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KINETICS, EQUILIBRIUM AND ISOTHERMS OF DIRECT RED 81 REMOVAL FROM AQUEOUS SOLUTION USING *BALSAMODENDRON CAUDATUM* WOOD WASTE ACTIVATED NANOPOROUS CARBON

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ABSTRACT
The sorption capability of *Balsamodendron caudatum* wood waste relative to Direct red 81 was evaluated to test its application in textile waste water management. *Balsamodendron caudatum* wood waste activated nano porous carbon material (BANC) was treated using sulphuric acid to pick up sorption capacity for the removal of Direct red 81(C.I. No 28160) from aqueous solution. The treated (BANC) using sulphuric acid was evaluated through SEM XRD and FT-IR. Present study deals with the use of BANC waste as adsorbent for the removal of Direct red 81 dye from its aqueous solutions. The studies indicate that sorption is powered by initial dye concentration, dye solution pH and adsorption temperature have been investigated in the present study. Isotherms for the sorption of Direct red 81 on (BANC) were analyzed by the Freundlich and Langmuir isotherm equations. A Kinetic study of dye followed the pseudo-first-order, pseudo second-order and Elovich models respectively. Consequences show that the pseudo first order kinetic model was established to compare the investigational report well.
Keywords*:* Sorption, Directred 81, Kinetics; Low-cost adsorbents, Aqueous solution.

INTRODUCTION

The earliest quality standards for drinking water deal almost exclusively with bacteriological aspects of water quality, the majority of chemical constituents being discussed only in relation to aesthetic properties. Although there was concern over the possibility of harmful health effects associated with water constituents developed with organomercury compounds[1].The contamination of water with Cadmium in relation to 'Ouch-ouch' disease in the Toyoma region[2]. In the last three decades, national and international bodies responsible for public health have become increasingly anxious about trace constituents of food and water and their
possible harmful effects on health. Although the discussion on long term health risks associated with drinking water centers on organic micro pollutants, there are several inorganic constituents that have been the subject of concern. In any part of the world nitrate level has been increasing (due to extensive application of nitrogenous fertilizers) particularly in ground water and possibility of carcinogenicity hazard due to endogenous synthesis of N-nitroso compounds has been referred[3]. It has been reported that high fluoride level in water can cause cancer also been reported[4].There has also been evidence of relationship between arsenic levels in water and incidence of skin cancer[5].Activated nano porous carbon is expensive and its regeneration and reuse make it more costly[6]. However, in view of the high cost and associated problems of regeneration, there is a constant search for alternate low cost adsorbents. Such types of adsorbents include pine tree leaves[7], bagasse fly ash[8], rice husk ash[9], agricultural waste and

timber industry waste carbons for the removal of various dyes from wastewaters[10].Critical review of low cost adsorbents for wastewater treatmenthas been presented by earlier researchers[11].

EXPERIMENTAL

Adsorbent

Balsamodendron caudatum wood waste was obtained from various regions of Coimbatore & Tirupur Districts, Tamil Nadu, and India. The study of *Balsamodendron caudatum* wood waste material is used as sorbent is expected to be inexpensive, environmentally safe and it has practical importance. To develop sorbents, the material was first ground and washed with distilled water and then dried. The dried material thus obtained was treated with hydrogen peroxide (40%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 H_2SO_4 solution for a period of 24 hours. At the end of 24 hrs the excess of H_2SO_4 solution were decanted off and air-dried. Then the materials were placed in the muffle furnace carbonized at 120-130°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 obtained carbon was washed sufficiently with large volume of water to remove free acid. Then obtained material was washed with plenty of water to remove excess of acid, dried then to desired particle size. The resulting carbon named as BANC.

Preparation of aqueous dye solution

The stock solutions of the dye (1000 ppm) were prepared by dissolving 1 g of dye in one litre of water without any more treatment, which were kept in dark colored glass bottles. For batch study, an aqueous solution of this dye was prepared from stock solutions in deionized water. NaOH and HCl solutions were used as buffers for pH studies.

