

Studies on adsorptive removal of cationic dyes using a novel non-conventional activated carbon

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ABSTRACT

*The present study establish the potential of activated carbon prepared from inexpensive, locally and abundantly available biomaterial **Euphorbia Tirucalli L** wood to remove cationic dyes Basic Violet3 and Basic Violet10 from aqueous solutions. Batch mode kinetic and isotherm studies were carried out to evaluate the effects of contact time, initial dye concentration, pH and temperature. The amount of dye adsorbed at equilibrium was 162.5 mg/g for BV3 and 150 mg/g for BV10. The maximum removal of cationic dyes observed at pH of 8. Adsorption of cationic dyes increased with temperature indicating endothermic nature of adsorption. Adsorption kinetic data has been studied using pseudo first order, second order and intra particle diffusion model to understand the reaction mechanism. Adsorption isothermal data could be interpreted by the Langmuir and Freundlich models. The maximum adsorption capacity Q_0 varies from 208.33 to 222.22 mg/g for BV3 and 204.08 to 217.39 mg/g while increasing the temperature from 30°C to 45°C. Thermodynamic parameters were also calculated and it was found to be spontaneous, endothermic and physical adsorption in nature. The activation energy for both cationic dyes studied were below 40 kJ/mole, indicates the physical adsorption. The isosteric heat of adsorption also supported the physisorption process.*

Key words: *Euphorbia tirucalli L*, cationic dyes, kinetics, adsorption, activated carbon, isotherm studies.

INTRODUCTION

Pollution caused by the textile industries is a common problem faced by many industrial countries. In India many textile industries discharge untreated or partially treated waste on land or in natural streams causing pollution to the surface water, ground water and soil [1-3]. The waste water disposed by textile industries is causing major hazards to environment and drinking water due to the presence of large number of contaminants like acids, bases, toxic organic, inorganic, dissolved solids and color [4]. Discharge of dyes in the environment is worrying for both toxicological and aesthetical reasons because these textile dyes damage the quality of receiving streams and is toxic to food chain organisms [5]. Among the various classes of dyes, basic dyes are the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high. Color removal from industrial waste water by adsorption techniques has been of growing importance due to the chemical and biological stability of dyestuffs to conventional water treatment methods and the growing need for high quality treatment. Many investigators have studied feasibility of using low cost substances such as *Euphorbia antiquorum L* wood [6], Jute and sunnhemp [7], Teak leaves [8] and Ashoka leaf powder [9] for the removal of dyes from aqueous solution. The use of renewable

sources as raw material for manufacturing activated carbon is advantageous as these are less expensive to manufacture.

In the present study, the adsorptions of basic dyes namely Basic Violet3 and Basic Violet10 have been investigated using ETAC as adsorbent. The kinetic and thermodynamic parameters were calculated to determine the adsorption mechanism. The effect of initial dye concentration, agitation time, pH and temperature has been evaluated to assess the possibility of ETAC for the removal of cationic dyes.

MATERIALS AND METHODS

Adsorbent

Activated carbon prepared from the precursor wood *Euphorbia Tirucalli L*. The wood cut into a pieces of 2 to 3 cm size and dried in sunlight for 10 days. The dried material soaked in a boiling solution of 35% H_3PO_4 for 1 hour and kept at room temperature for 24 hours. The wood material separated, air dried and carbonized in muffle furnace at 550 °C for 1½ hour. The carbonized material powdered and activated at 800°C for 10 minutes. The resulting carbon was washed with plenty of water until the residual acid was removed. The dried material was ground well to fine powder and sieved into a particle size of 180 to 300 micron [10].

Adsorbate

The cationic dyes used in this experiment are Basic Violet 3 (M.Formula: $C_{25}H_{30}ClN_3$, M.Wt: 407.97, λ_{max} : 540nm), Basic Violet 10 (M.Formula: $C_{28}H_{31}ClN_2O_3$, M.Wt: 479.02, λ_{max} : 479nm) which are used without further purification. All other chemicals used in this experiment are of analytical grade. The structures of cationic dyes used are shown in Fig.1a and 1b. A stock solution of 1000 mg/L was prepared by dissolving appropriate amount of dye in one litre of distilled water. The percentage purity of dye is also taken in to consideration for the preparation of stock solution.

