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# Balance, Kinetics, Isotherm and Thermodynamic Modeling of Adsorption of Reactive Yellow 107on to *Balsamodendroncaudatum* Wood Squander Activated Carbon Material

**B Sivakumar[1] J Jebaramya[2] and C Chelladurai[3]**
[1, 2 & 3] Department of Chemistry, Angel College of Engineering and Technology, Tirupur, TamilNadu, India.

**Abstract**: *Balsamodendron caudatum wood waste activated carbon (BACM) has the potential to take up the dyes from aqueous solution. The inappropriate discarding of dyes in waste water constitutes an environmental problem and can cause harm to the flora and fauna. Present examination deals with the exploitation of (BACM) waste as adsorbent for the elimination of Reactive Yellow 107dye from its aqueous solutions. The treated (BACM) using sodium sulphate was evaluated through SEM and XRD. The analysis indicates that adsorption is inclined 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 correspondingly. Conclusions show that the pseudo first order kinetic model was found to compare the investigational data fit.*

**Keywords**: *BACM, Adsorption, Reactive Yellow 107, kinetics, isotherm; low-priced sorbents; aqueous solution.*

## INTRODUCTION

Water is the most essential requirement in daily life that has been contaminated by the disposal of domestic, municipal, and industrial wastes. Anything, which is not needed, finds its way to the nearest watercourse or land, which further pollutes the ground water. So, there is a need to utilize the available resources effectively without polluting the water. Textile 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, sporadic fever, renal damage, and cramps etc., which are hazardous to human as well as animal health. 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. So, there is a need to utilize the available resources effectively without polluting the water (Prasad and Kumar 2010). Textile industries have shown a significant increase in the use of synthetic complex organic dyes as coloring materials (Talarposhti et al. 2001). A dye is carcinogenic, affects reproductive organs and develops toxicity and neurotoxicity (Lakshmi 1987). Therefore, the dyes are to be necessarily removed from water and wastewater. Different processes for color removal typically include physical, chemical, and biological schemes. Some processes such as electrochemical techniques and ion-pair extractions are relatively new for textile waste treatment, while others have been used in the industry for a long time.Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, simplicity of design, use of operation, and insensitivity to toxic substances (Meshko et al. 2001). The lower generation of residues, easy metal recovery, and the possibility to reuse adsorbent are the greatest advantages of this method (Gurnani et al. 2003). 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. Bamboo (Ahmad et al., 2009 ) , sugar cane bagasse ash (Kanawade et al., 2011), bone

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char (Alvin et al., 2010), fly ash(Sell et al., 1994), peat moss( Allen and McKay 2001; Chen et al.,2001), ipomoea carnia stem waste (Karthikeyan et al., 2007) , jujuba seeds (Somasekhara Reddy et al., 2012) and potatoes ,egg Husk ( Hila et al., 2012) and solid coal (Katarzyna Czerw et al., 2016) are some of the waste materials which have been fruitfully tried for this purpose.

## 1 Experimental

### 1.1 Adsorbent

*Balsamodendron caudatum* wood waste was obtained from various regions of Erode & Tirupur Districts, 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 $Na_2SO_4$ solution for a period of 24 hours. At the end of 24 hrs the excess of $Na_2SO_4$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 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 BACM.

### 1.2 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.

### 1.3Amount of dye Adsorbed

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

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

$Q_e$ (mg/g) is the amount of dye adsorbed at equilibrium, *V* (L), isthe volume of the solution dye, *Co* (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)

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

The initial concentration of Reactive Yellow 107pH and temperature was investigated by varying any one parameters and keeping the other parameters constant

### 1.4 The Pseudo First – Order Equation

The pseudo first - order equation (Lagergren 1898) is generally expressed as follows.

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

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.

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

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 determined from the slope and intercept of the plot, respectively.

### 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.

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

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.

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

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

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

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

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

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 form the slope and intercept of the plot, respectively.

### 1.6 The Elovich Equation

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

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

Where, $\alpha$ is the initial adsorption rate (mg.$g^{-1}$ $min^{-1}$), $\beta$ is the adsorption 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 Reactive Yellow 107adsorption fits the Elovich model a plot of qt vs ln t should yield a linear relationship with slope of $(1/\beta)$ and an intercept of $(1/\beta)$ In $(\alpha\beta)$

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## 2 Results and Discussions

### 2.1 Characterization of Adsorbent

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

Table 1 Characteristics of the Activated Carbon BACM

| Parameter | BACM |
|---|---|
| pH | 6.5 |
| Surface area ($m^2/g$) | 339.64 |
| $pH_{zpc}$ | 4.5 |

The surface area of the BACM was measured through $N_2$ adsorption at 77K using a NOVA1000, Quanta chrome Corporation. The pH of BACM 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 BACM obtained from the $N_2$ equilibrium adsorption isotherms was found to be 339.64 $m^2/g$. The results of "pH drift" experiment, from which the pHpzc of BACM studied in this test was found to be 4.5.

### 2.2 Effect of pH

From the set of experiments conducted to find the effect of pH on adsorption phenomenon, it was observed that pH influences BACM surface dye binding sites and the dye chemistry in water. Figure 1 shows the amount of dye adsorbed, $q_e$ using acid activated absorbent 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 6.5 .The uptake of Reactive Yellow 37was found to be optimal at pH 6.5 with the maximum dye uptake of 81.6 mg/g .