Table -1: Individuality of the dye used

Class	Sample	General name	C.I. No.	$\lambda_{max\ nm}$	Fw
Direct	DR81	Direct Red 81	28160	508	675.61

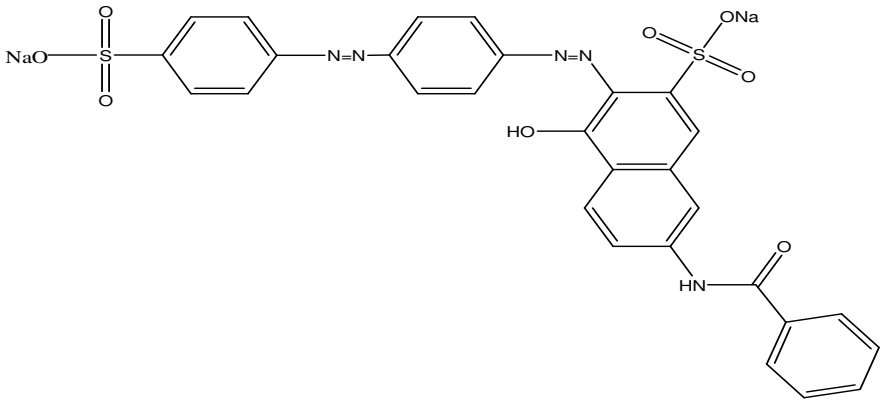

Fig.-1: Structure of Direct Red 81

The pseudo first – order equation

The pseudo first - order equation[12] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

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}).

The Pseudo Second – Order Equation

The pseudo second – order adsorption kinetic rate equation is expressed as-[13]

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

Where, k_2 is the rate constant of pseudo second order adsorption (g. mg^{-1}. min^{-1}). Where, k_2 is the rate constant of pseudo second order adsorption (g. mg^{-1}. min^{-1}). If the initial adsorption rate h (mg g^{-1} min^{-1}) is-

$$h = k_2 q_e^2 \quad (3)$$

The Elovich Equation

The Elovich model equation is normally expressed[14]as-

$$\frac{dq_t}{d_t} = \alpha \exp(-\beta q_t) \quad (4)$$

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

RESULTS AND DISCUSSION

Characterization of adsorbent

The surface area of the BANC was calculated through N_2 adsorption at 77K using a NOVA1000, Quanta chrome company. The pH of BANC was measured by a PHS-3C pH meter. pH of zero charge (pHpzc) of the samples was resolute using pH drift method [15]. The surface area of the BANC obtained from the N_2 equilibrium adsorption isotherms was found to be 760 m^2/g. The results of "pH drift" test, from which the pHpzc of BANC studied in this test was found to be 4.5.The better color removal of the dye, Direct red 81, was observed at pH of 6.5.

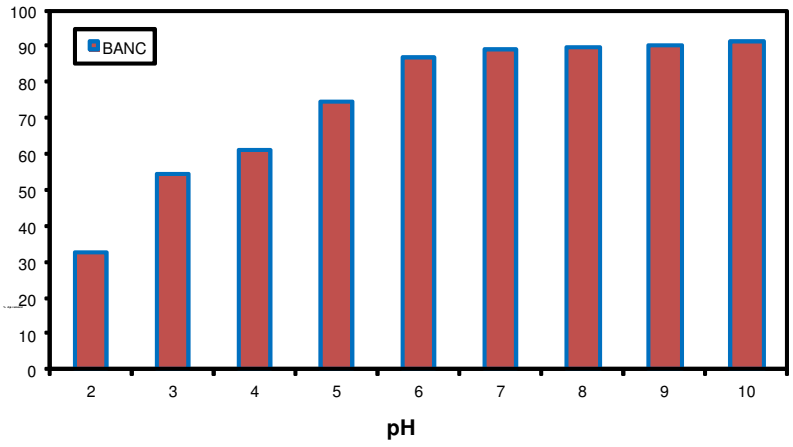

Fig. - 2: Effect of of pH on % of removal of Direct red 81 by BANC

Impact of pH

From the set of experiments conducted to find the effect of pH on sorption phenomenon, it was observed that pH influences BANC surface dye binding sites and the dye chemistry in water. Figure 2 show the quantity of dye removed, using acid activated sorbent at initial pH value. In this experiment, the initial dye concentration was fixed at 20 ppm. From the shake flask experiments, better color removal of the dye, Direct red 81, was observed at pH of 6.5 .The uptake of Direct red 81was establish to be optimal at pH 6.5 with the utmost dye uptake of 89 %. As the surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye and the surfaces of sorbent is reduced, this causes more sorption [16]. At pH above pH_{zpc}, the surface of adsorbent may acquire a negative charge leading to an increased cationic dye adsorption, due to electrostatic attraction.

