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Kinetics, equilibrium, isotherm and thermodynamic modeling of sorption of Reactive Yellow 37 on to *balsamodendroncaudatum* wood waste activated carbon

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Abstract

Balsamodendron caudatum wood waste activated carbon (BAC) have the capability to absorb the dyes from aqueous solution. The unsuitable dumping of dyes in waste water constitutes an ecological trouble and can cause damage to the ecosystem. Present investigation deals with the utilization of (BAC) waste as adsorbent for the exclusion of Reactive Yellow 37 dye from its aqueous solutions. The investigation indicates that adsorption is influenced 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. Equilibrium isotherms for the adsorption of Reactive Yellow 37 on BAC were analyzed by the Langmuir isotherm. Outcome show that the pseudo first order kinetic model was found to compare the investigational data fit.

Keywords: BAC, Adsorption, Reactive Yellow 37, kinetics, isotherm; low-cost adsorbents; aqueous solution.

Introduction

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, 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 .Water is essential to all forms of life so water treatment technique for the removal of dyes important. In nature, a number of regulatory mechanisms play an important role in controlling the physico-chemical properties of important as well as the number and types of its biological populations. Irrespective of origin, it always contains a complex mixture of organic and inorganic substances most of which are of natural origin resulting from complex interaction between water, soil and underlying geological status. Biological and microbiological process occurring in soil and water. Suspended and colloidal mineral matter, plant detritus, algae and protosozoa are also frequently found in water. Activated carbon with large surface area, micro porous character and chemical nature of their surface have made them potential adsorbents 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 (Benefield et al., 1982). 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), fly ash(Sell et al., 1994), peat moss(Allen and McKay 2001), jujuba seeds (Somasekhara Reddy et al., 2012) and potatoes and egg Husk (Hila et al., 2012), are some of the waste materials which have been fruitfully tried for this purpose.

1 Experimental

1.1Adsorbent

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.

One portion of the above material was soaked well with $H_2 SO_4$ solution for a period of 24 hours. At the end of 24 hrs the excess of $H_2 SO_4$ 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 BAC.

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:

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

 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 percentage of removed anionic dye (R %) in solution was calculated using eqn. (2)

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

The initial concentration of Reactive Yellow 37 pH 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.

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

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 (1 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.

$$\log(q_{e} - q_{t}) = \frac{\log(q_{e}) - k_{1}}{2.303} \times t$$
(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)

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

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.

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

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

where, α is the initial adsorption rate (mg.g⁻¹ min⁻¹), β 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;

$$\begin{array}{cccc}
1 & 1 \\
q_t &= & - & \ln(\alpha \beta) + & - & \ln t \\
& \beta & \beta \\
\end{array}$$
(11)

If Reactive Yellow 37 adsorption 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 $(\alpha \beta)$

2 Results and Discussions

2.1 Characterization of adsorbent

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

Parameter	BAC
рН	6.5
Surface area (m²/g)	502
pH _{zpc}	4.5

Table 1 Characteristics of the Activated Carbon BAC

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 m²/g. The results of "pH drift" experiment, from which the pHpzc of BAC 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 BAC 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.

2.3 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.



Fig. 1 Impact of pH on equilibrium uptake of Reactive Yellow 37 sorption onto BAC. M, 100 mg; V, 50 ml; $C_0 20 \text{ mg/L}$; temperature, 30°C).

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 BAC at room temperature. The speed of agitation was maintained constant at 250 rpm. The colour reduction profiles were obtained using the absorbance measurements.

2.5 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 0.98.

2.6 Isotherm

The Freundlich isotherm is 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

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	βg min ⁻¹	α mg g ⁻ 1	r ²
BAC	30ºC	0.0173	0.9897	0.0036	0.3354	0.9867	0.1912	0.8574	0.9340
	45°C	0.0052	0.8576	0.0390	5.3686	0.3619	0.7834	0.5587	0.9571
	60ºC	0.0266	0.6047	0.0532	0.1559	0.6389	0.0993	0.4737	0.8943

surface with a finite number of identical sites.

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

2.7 Langmuir Model

The Langmuir model was developed based on the assumption of the formation of a monolayer of the adsorbate species onto the surface of the particle of the adsorbent. It has also been assumed that the surface sites are completely energetically homogeneous. But in the true sense, the adsorbent surface is energetically heterogeneous (Langmuir, 1918). 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 adsorption. In this respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well recognized.

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This model is the most widely used two-parameter equation, generally expressed in the form by the following equation

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

Ce/qe was plotted against Ce using linear regression analysis, as shown in Fig. 2. 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 44.05 mg/g for Reactive Yellow 37. The values of K_L it could be concluded that adsorptions of acid dye ($K_L = 0.08926$). The essential characteristic of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L (Wang et al., 2005).

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 shape of isotherm as given in Table 4.

R _L	Type of isotherm		
$R_L > 1$	Unfavourable		
RL = 1	Linear		
0 < RL < 1	Favourable		
$\mathbf{RL} = 0$	Irreversible		

Table 3 Parameters for types of isotherm

In the present research work, the investigator aims at determining how well the Langmuir model can be applied to the chosen adsorbate – adsorbent system.

		Langmuir isotherm	
$K_f(\mathrm{mg/g})$	K_L l/mg	$q_o \mathrm{mg/g}$	\mathbf{R}^2
5.0354	0.08926	44.052	0.9933

Table 4 Equilibrium isotherm constants at 30°C.

$$R_{\rm L} = (1/1 + K_{\rm L}C_0) \tag{13}$$

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 0.3767, 0.3385 and 0.3450 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 adsorption of each of the dye under consideration.



Fig. 2 Langmuir plot for Acid Orange 7 sorption onto BAC. M, 100 mg; V, 50 ml; C₀, 20 mg/L; pH, 6.5; temperature, 30°C).

2.9 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 (Δ H), free energy change (Δ G) due to transfer of unit mole of solute from solution to the solid liquid interface and entropy (Δ S) of adsorption.

The thermodynamic parameters obtained for the adsorption systems were calculated using the following equation (Inbaraj and Sulochana 2002).

$$K_c = \frac{C_{Ae}}{C_c} \tag{16}$$

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

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

 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 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.

Adsorbent	$\Delta \mathbf{G} \ (\mathbf{J} \ \mathbf{mol}^{-1})$			$\Delta \mathbf{H}$	$\Delta \mathbf{S}$
	30 ⁰ C	45 ⁰ C	60 ⁰ C	(J mol ⁻¹ K ⁻¹)	
BAC	-3256.83	-4252.26	-7099.0	69.27	246.46

Table 5 Thermodyanamic parameters forReactive Yellow 37, BAC adsorption.

3 CONCLUSIONS

Adsorption of reactive dye on the BAC was found to be dependent on the pH, (The optimal pH of Reactive Yellow 37 was 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 37 adsorption on adsorbent was found to follow a pseudo first -order rate equation. An equilibrium isotherm for the adsorption of Reactive Yellow 37 on BAC was analyzed by the Langmuir isotherm equations. Result showed that the Langmuir isotherm best-fit the Reactive Yellow 37 adsorption. **References**

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