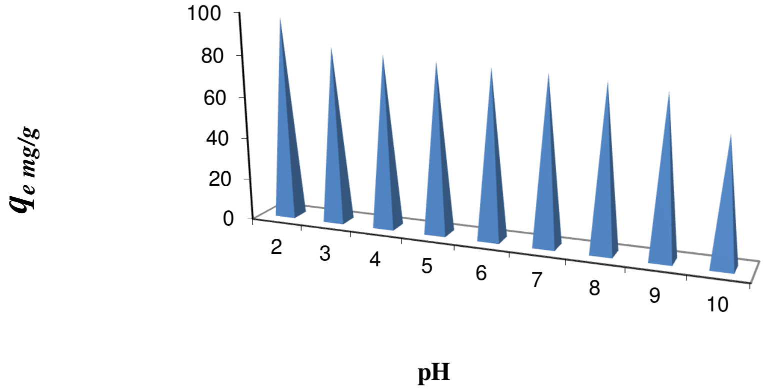

Figure.1 Influence of pH on stability uptake of Reactive Yellow 107 adsorption onto BACM.100 mg; V, 50 ml;$C_0$ 20 mg/L; temperature, 30°C).

### 2.3 Effect of Adsorbent Dosage

\The effect of quantity of acid treated BACM 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.

### 2.4 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 with100 mg of BACM at room temperature. The rate of agitation was maintained constant at 250 rpm. The colour reduction profiles were obtained using the absorbance capacity.

### 2.5 Influence of Temperature on Kinetic Rate Constant and Rate Parameters

Sorption experiment was established out with preset initial dye concentration (20mg/L) at pH 6.5 and at different temperature viz. 30 °C. 45 °C and 60 °C. The study of the data in (Table 2) reveals that the effect of temperature of the dye has very little influence on the pseudo second order rate constants. The table 2 also reveals that the effect of the temperature of dye on Elovich and pseudo first

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order rate constant is neither considerable nor little. It is evident that the adsorption of dye on the BACM waste activated carbon is best described by first order rate equation with regression coefficient value is greater than 0.98.

Table 2. The adsorption kinetic model rate constants for BACM 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$^{-1}$ min$^{-1}$ | $r^2$ |
| BACM | $30^0$C | 0.0234 | 0.9986 | 0.0017 | 0.4572 | 0.8521 | 0.1438 | 0.8547 | 0.9356 |
| | $45^0$C | 0.0128 | 0.9767 | 0.0670 | 4.3547 | 0.4016 | 0.1578 | 0.4689 | 0.9093 |
| | $60^0$C | 0.03467 | 0.7096 | 0.0056 | 0.1435 | 0.6458 | 0.1345 | 0.4345 | 0.8654 |

## 2.6. Morphology

The study by SEM of the adsorbent shown in the fig. 1 exposed that, it is highly permeable in nature. From the SEM results, it was found that there are uniform holes and cave type openings on the surface of the specimen that would definitely have increased the surface area (Khattri et al. 2000)

## 2.7. XRD Analysis

Fig. 2 shows the wide angle XRD pattern for porous carbon sample. The XRD analysis of permeable 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 (Syed 2011).

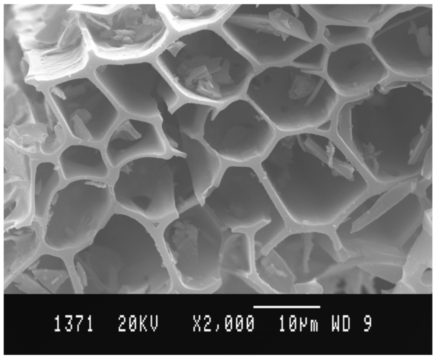

Figure. 2 SEM analysis for BACM

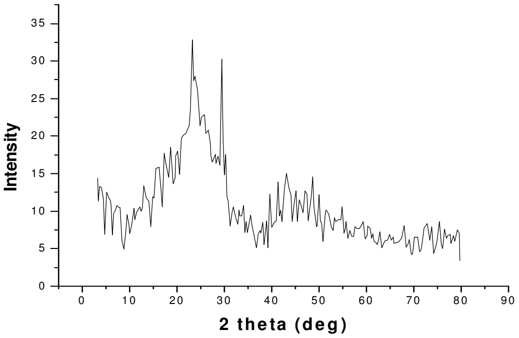

Figure. 3 XRD pattern for BACM

## 3.0 Adsorption Thermodynamics

The rate 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 (Inbaraj and Sulochana 2002).

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

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$$\Delta G = -RT \ln K_c \tag{17}$$

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

$K_C$ 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 5 gives the value of ΔG, ΔS and ΔH for the adsorption of BACM. The negative values of free energy change (ΔG) indicate the feasibility and spontaneous nature of adsorption of BACM. The positive value of ΔS is due to the increased randomness during the adsorption of adsorbents.

Table 3 Thermodyanamic parameters forReactive Yellow 37, BACM adsorption.

| Adsorbent | ΔG (J mol$^{-1}$) | | | Δ | ΔS |
|---|---|---|---|---|---|
| | $30^0$C | $45^0$C | $60^0$C | (J mol$^{-1}$ K$^{-1}$) | (J mol$^{-1}$ K$^{-1}$) |
| BACM | -3245.84 | -5652.28 | -7569.07 | 79.77 | 256.79 |

## 3. Conclusions

The sorption of reactive dye on the BACM was originate to be reliant on the pH, (The most favourable pH of Reactive Yellow 107was 6.5), temperature and concentration for adsorbent. Thermodynamic parameters obtained for the adsorbent accounts for feasibility of the process at each concentration. Adsorption equilibriums 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 107 sorption on adsorbent was found to follow a pseudo first -order rate equation. An equilibrium isotherm for the adsorption of Reactive Yellow 107on BACM was analysed by the Langmuir isotherm equations. Result showed that the Langmuir isotherm best-fit the Reactive Yellow 107adsorption.

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