Impact of concentration

The batch adsorption experiments were carried out by using three different concentrations of dye viz. 20mg/L, 40mg/L and 60mg/L at pH 6.5 at the reaction temperature of 30 °C were selected for adsorbent. The rate of agitation was maintained constant at 200 rpm. The color fall profiles were obtained using the absorbance measurements.

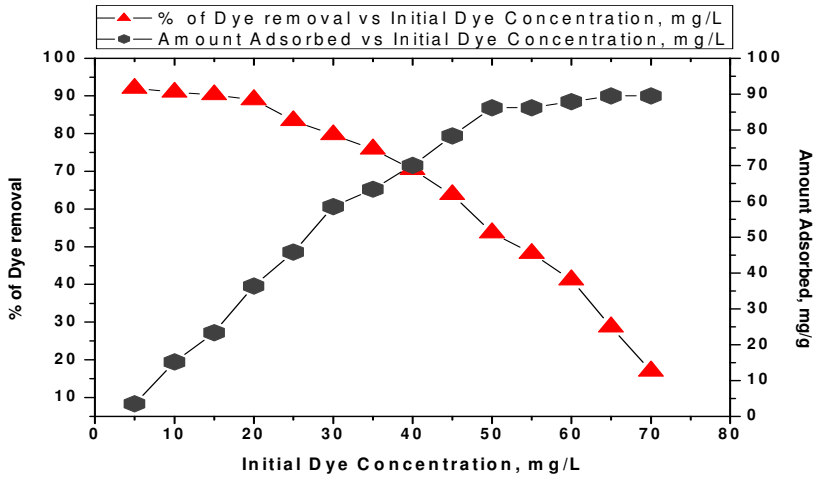

Fig. - 3: Effect of concentration on adsorption of Direct red 81 on BANC at pH 6.5.

SEM analysis

The morphological study by SEM of the adsorbent shown in the Figure 4 exposed that, it is extremely porous in nature. From the SEM results, it was found that there are identical holes and cave type openings on the surface of the sample that would absolutely have greater than before the surface area [17].

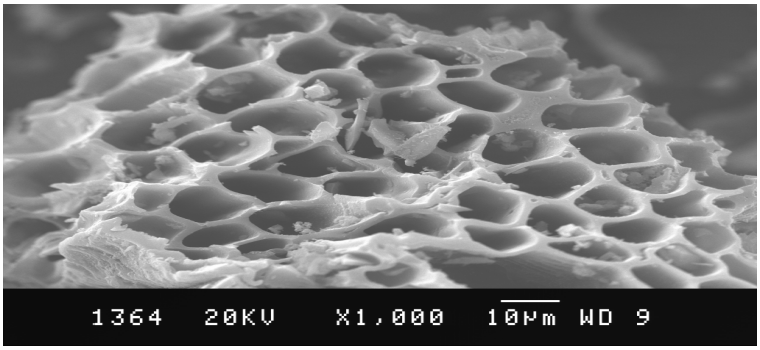

Fig.-4: SEM analysis for BANC

XRD analysis

Figure-5 shows the wide angle XRD pattern for nano porous carbon sample. The XRD analysis of nano porous carbon proved that the carbon prepared by acid treatment shows the X-ray diffraction angle 2Θ = 23 it is similar to the reported graphitization wood waste [18].

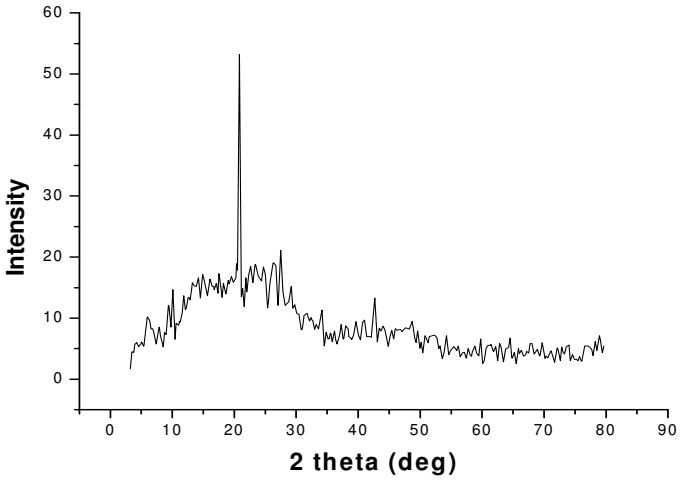

Fig. - 5: XRD pattern for BANC

FT-IR analysis

The FT-IR spectrum of the *Balsamodendron caudatum* wood waste activated nano porous carbon prepared by a range of treatment processes shown in the Figure 6 revealed that the carbons evaluated contain four classes of surface groups: carboxyls, lactones, phenols and carbonyls. The task of the exact wave number to a given functional group was not possible because the sorption bands of different functional groups overlap and shift depending on their molecular structure and environment. Shifts in absorption position may be caused by factors such as intramolecular and intermolecular hydrogen bonding, steric effect and degree of-conjugation[19,20].

