Thermodynamic, kinetic, and isothermal modelling of acid orange 17 sorption onto activated carbon made from Balsamo dendron caudatum wood waste

Dr.RAMACHANDRA C G

[1*&2] Department of Chemistry, Coimbatore Institute of Engineering and Technology, Narasipuram,
Coimbatore, 641109, Tamil Nadu, India.

Authors to whom all Correspondence should be addressed.

Abstract

The wood waste activated carbon from Balsamodendron caudatum (BAC) can absorb dyes from aqueous solutions. Dye improper disposal in wastewater creates environmental issues and has the potential to harm ecosystems. The current study focuses on using BAC waste as an adsorbent to remove Acid Orange 17 dye from its aqueous solutions. The results of the inquiry show that the initial dye concentration, contact time, pH of the dye solution, and thermodynamic parameters including free energy, enthalpy, entropy, and adsorption temperature all have an impact on adsorption. The Elovich, pseudo-second-order, and pseudo-first-order models were followed, correspondingly, by a kinetic analysis of dye. The Freundlich method was used to examine the equilibrium isotherms for the adsorption of Acid Orange 17 on BAC.

Keywords: BAC; Adsorption; Acid Orange 17; kinetics; isotherm; low-cost adsorbents; aqueous solution.

Introduction

Water is essential to all living organisms. It functions as a participant, catalyst, or mediator in all chemical reactions that occur in our environment. Nature regulates not only the physico-chemical properties of its living populations, but also their amount and variety through a multitude of regulatory systems. No matter where it came from, it always contains a complex mixture of both inorganic and organic components, most of which are the result of intricate interactions between underlying geological conditions, water, and soil. biological and microbiological processes that take place in soil and water. Other often found materials include algae, protozoa, suspended and colloidal mineral particles, and plant debris. Its activated carbon's enormous surface area, microporous structure, and chemical composition Summary.

They are prospective adsorbents for the removal of colors from industrial effluent because water is essential to their surface. It is commonly known that active carbon has the ability to absorb contaminants and remove them from the environment (Macias et al., 1993). Wastewater technology has gained a new dimension through the adsorption of hazardous soluble compounds from wastewater onto the surface of a solid adsorbent (Benefield et al., 1982). The cost-effectiveness of activated carbon adsorption is one of the main problems. Therefore, the majority of current research has been on using waste materials as activated carbon substitutes. Fly ash (Sell et al., 1994), peat moss (Allan and McKay 2001; Chen et al., 2001), bamboo (Ahmad et al., 2009), sugar cane bagasse ash (Kanawade et al., 2011), bone char (Alvin et al., 2010), jujuba seeds (Somasekhara Reddy et al., 2012), fly ash (Sell et al., 1994), peat moss (Allen and McKay 2001; Chen et al., 2001), ipomoea carnia stem waste (Karthikeyan et al., 2007), potatoes and egg husk (Hila et al., 2012), coconut shell (Bangfu_Huangeand et al., 2024) adsorption-membrane (Jemal Fito Nure et al., 2023) , (Bangfu_Huangeand et al., 2024) adsorption-membrane (Jemal Fito Nure et al., 2022) paper (Mengxiao Zhao et al., 2022) , metal nanoparticlesother (James dean et al., 2019) , waste materials have been successfully tried for this purpose.

1 Experiment

1.1 Adsorbent

Waste wood from Balsam dendron caudatum was collected from different areas in the Tamil Nadu districts of Erode and Tirupur. It is anticipated that the study of Balsamo dendron caudatum wood waste material utilized as an adsorbent will be affordable, safe for the environment, and useful. The material was first pulverized, rinsed with double-distilled water, then dried in order to create adsorbents. After that, the dry material was treated with 30% W/V hydrogen peroxide at ried to the appropriate particle size after being thoroughly cleaned with water to get rid of extra acid.