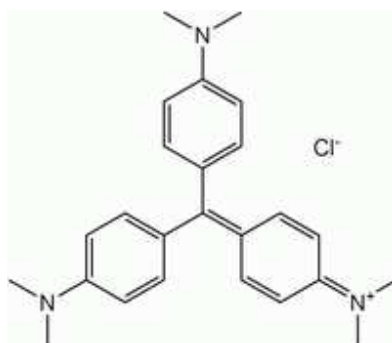


Figure 1a - Structures of Basic Violet 3

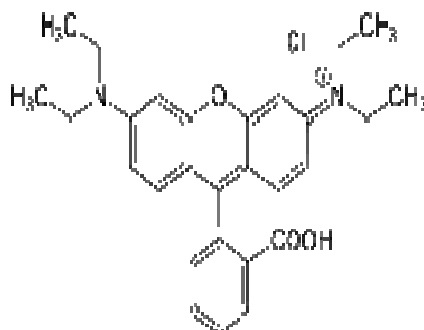


Figure 1b - Structures of Basic violet 10

Characterisation studies

Physico-chemical characteristics of activated carbon prepared from *Euphorbia Tirucalli L* wood were studied as per the standard testing methods [11-12].

Batch adsorption studies

Batch adsorption studies were carried out at different temperature by shaking 100 ml of dye solution having concentration in the range between 25-100 mg/L with 100 mg of adsorbent. At different time intervals the dye solution were taken and centrifuged. Absorbance of supernatant solution was noted using spectrophotometer (Elico make : model BL 198) and analysed for residual dye concentrations. The experiments were carried out at different experimental conditions by varying initial dye concentration, contact time, pH and temperature.

Dye Adsorption by varying pH

The effects of pH on cationic dye adsorption were investigated using 100 ml of 50 mg/L dye solution and 0.1 g of ETAC. The initial pH in the range 1-12 was adjusted using 0.1M HCl or 0.1M NaOH. The experiment was conducted at room temperature and equilibrium time reached at 80 min for BV3 and BV10 and the amount of dye adsorbed were determined.

Adsorption isotherm

Adsorption experiments were carried out at different temperatures (30-45°C) by using 100ml of dye solutions with varying concentration in the range between 10-170 mg/L and fixed amount of ETAC (0.1 g). The amount of dye adsorbed at equilibrium time was measured.

RESULTS AND DISCUSSION

Analysis of adsorbent characteristics

The Physico-chemical characteristics of activated carbon (ETAC) prepared from *Euphorbia Tirucalli L* wood using H_3PO_4 were summarized in Table.1 and the adsorbent was analysed for the adsorption of cationic Dyes (Basic violet3 and Basic Violet10).

Table.1 Physico-chemical characteristics of Adsorbents

S. No	Properties	ETAC
1	pH	6.48
2	Conductivity, $\mu S/cm$	0.187
3	Moisture content, %	10.4
4	Ash, %	10.8
5	Volatile matter, %	22.2
6	Bulk density, g/ml	0.56
7	Specific gravity	1.18
8	Porosity, %	52.54
9	Methylene Blue value, mg/g	405
10	Iodine Number, mg/g	932
11	Surface area(BET), m^2/g	857.85

Effect of initial dye concentration and agitation time

The adsorption of all three cationic dyes onto ETAC were rapid in the first 15min, later it slows down on and finally reached the equilibrium at 80 minutes for BV3 and BV10. When the concentration of dye solution increased from 25 to 100 mg/L, the percentage of dye adsorption decreased from 93.75 to 81.25% and 91.84 to 75% for BV3 and BV10 respectively and lower adsorption is due to the saturation of adsorption sites. Though, the percentage of adsorption decreases on increasing the concentration, the equilibrium amount of dye adsorbed increased from 46.88 to 162.5 mg/g for BV3 and 45.92 to 150 mg/g for BV10. This is due to the fact that at higher concentration lower adsorption percentage is due to the saturation of adsorption sites [13]. Similar results were observed for removal of basic dyes by sugar cane stalks [14] and jute fibre carbon [15].