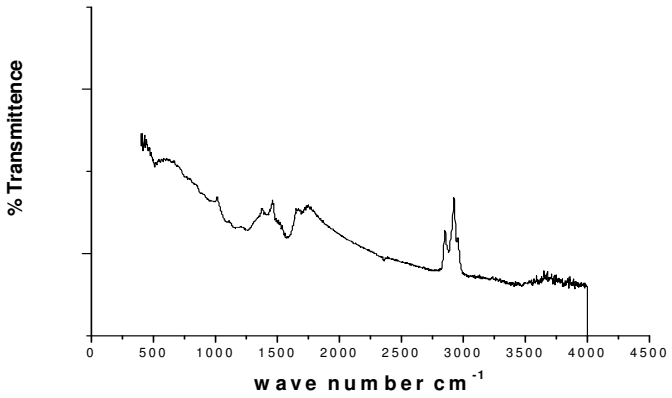

Fig.-6: FTIR Spectra for BANC

Impact of Temperature on Kinetic Rate Constant and Rate Parameters

Sorption experiment was conceded out with fixed initial dye concentration (20mg/L) at pH 6.5 and at various temperatures viz. 30 °C, 45 °C and 60 °C. The investigation of the data in (Table 1) reveals that

the influence of temperature of the dye has very little influence on the pseudo second order rate constants. The table 2 also reveals that the influence of the temperature of dye on Elovich and pseudo first order rate constant is neither considerable nor small. It is obvious that the sorption of dye on the BANC waste activated carbon is best described by first order rate equation with regression coefficient value is larger than 0.98.

Table- 2: The sorption kinetic model rate constants for banc various temperature

Adsorbent	Initial Temperature	Pseudo first order		Pseudo Second order			Elorich Model		
		k_1 $l\,min^{-1}$	r^2	k_2 $g\,mg^{-1}\,min^{-1}$	h $mg_1\,g^{-}$	r^2	β $g\,min^{-1}$	α $mg\,g^{-1}\,min^{-1}$	r^2
BANC	30^0C	0.0185	0.9265	0.00257	0.4791	0.9913	0.1944	0.5899	0.9844
	45^0C	0.0072	0.8366	0.0451	5.4520	0.4513	0.1927	0.6280	0.9817
	60^0C	0.0343	0.6546	0.0323	0.1155	0.6352	0.4944	0.4328	0.9716

Isotherms

The Langmuir, Freundlich isotherms are the most regularly used two parameter models in the literature relating the non-linear equilibrium between amount of dye adsorbed on the acid treated (BANC) (q_e) and equilibrium concentration of solution (*Ce)* at a constant temperature (30°C). The Langmuir equation, which is valid for monolayer sorption onto a uniform surface with a finite number of identical sites.

Langmuir Model

The Langmuir model was developed based on the hypothesis of the formation of a monolayer of the sorbate species onto the surface of the particle of the sorbent. It has also been assumed that the surface sites are completely actively homogeneous. But in the true sense, the sorbent surface is energetically heterogeneous[21]. The study of the Langmuir isotherms is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing the operating conditions for effective sorption. In this respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well documented. This model is the most widely used two-parameter equation, generally expressed in the form by the following equation-

$$\frac{1}{q_e} = \frac{1}{Q_o K_L}. + \frac{C_e}{Q_o} \qquad (5)$$

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)
K_L = direct measure of the intensity of the sorption (L / mg)

Ce/qe was plotted against Ce using linear regression examination, as shown in Figure 7. The constants Q_0 and K_L were determined from the intercept and slope of the linear plots, respectively. As shown in Table 4, the Qo from the Langmuir isotherm were 147.05mg/g for Direct red 81. The values of K_L it could be concluded that sorptions of acid dye (K_L = 0.08825). The essential characteristic of Langmuir equation can be uttered in terms of a dimensionless separation factor R_L[22].The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless parameter, R_L, which is defined by R_L =

$1/1+ bC_0$, where, C_0 is the initial dye concentration (mg/L) and b is the Langmuir constant (L/mg). The parameter indicates the form of isotherm as given in Table-3.