For a full day, a section of the material mentioned above was thoroughly immersed in H_2 SO_4 solution. The extra H_2 SO_4 solution was decanted off and allowed to air dry after the whole day. Subsequently, the materials were carbonized at 120–130°C in a muffle furnace. After being dehydrated, the materials were ground into a powder and heated to 800°C for 60 minutes in a muffle furnace. Following activation, the carbon in the result was thoroughly cleaned with a lot of water to get rid of any free acid. Then, the material was dried to the appropriate size using a lot of water to get rid of any remaining acid. The carbon that is produced is called BAC.

1.2 Preparation of aqueous dye solution

The International Color Index (1998) presents Table 1. The corresponding structure is depicted in Figure 1. The details of the dye employed and its qualities are described in Table 1. Without any additional processing, one litre of water was used to dissolve one gram of the relevant dye to create the stock solutions (1000 mg/L), which were then stored in glass bottles with a dark hue. An aqueous solution of this dye was made using stock solutions in deionized water for the batch research. Solutions of HCl and NaOH were utilized as buffers for pH investigations.

Table 1 Characteristics of the dye used

Class	Sample	Generic name	C.I. No.	$\lambda_{\max\ nm}$	Fw
Acid	AO7	Acid Orange17	16020	388	378.38

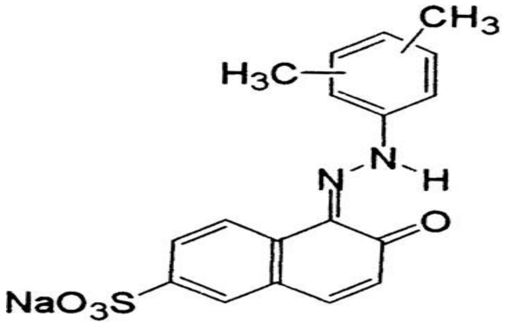

Fig. 1 Structure of Acid Orange 17

1.3 Amount of dye adsorbed

The method used to find the Amount of dye adsorbed, Q_e , was as revealed below:

$$Q_e = \frac{C_0 - C}{M} \times \mathrm{V} \tag{1}$$

Q_e (mg/g) is the amount of dye adsorbed at equilibrium, V (L), is the volume of the solution dye, C_o (mg/L) is the initial dye concentration, C (mg/L) is the dye concentration at any time and M (g) is the adsorbent dosage.

The proportion of detached anionic dye (R %) in solution was calculated using eqn. (2)

$$\%\ \text{Removal} = \frac{C_0 - C_t}{C_0} \times 100 \tag{2}$$

The initial attentiveness of Acid Orange 17 pH and temperature was examined by varying any one parameters and possession the other limitations constant

1.4 The pseudo first – order equation

The pseudo first - order calculation (Lagergren 1898) is generally spoken as follows.

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

where,

q_e and q_t are the sorption volume 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 incorporation 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 relationship from which k_1 and q_e can be resolute from the slope and intercept of the plot, individually.

1.5 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.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_t \tag{6}$$

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.

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

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

$$h = k_2 q_e^2 \tag{8}$$

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

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

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 gritty form the slope and intercept of the plot, respectively.

1.6 The Elovich equation

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

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

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

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

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

If Acid Orange 17 adsorption fits the Elovich model a plot of qt vs ln t should yield a linear association with slope of (1/β) and an intercept of (1/β) In (α β)

2 Results and discussion

2.1 Characterization of adsorbent

Physico-chemical categorizations of the adsorbents were presented in Table 2.

Table 2 Characteristics of the Activated Carbon BAC

Parameter	**BAC**
pH	6.5
Surface area (m^2/g)	458
pH_{zpc}	4.2

N2 adsorption at 77K was used to measure the BAC's surface area using a NOVA1000 from Quanta Chrome Corporation. A PHS-3C pH meter was used to determine the pH of BAC. Using the pH drift method, the samples' pH of zero charge (pHpzc) was ascertained (Fariaa et al., 2004). Based on the N2 equilibrium adsorption isotherms, the surface area of the BAC was determined to be 458 m2/g. The pHpzc of the BAC under investigation in this test was discovered to be 4.2 based on the findings of the "pH drift" experiment.