Effect of temperature

It is important to analyze the temperature effect for adsorption of cationic dyes onto ETAC. From the results of temperature studies, the dye adsorbed at equilibrium was increased with increasing temperature indicated that the adsorption is endothermic and high temperature is favorable for the adsorption of all the three cationic dyes. The

enhanced adsorption of cationic dyes with temperature is due to increased mobility of dye molecules and enlargement of pore size due to activated diffusion which causes pores to widen and deepen there by creating more surfaces for adsorption [16].

Effect of pH

It is the most important parameter controlling the adsorption process. When the pH of the dye solution increased, the amount of dye adsorbed also increases. The experiments were carried out at an initial pH of 1 to 12 and the results indicate that there is a strong electrostatic interaction between adsorbent and adsorbate. From the figure.2 both the cationic dyes studied show higher percentage of adsorption at pH 8 to 9. At high pH the carbon surface become negative which enhances the positively charged cationic dyes [17].

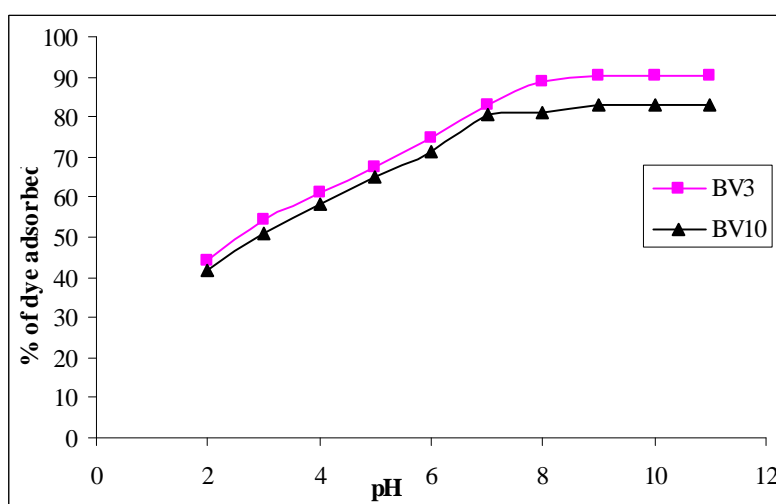


Figure 2 – Effect of pH

Adsorption kinetics

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for the validation of the efficiency of the process. In the present work, the kinetic data obtained from batch studies have been analyzed by using pseudo-first order, second order and intra particle diffusion models.

Pseudo-first order model

The pseudo-first order equation of Lagergren [18] is generally as follows

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

The integrated form of equation

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \dots (2)$$

The amount of dye adsorbed at equilibrium q_e and first order rate constant k_1 calculated from intercept and slope of the plot $\log(q_e - q_t)$ vs time and the results are summarized in table 2. From the values of r^2 , it is clear that pseudo first order equation does not fit well for whole range of adsorption process, as it is applicable for the initial stages of adsorption processes [19].

Pseudo-second order model

The second order equation for the equilibrium adsorption is expressed as Ho and Mckay [20]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots (3)$$

The r^2 values obtained for various initial dye concentrations were above 0.98 indicating that the second order kinetic model describes very well for adsorption of cationic dyes onto ETAC. Figure 3a and 3b showed the pseudo-second order kinetic model for BV3 and BV10 respectively. The values of second order rate constant k_2 and q_e were calculated from the intercepts and slopes of the plot of t/q_t vs t and the results are presented in table 2. The value of k_2 decreases with increase in dye concentration due to decrease in available vacant sites for adsorption. Based on the values of co-relation co-efficient, the second order kinetic model was more suitable to describe the adsorption process for cationic dye adsorption than pseudo-first order model.