Table -3: Parameters for types of Isotherm

R_L	Type of isotherm
$R_L > 1$	Unfavorable
RL = 1	Linear
0 < RL < 1	Favorable
RL = 0	Irreversible

In the present research work, the investigator aims at shaping how well the Langmuir model can be applied to the chosen sorbate –sorbent system.

$R_L = (1/1+K_LC_0)$ (6)

Table- 4: Equilibrium isotherm constants at 30°c.

Freundlich isotherm			Langmuir isotherm		
K_f(mg/g)	1/n	R^2	K_L l/mg	q_o mg/g	R^2
5.0354	0.5789	0.9972	0.08825	147.05	0.9933

Where,

C_0 = (mg /L) is the initial dye concentration.

R_L= the nature of the adsorption process.

The calculated R_L values of acid dye is found to be between 0.3868, 0.3395 and 0.3471 for dye concentrations viz. 20 mg/L, 40 mg/L and 60 mg/L, respectively (data not shown). The magnitude of the R_L values, i.e., $0 < R_L < 1$, indicated the favorable sorption of each of the dye under deliberation.

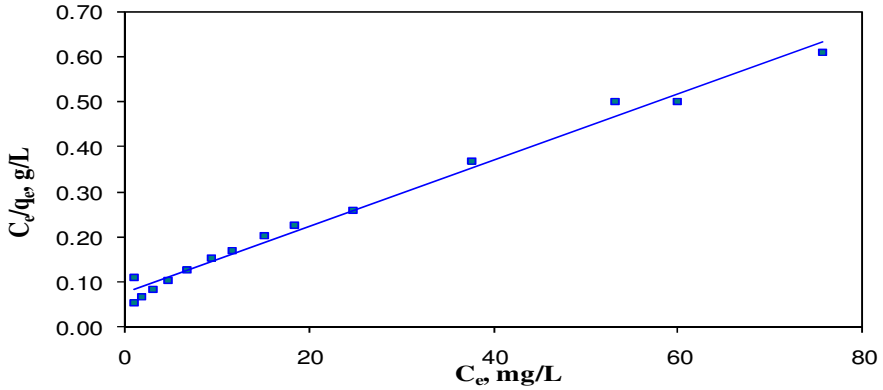

Fig.-7: Langmuir plot for Direct red 81 absorption onto BANC. M, 100 mg; V, 50 ml; C_0, 20 mg/L; pH, 6.5; temperature, 30°C).

Freundlich Model

At Equilibrium conditions, the adsorbed amount, q_e can also be predicted by using the Freundlich equation[23].

$$q_e = k_f C_e^{1/n} \quad (7)$$

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-

$$\log q_e = \log k_f + (1/n) \log C_e \quad (8)$$

The values of n and k_f were resolute from the plot log C_e v_s log q_e .Where, k_f is the suggestion of the sorbent 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. The Freundlich equation predicts that the dye concentration on the adsorbent will rise so long as there is an enlarge in the dye concentration in the liquid. The experimental evidence indicates that an isotherm is reached at a limiting value of the solid phase concentration. The equation itself does not have any real physical significance. Freundlich isotherm fitted well to the data with correlation coefficient value 0.9972. The designed Freundlich isotherm constants at 30°C are as shown in Table 4. The value of Freundlich exponent n = 1.7275 lying in the range of 1 - 10, indicate favorable adsorption.

CONCLUSIONS

Sorption of Direct red 81 dye on the BANC was establish to be dependent on the pH, (The optimal pH of Direct red 81 was 6.5), temperature and concentration for sorbent. Sorption equilibriums were reached within 220 min contact time for Direct red 81 dye used in this test. The percentage saturation was found to be almost 89% for the BANC respectively. The kinetics of Direct red 81 adsorption on adsorbent was found to follow a pseudo first-order rate equation. The adsorbent was employed to adsorb Direct red 81 from aqueous solution openly and showed high removal competence at suitable conditions, indicating that the secondary adsorption was an efficient and inexpensive way for reuse of the used sorbents. An equilibrium isotherm for the sorption of Direct red 81 on BANC was analyzed by the Freundlich, and Langmuir isotherm equations. Final result showed that the Freundlich isotherm best-fit the Direct red 81 sorption.

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