2.2 Effect of pH

The set of tests designed to determine how pH affects the adsorption phenomenon revealed that pH has an impact on the dye chemistry in water as well as the BAC surface dye binding sites. The amount of dye adsorbed at the initial pH value using an acid-activated absorbent is depicted in Figure 1. The starting dye concentration in this experiment was set at 20 mg/L. Better color removal of the dye, Acid Orange 7, was noted at pH 6.5 in the shake flask studies. With a maximum dye uptake of 81.6 mg/g, pH 6.5 was shown to be the ideal level for Acid Orange 7 uptake. A tendency of declining qe values was noted in the pH range of 5.5 to 8.0. The qe values were discovered to be identical to reduction in the pH alkaline range of 7.0–10.1. Reported outcomes are comparable (Low et al. 1995).

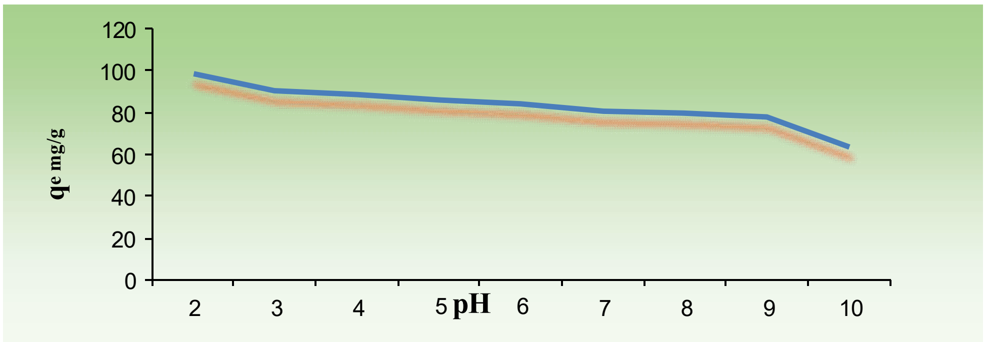

Fig. 2 Impact of pH on equilibrium uptake of Acid Orange 17 sorption onto BAC. M, 100 mg; V, 50 ml; C_0 20 mg/L; temperature, 30°C).

2.3 Effect of adsorbent dosage

By agitating 50 ml of a 20 mg/L dye solution with 100 mg of sorbent added, the impact of the amount of acid-treated BAC on the amount of color adsorbed was investigated. These investigations were all carried out at room temperature and 200 rpm constant speed. An increase in the dosage of adsorbent was found to result in a higher percentage of color removal.

2.4 Effect of initial dye concentration and contact time

The dye was stirred at equal intervals in order to conduct the kinetic tests. Contact time studies were performed by agitating 50 ml of dye solutions containing 100 mg of BAC at room temperature and concentrations of 20 mg/L, 40 mg/L, and 60 mg/L at an ideal pH of 6.5. The agitation speed was kept constant at 200 rpm. By applying the absorbance measurements, the color reduction profiles were produced.

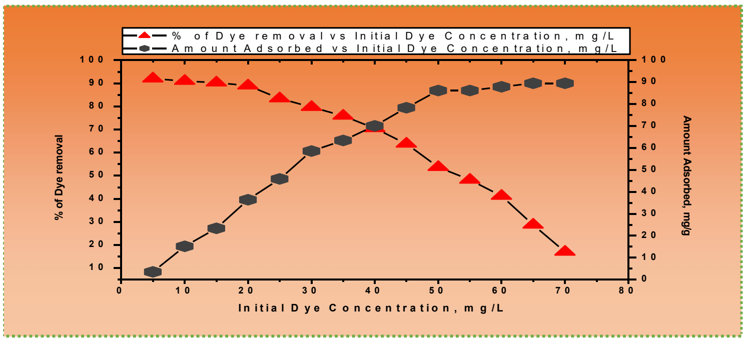

Fig. 3 Effect of Initial Concentration of Acid Orange 17 Solution

2.5 Effect of Temperature on kinetic rate constant and rate parameters

The adsorption experiment was conducted at a different temperature of 30 °C and with a fixed starting dye concentration of 20 mg/L at pH 6.5. between 45 and 60 degrees Celsius. The pseudo second order rate constants are mostly unaffected by the dye's temperature, according to a study of the data in (Table 3). Table 3 further shows that the dye's temperature has no discernible effect on the Elovich and pseudo-first order rate constants.It is clear that the first order rate equation, with a regression coefficient value greater than 0.98, best describes the dye adsorption on the BAC waste activated carbon.