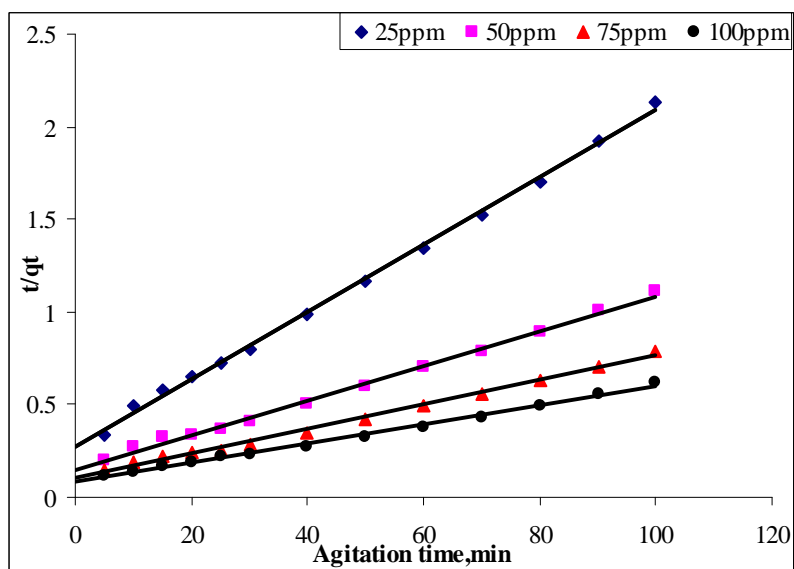


Figure 3a- Pseudo-second order plot for Adsorption of BV3 onto ETAC

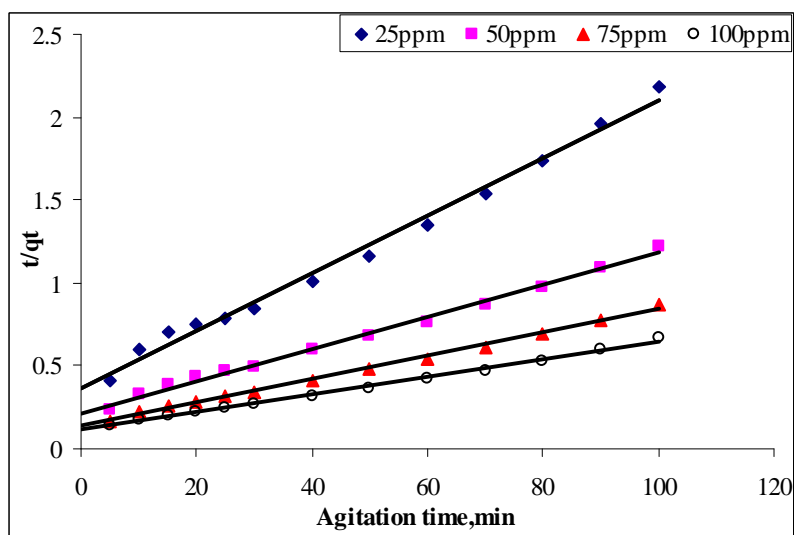


Figure 3b- Pseudo-second order plot for Adsorption of BV10 onto ETAC

Table 2. Kinetic Model values for adsorption of Basic Dyes onto ETAC

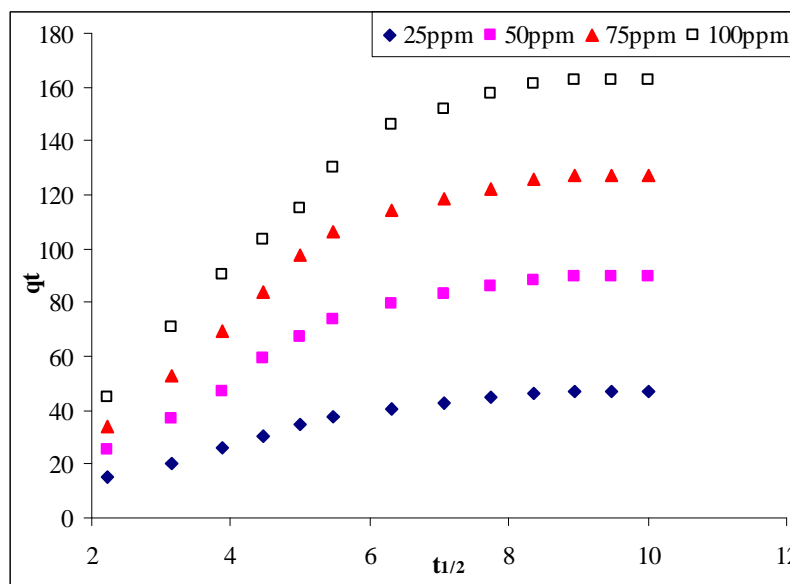
Dyes	Concn mg/L	First Order Kinetics			Second Order Kinetics			Intra Particle Diffusion model	
		k_1 (min^{-1})	$q_e(\text{cal})$ (mg/g)	r^2	$k_2 \times 10^4$ (g/mgmin)	$q_e(\text{cal})$ (mg/g)	r^2	k_{id} (mg/g min)	r^2
BV3	25	0.0534	46.95	0.9848	11.9342	55.24	0.9980	4.6848	0.9248
	50	0.0566	92.57	0.9885	5.9625	106.38	0.9957	9.1490	0.9104
	75	0.0575	130.70	0.9893	4.2459	151.51	0.9956	12.9820	0.9034
	100	0.0651	196.92	0.9644	3.2778	192.30	0.9964	16.6379	0.9202
BV10	25	0.0612	57.03	0.9796	8.4455	57.47	0.9991	4.8939	0.9352
	50	0.0522	93.77	0.9774	4.4070	103.09	0.9951	8.7074	0.9565
	75	0.0522	125.63	0.9829	3.6139	142.85	0.9973	12.060	0.9448
	100	0.0601	189.10	0.9488	2.5147	188.67	0.9954	15.9247	0.9452

Intra particle diffusion model

The pseudo-first order and second order kinetic models could not identify the diffusion mechanism, so that the kinetic results were further analysed using intra particle diffusion model [21-22]. In batch mode adsorption process there is a possibility that the transport of dye molecules from the solution into the pores of the adsorbent is the rate controlling step .

$$t^{1/2} = k_{id} + C \quad \dots (4)$$

This possibility was tested by plotting a graph between qt and $t^{1/2}$ at different initial dye concentration and shown in Figure.4a and 4b. All the plots have initial curved portion followed by an intermediate linear portion. The initial portion is related to mass transfer and linear part is due to intra particle diffusion. The values of k_{id} for all concentrations studied were determined from the slopes of respective plots and the results are presented in table 2. If the intra particle diffusion was the only rate controlling step, the plot passed through the origin, if not the boundary layer diffusion controlled the adsorption to some degree [23]. But the plots obtained were not linear over the whole time range, implying that more than one process affected the adsorption ie the mechanism of removal of cationic dyes is complex and both surface adsorption as well as intra particle diffusion contribute to the rate determining step.

