through a film diffusion process at all the concentrations and temperature for BAC. The percentage saturation was found to be almost 98.2 % for the BAC respectively. Thus, it is safe to conclude that the waste material can be used as adsorbent. Direct Red 81 exist mostly as the most easily adsorbed form, increases as the initial Direct Red 81 concentration and temperature were found to increase the percentage removal of Direct Red 81. The kinetics of Direct Red 81 adsorption on adsorbent was found to follow a pseudo second -order rate equation.

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