Table 3 The adsorption kinetic model rate constants for BAC at different 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 g^{-1} min^{-1}**	**r^2**	**β g min^{-1}**	**α mg g^{-1}**	**r^2**
BAC	30^0C	0.0187	0.9576	0.0009	0.3345	0.9866	0.1234	0.8342	0.9612
	45^0C	0.0157	0.8578	0.0312	5.3012	0.3234	0.1754	0.4234	0.9234
	60^0C	0.0224	0.6045	0.0024	0.1456	0.6345	0.1890	0.4678	0.9567

2.6 Isotherm

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

R_L	Types of adsorption
$R_L > 1$	Disapproving
RL = 1	Lined
0 < RL < 1	Auspicious
RL = 0	Irretrievable

2.7 Langmuir Model

The Langmuir model was created under the presumption that an adsorbate species monolayer would form on the surface of an adsorbent particle. Furthermore, the assumption has been made that the surface sites are totally uniform in terms of energy. However, as Langmuir 1918 states, the adsorbent surface is actually energetically heterogeneous. Analyzing the Langmuir isotherms is crucial for determining the adsorbent's adsorption effectiveness. Optimizing the operating conditions for efficient adsorption is another benefit of this study.

The most popular two-parameter equation is this one, which is typically stated as follows:

$$\frac{1}{q_e} = \frac{1}{Q_o K_L} \cdot + \frac{C_e}{Q_o} \tag{12}$$

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)

As seen in Fig. 3, Ce/qe was plotted against Ce using linear regression analysis. The linear plots' intercept and slope provided the constants Q0 and KL, respectively. Table 5 illustrates that Acid Orange 7's Qo from the Langmuir isotherm was 44.05 mg/g. Based on the KL values (KL = 0.08926), it is possible to conclude that acid dye adsorptions occurred. A dimensionless separation factor, RL, can be used to express the fundamental property of the Langmuir equation (Wang et al., 2005).

A dimensionless parameter called RL, defined by RL = 1/1+ bC0, where C0 is the initial dye concentration (mg/L) and b is the Langmuir constant (L/mg), can be used to characterize the key features of a Langmuir isotherm. The variable shows the isotherm's form as shown in Table 4.

The goal of the current study is to ascertain how effectively the selected adsorbate-adsorbent system can be fitted using the Langmuir model.

$$R_L = (1/1+K_LC_0) \qquad (13)$$

Table 5 Equilibrium isotherm constants at 30°C.

	Freundlich isotherm			**Langmuir isotherm**	
K_f(mg/g)	**n**	**R^2**	**K_L l/mg**	**q_o mg/g**	**R^2**
5.0354	0.6186	0.9871	0.08926	44.052	0.9933

where,

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

R_L= the nature of the adsorption process.

The determined relative linearities (RL values) of acid dye for dye concentrations of 20 mg/L, 40 mg/L, and 60 mg/L, respectively, are found to be 0.3767, 0.3385, and 0.3450 (data not shown). The favorable adsorption of each dye under examination was indicated by the magnitude of the RL values, that is, 0 < RL < 1.

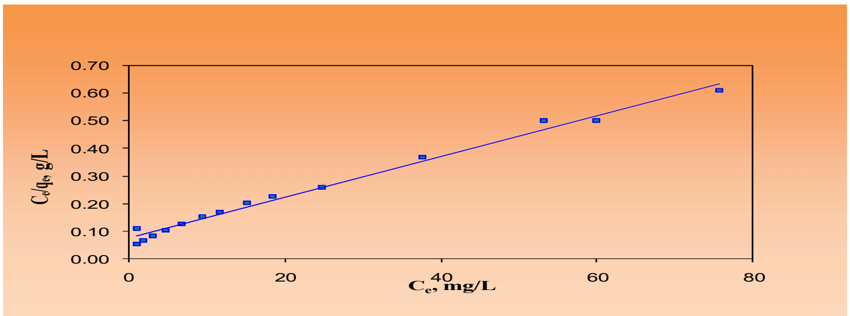

Fig. 4 Langmuir plot for Acid Orange 17 sorption onto BAC. M, 100 mg; V, 50 ml; C_0, 20 mg/L; pH, 6.5; temperature, 30°C).