**Figure 4a- Intra particle Diffusion plot for Adsorption of BV3 onto ETAC**

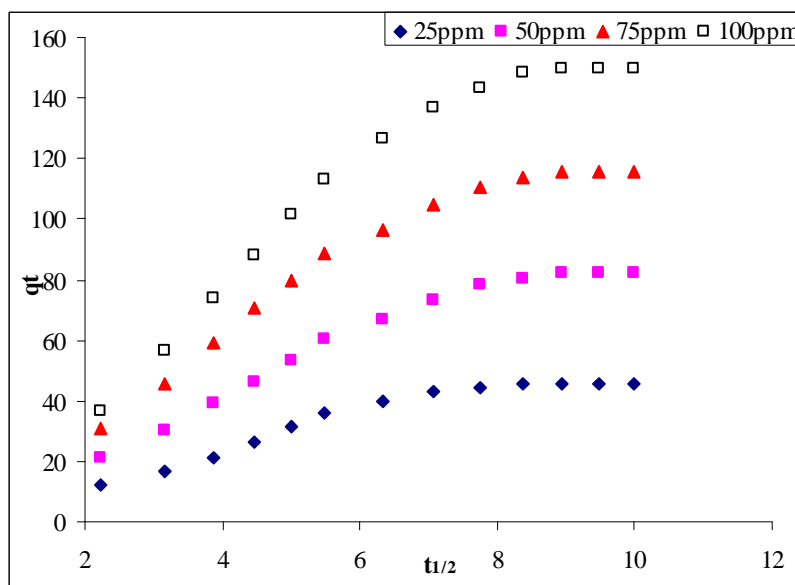


Figure 4b- Intra particle Diffusion plot for Adsorption of BV10 onto ETAC

Adsorption isotherm

Isotherms are the equilibrium relation between the concentration of the adsorbate on the solid phase and in the liquid phase. It is the most important data to understand the mechanism of adsorption systems. In this study, Langmuir [24] and Freundlich [25] isotherm models were used to describe the basic dye equilibrium.

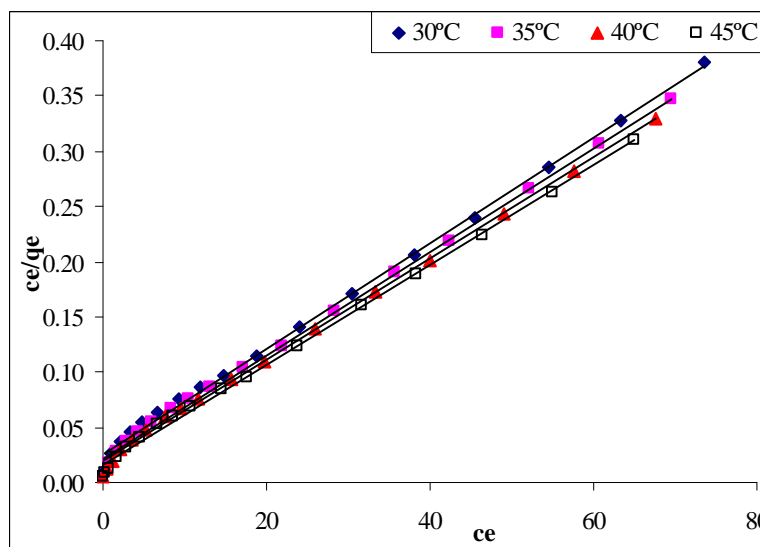


Figure 5a- Langmuir Adsorption Isotherm for Adsorption of BV3 onto ETAC

Langmuir isotherm

The Langmuir isotherm equation is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of adsorbate dye molecule on the adsorbent surface. The energy of adsorption is constant and there is no transmigration of the adsorbate in the plane of the surface [26]. The linearised form of Langmuir isotherm is presented by the equation.

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{c_e}{Q_0} \quad \dots (5)$$

Where, C_e is the equilibrium concentration (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b_L (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. Figure 5a and 5b showed the Langmuir plot for BV3 and BV10 respectively. The values of Q_0 and b_L calculated from the slopes and intercepts of the linear plots of C_e/q_e vs C_e and the results are presented in table 3. The results show that the value of adsorption efficiency Q_0 and adsorption energy b_L of ETAC increases with increasing the temperature suggests that the maximum adsorption corresponds to a saturated monolayer of dye molecules on adsorbent. Further it confirms the endothermic nature of processes involved in the system [27]. The maximum adsorption capacity Q_0 varies from 208.33 to 222.22 mg/g for BV3 and 204.08 to 217.39 mg/g while increasing the temperature from 30°C to 45°C.

