

Arithmetical Modeling Kinetics and Thermodynamics on the Adsorption of Reactive Yellow 17 by a Low-Cost Adsorbent: *balsamodendroncaudatum* wood waste- Based Activated Carbon Using Sulfuric Acid Activator-Assisted Thermal establishment

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Abstract-- *Balsamodendron caudatum* wood waste activated carbon (BAC) has the potential to absorb the dyes from aqueous solution. The inappropriate dumping of dyes in waste water constitutes an environmental trouble and can cause harm to the ecosystem. Present examination deals with the utilization of (BAC) waste as a sorbent for the exclusion of Reactive Yellow 17 dye from its aqueous solutions. The research indicates that sorption is subjective by initial dye concentration, contact time, dye solution pH, thermodynamic parameters such as the free energy, enthalpy, entropy and adsorption temperature have been investigated in the present study. A Kinetic study of dye followed the pseudo-first-order, pseudo second-order and Elovich models respectively. Outcome show that the pseudo first order kinetic model was found to compare the new data well.

Keywords-- BAC, Adsorption, Reactive Yellow 17, kinetics, low-cost adsorbents; aqueous solution.

I. INTRODUCTION

In recent years, the use of synthetic dyes in industries has increased dramatically due to low-cost in synthesis, efficient synthesis process, high stability and resistance to temperature, light and detergent, and other factors in comparison to natural dyes (Kooh et al., 2016). Synthetic dyes are widely used in different industries such as paper, textile, food, plastic, leather, and cosmetic (Kooh et al., 2018). Fabric effluents are known toxicants, which inflict acute disorders in aquatic organisms. Uptake of textile effluents through food chain in aquatic organisms may cause various physiological disorders like hyper tension, irregular fever, renal damage, cramps etc, which are dangerous to human as well as animal physical condition. Dyes are the most common water pollutants. Various sources of dye effluents are from pickling industries, paper and pulp industries, dye stuff industries, tanning, and textile industries. Water is necessary to all forms of life so water achievement technique for the removal of dyes important. Organic and microbiological procedure occurring in soil and water. Suspended and colloidal mineral matter, plant detritus, algae and protozoa are also regularly found in water. Activated carbon with large surface area, micro porous character and chemical nature of their surface have made them potential sorbents for removal of dyes from

industrial wastewater. The adsorptive properties of active carbon for removal of pollutants are well documented. Adsorption of hazardous soluble chemicals from wastewater in to surface of a solid adsorbent has provided a new dimension to wastewater technology. sugar cane bagasse ash (Kanawade et al., 2011), fly ash (Sell et al., 1994), peat moss (Allen and McKay 2001), jujuba seeds (Somasekhara Reddy et al., 2012), potatoes and egg Husk (Hila et al., 2012), and Grape Waste (Seyyed Alireza Mousavi et al., 2021), different water content on activated carbon. (Rösler et al 2021) are some of the waste materials which have been fruitfully tried for this purpose.

II. EXPERIMENTAL

A. Adsorbent

Balsamodendron caudatum wood waste was obtained from various regions of Erode & Tirupur Districts, Tamil Nadu, 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. portion of the above material was soaked well with H₂ SO₄ solution for a period of 24 hours. At the end of 24 hrs the excess of H₂ SO₄ 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 carbon of obtained were washed sufficiently with large volume of water to remove free acid, Then the obtained material was washed with plenty of water to remove excess of acid, dried then to desired particle size and named as BAC.

B. Preparation of aqueous dye solution

The stock solutions of the dye (1000 mg/L) were prepared by dissolving 1 g of respective dye in one litre of water without any further treatment, which were kept in dark coloured 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.

C. Amount of dye adsorbed

The formula used to find the Amount of dye adsorbed, Q_e , was as shown below:

$$Q_e = \frac{C_0 - C}{M} \times V \quad (1)$$

Q_e (mg/g) is the amount of dye adsorbed at equilibrium, V (L), is the volume of the solution dye, C_0 (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 percentage of removed anionic dye (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 Reactive Yellow 17pH and temperature was investigated by varying any one parameters and keeping the other parameters constant

E. The pseudo first order equation

The pseudo first - order equation (Lagergren 1898) 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 $q_t = q_e$, 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 relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

F. The pseudo second – order equation.

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

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

where, k_2 is the rate constant of pseudo second order adsorption ($\text{g. mg}^{-1} \cdot \text{min}^{-1}$). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_e$, the integrated form of equation (5) becomes.

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

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.

G. The Elovich equation

The Elovich model equation is generally expressed (Chien and Clayton 1980) 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.

III. RESULTS AND DISCUSSIONS

A. Characterization of adsorbent

Physico-chemical characterizations of the adsorbents were presented in Table 1.

TABLE 1 CHARACTERISTICS OF THE ACTIVATED CARBON BAC

Parameter	BAC
pH	6.0
Surface area (m^2/g)	502
pH _{zpc}	4.5

The surface area of the BAC was measured through N_2 adsorption at 77K using a NOVA1000, Quanta chrome Corporation. The pH of BAC was measured by a PHS-3C pH meter. pH of zero charge (pHpzc) of the samples was determined using pH drift method (Fariaa et al., 2004). The surface area of the BAC obtained from the N_2 equilibrium adsorption isotherms was found to be $502 \text{ m}^2/\text{g}$. The results of “pH drift” experiment, from which the pHpzc of BAC studied in this test was found to be 4.5.