2.8 Freundlich Model

At Equilibrium conditions, the adsorbed amount, q_e can also be predicted by using the Freundlich equation (Freundlich, 1926).

$$q_e = k_f C_e^{1/n} \tag{14}$$

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

$$\log q_e = \log k_f + (1/n) \log C_e \tag{15}$$

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

where 1/n, a measure of surface heterogeneity that ranges from 0 to 1, becomes more heterogeneous as its value approaches zero, and kf indicates the adsorbent capacity.According to the Freundlich equation, as long as the dye concentration in the liquid rises, so will the dye concentration on the adsorbent. An isotherm is reached at a limiting value of the solid phase concentration, according to the experimental data. There isn't much physical meaning to the equation itself. Freundlich isotherm with a correlation coefficient of 0.9871 demonstrated good data fitting. Table 5 displays the determined Freundlich isotherm constants at 30°C. Freundlich exponent n = 1.6165 has a value between 1 and 10, show an advantageous adsorption. where 1/n is a m, denotes favorable adsorption, and kf is a measure of the adsorbent capacity.

2.9 Adsorption Thermodynamics

The understanding of kinetic studies can be used to compute the rate or speed of a reaction. However, a basic understanding of thermodynamic factors is necessary to anticipate the changes in response that occur during the sorption process. Entropy (ΔS) of adsorption, free energy change (ΔG) resulting from the transfer of a unit mole of solute from solution to the solid-liquid interface, and enthalpy of adsorption (ΔH) are the three primary thermodynamic parameters.Equation (Inbaraj and Sulochana 2002) was used to compute the thermodynamic parameters acquired for the adsorption systems.

$$\Delta G = -RT \ln K_c \tag{16}$$

$$K_c = \frac{C_{Ae}}{C_e} \tag{17}$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{18}$$

R is the gas constant (J/mole), T is the temperature in Kelvin, C Ae is the solid phase concentration at equilibrium, and Ce is the residual concentration at equilibrium. KC is the equilibrium constant. The Vant Hoff plot's slope and intercept (1/t Vs ln kc) were used to calculate Δ**H** and Δ**S**. For the adsorption of BAC, Table 6 provides the values of Δ**G** , Δ**S**, and Δ**H**. The possibility and spontaneous nature of BAC adsorption are indicated by the negative values of free energy change (Δ**G**). The enhanced unpredictability during the adsorption of adsorbents is the cause of the positive value of S.

Table 6 Thermodynamic parameters for Acid Orange 17, BAC $_{\text{adsorption}}$.

Adsorbent	**ΔG (J mol^{-1})**			**ΔH**	**ΔS**
	30^0C	**45^0C**	**60^0C**	**(J mol^{-1} K^{-1})**	**(J mol^{-1} K^{-1})**
BAC	-3256.83	-4252.26	-7099.0	69.27	246.46

3 conclusions

It was discovered that the pH, temperature, and adsorbent concentration all affected the adsorption of anionic dye on the BAC (pH 6.5 was determined to be ideal for Acid Orange 7). The process viability at each concentration is taken into account by the thermodynamic parameters found for the adsorbent. For the anionic dye employed in this test, adsorption equilibriums were obtained in 102 minutes of contact time. The process viability at each concentration is taken into account by the thermodynamic parameters found for the adsorbent. It was discovered that the adsorbent's Acid Orange17 adsorption kinetics followed a pseudo-first-order rate equation. An equilibrium isotherm was examined using the Freundlich and Langmuir isotherm equations to examine the adsorption of Acid Orange17 on BAC. The adsorption of Acid Orange7 was shown to be best-fit by the Freundlich isotherm.

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