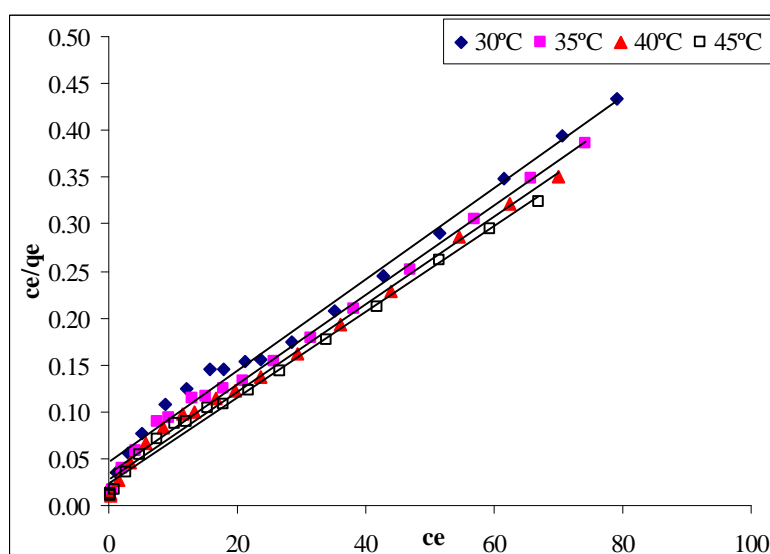


Figure 5b- Langmuir Adsorption Isotherm for Adsorption of BV10 onto ETAC

Table.3 Comparison of the coefficients of Isotherm parameters of Basic dyes

Dyes	Temp °C	Isotherm Models					
		Langmuir			Freundlich		
		Q_0 (mg/g)	b (L/mg)	r^2	n	k_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$)	r^2
BV3	30	208.33	0.1867	0.9978	2.6673	47.2063	0.9362
	35	212.76	0.2175	0.9972	2.7948	52.7351	0.9502
	40	217.39	0.2527	0.9974	2.9222	58.3848	0.9565
	45	222.22	0.2980	0.9973	3.1397	65.9173	0.9655
BV10	30	204.08	0.1084	0.9873	2.4330	35.5385	0.9622
	35	208.33	0.1407	0.9891	2.6961	44.6580	0.9769
	40	212.76	0.1649	0.9912	2.8801	51.2035	0.9682
	45	217.39	0.1869	0.9918	2.9620	55.8598	0.9622

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter R_L [28] that is defined by the following equation

$$R_L = \frac{1}{(1 + bC_0)} \quad \dots (6)$$

Where, C_0 is the initial solute concentration. The R_L value indicated the type of adsorption isotherm to be either unfavourable ($R_L > 1$), favourable ($R_L < 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). Langmuir model is more appropriate to explain the nature of adsorption of cationic dyes with correlation coefficient of 0.9978 to 0.9973 for BV3 and 0.9873 to .9918 for BV10.

Freundlich isotherm

The Freundlich isotherm is an empirical equation derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces.

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \quad \dots (7)$$

Where, K_f and $1/n$ are Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent respectively. The q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L). The values of K_f and $1/n$ are calculated from intercept and slopes of linear plot of $\log q_e$ vs $\log c_e$ (figure not shown) and the results are presented in table 3. The value of $1/n$ is below one for all three dyes studied indicating that the adsorption of cationic dyes on ETAC is favourable. But it poorly fits with the experimental data with correlation coefficient 0.9362 to 0.9655 for BV3 and 0.9622 to 0.9622 for BV10.

Thermodynamic parameters

Activation energy

The second order rate constant of the dye adsorption is expressed as a function of temperature by Arrhenius relationship.

$$\ln k_2 = \ln A - \frac{E_a}{RT} \quad \dots (10)$$

Where E_a and A refers to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting $\ln k_2$ vs $1/T$ shown in figure 6. The activation energies were found to be 27.1967 kJ/mole and 33.0255 for BV3 and BV10 respectively. The minimum value of E_a (27.1967 kJ/mole) for sorption of BV3 onto ETAC indicated the higher adsorption due to lesser energy barrier. The physisorption usually have energies in the range of 5-40 kJ/mole, while higher activation energies 40-800 kJ/mole suggests chemisorption [29]. The activation energy < 40 kJ/mole for both the dyes indicates the diffusion controlled physisorption.