B. Effect of pH

From the set of experiments conducted to find the effect of pH on adsorption phenomenon, it was observed that pH influences BAC surface dye binding sites and the dye chemistry in water. Figure 1 shows the amount of dye adsorbed, q_e using acid activated adsorbent at initial pH value. In this experiment, the initial dye concentration was fixed at 20 mg/L . From the shake flask experiments, better

colour removal of the dye, Reactive Yellow 37, was observed at pH of 6.0. The uptake of Reactive Yellow 37 was found to be optimal at pH 6.0 with the maximum dye uptake of 89.6 mg/g.

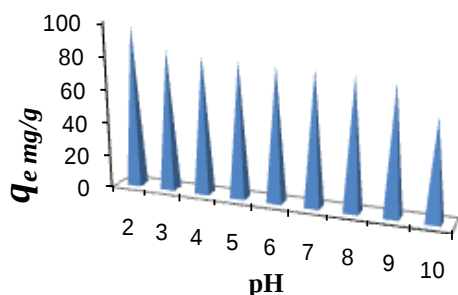


Figure. 1 Impact of pH on equilibrium uptake of Reactive Yellow 17 sorption onto BAC. M, 100 mg; V, 50 ml; C_0 20 mg/L; temperature, 30°C).

C. Effect of adsorbent dosage

The effect of quantity of acid treated BAC on the amount of color adsorbed was studied by agitating 50 ml of 20 mg/L dye solution with amount of sorbent addition was 100 mg. All these studies were conducted at room temperature and at a constant speed of 200 rpm. An increase in % colour removal was observed with an increase in adsorbent dosage.

D. Effect of initial dye concentration and contact time

For conducting the kinetic studies, the dye is agitating at equal time intervals were used. Contact time experiments were carried out by agitating with 50 ml of dye solutions whose concentrations viz. 20 mg/L, 40 mg/L and 60 mg/L at an optimum pH of 6.5 with 100 mg of BAC at room temperature. The speed of agitation was maintained constant at 250 rpm. The colour reduction profiles were obtained using the absorbance measurements.

E. Effect of Temperature on kinetic rate constant and rate parameters

Adsorption experiment was carried out with fixed initial dye concentration (20mg/L) at pH 6.5 and at different temperature viz. 30 °C, 45 °C and 60 °C. The analysis of the data in (Table 2) 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 appreciable nor little. It is obvious that the adsorption of dye on the BAC waste activated carbon is best described by first order rate equation with regression coefficient value is greater than 0.99.

Adsorbent	Initial Temperature	Pseudo first order						Elorich Model	
		k_1 $l\ min^{-1}$	r^2	k_2 $g\ mg^{-1}\ min^{-1}$	h $mg\ g^{-1}$	r^2	$\beta\ g$ min^{-1}	α $mg\ g^{-1}$	r^2
BAC	30°C	0.0189	0.7645	0.0073	0.3543	0.9098	0.1198	0.8982	0.9093
	45°C	0.0074	0.2589	0.0452	5.8764	0.6543	0.8245	0.56745	0.9286

	60°C	0.0654	0.6245	0.0876	0.9879	0.8765	0.0976	0.4765	0.8654
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TABLE 2 THE ADSORPTION KINETIC MODEL RATE CONSTANTS FOR BAC AT DIFFERENT TEMPERATURE

F. Adsorption Thermodynamics

The speed of a reaction or the reaction rate can be calculated from the knowledge of kinetic studies. But the changes in reaction that can be expected during sorption process require the brief idea of thermodynamic parameters. The three main thermodynamic parameters include, enthalpy of adsorption (ΔH), free energy change (ΔG) due to transfer of unit mole of solute from solution

to the solid liquid interface and entropy (ΔS) of adsorption.

The thermodynamic parameters obtained for the adsorption systems were calculated using the following equation (Sivakumar et al., 2012).

$$K_c = \frac{C_{Ae}}{C_e} \quad (16)$$

$$\Delta G = -RT \ln K_c \quad (17)$$

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

K_c is equilibrium constant, C_{Ae} is the solid phase concentration at equilibrium, C_e is residual concentration at equilibrium, R is gas constant (J/mole) and T is the temperature in Kelvin. ΔH and ΔS was obtained from the slope and intercept of Vant Hoff plot ($1/t$ Vs $\ln K_c$). Table 6 gives the value of ΔG , ΔS and ΔH for the adsorption of BAC. The negative values of free energy change (ΔG) indicate the feasibility and spontaneous nature of adsorption of BAC. The positive value of ΔS is due to the increased randomness during the adsorption of adsorbents.

TABLE 3 THERMODYNAMIC PARAMETERS FOR REACTIVE YELLOW 17, BAC ADSORPTION.

Adsorbent	ΔG (J mol ⁻¹)			ΔH	ΔS
	30°C	45°C	60°C	(J mol ⁻¹ K ⁻¹)	(J mol ⁻¹ K ⁻¹)
BAC	-4769.45	-4565.45	-7345.0	78.28	249.57

III. CONCLUSIONS

Adsorption of reactive dye on the BAC was found to be dependent on the pH, (The optimal pH of Reactive Yellow 17 was 6.5), temperature and concentration for adsorbent. Thermodynamic parameters obtained for the adsorbent accounts for feasibility of the process at each concentration. Adsorption equilibria were reached within 105 min contact time for reactive dye used in this test.

Thermodynamic parameters obtained for the adsorbent accounts for feasibility of the process at each concentration. The kinetics of Reactive Yellow

17adsorption on adsorbent was found to follow a pseudo first -order rate equation. An equilibrium isotherm for the adsorption of Reactive Yellow 17 on BAC was analyzed by the Langmuir isotherm

equations. Result showed that the Langmuir isotherm best-fit the Reactive Yellow 17 adsorption.

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