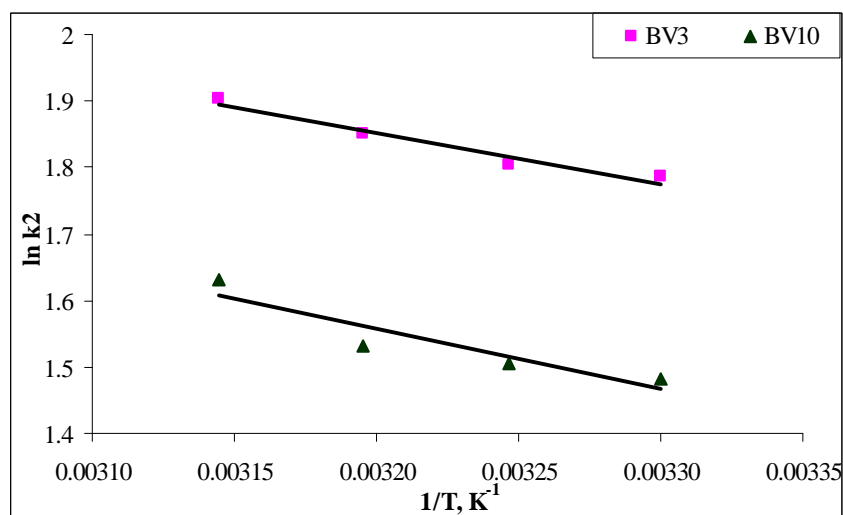


Figure 6- Arrhenius plot for adsorption of Cationic dyes

The thermodynamic parameters such as change in standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) can be determined by using VantHoff equation

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots (9)$$

Where, T is the absolute temperature and K_L (L/g) is the standard thermodynamic equilibrium constant. By plotting a graph of $\ln K_L$ vs $1/T$, the values of ΔS° and ΔH° can be estimated from the slopes and intercepts (figure not shown). The results are given in table 4. The positive values of ΔS° confirming physical adsorption nature and increased randomness at the solid-solution interface during adsorption and indicate affinity of the dye onto adsorbents [30]. The value of enthalpy of a sorption process may be used to distinguish between chemical and physical adsorption [31-32]. For chemical adsorption enthalpy value ranges from 83-830 KJ/mole [33].

Table.4 Thermodynamic Parameters at different Temperatures

Dye	Temp°C	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° kJ/K/mol	Ea kJ/mole	ΔH_x kJ/mole
BV3	30	-9.2107	28.2942	0.1237	27.1951	27.1967
	35	-9.8296				
	40	-10.4486				
	45	-11.0675				
BV10	30	-7.8750	32.1793	0.1321	33.0232	33.0255
	35	-8.5359				
	40	-9.1969				
	45	-9.8579				

Isosteric heat of adsorption

It is the basic requirements for the characterization and optimization of an adsorption process and also very important for equipment and process design.

The isosteric heat of adsorption at constant coverage is calculated using Clausius- Clapeyron equation [34].

$$\ln C_e = \frac{\Delta H_x}{RT} + K \quad \dots (10)$$

Where C_e is the equilibrium dye concentration in solution (mg/L), ΔH_x is the isosteric heat of adsorption (kJ/mole). The isosteric heat of adsorption is calculated from the slope of the plot $\ln C_e$ versus $1/T$. The magnitude ΔH_x of provides an information about the nature and mechanism of the process. For physical adsorption ΔH_x should be below 80 kJ/mole and for chemical adsorption it ranges between 80 and 400 kJ/mole [35]. The values of ΔH_x for the adsorption of BV3 and BV10 onto ETAC are 27.1967 kJ/mole and 33.0255 kJ/mole which are within the range of physisorption and suggested that the adsorption process is physisorption.

CONCLUSION

The present study confirmed that the activated carbon prepared from *Euphorbia Tirucalli L* wood was found to be suitable adsorbent for the removal of cationic dyes. The equilibrium adsorption occurs within 70 minutes. Removal of cationic dyes is pH dependent and maximum removal occurs at pH 8-9. The kinetic studies revealed that the adsorption data was controlled by both surface adsorption and intra particle diffusion. The experimental adsorption equilibrium data were in good agreement with Langmuir model. The determination of thermodynamic parameters indicates the spontaneous and endothermic nature of adsorption process. The activation energy for all the three cationic dyes studied was below 40 kJ/mole, isosteric heat of adsorption indicates the physical nature of adsorption process.

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