

# **Adsorptive Removal of Basic Violet Dye from Aqueous Solution by Activated Carbon Prepared From Tea Dust Material**

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**ABSTRACT:** In the present investigation, the activated carbon was prepared from tea dust material and utilized for the removal of Basic violet-14 from aqueous solution. The experimental studies were carried out in a batch mode by varying the parameters such as initial dye concentration, adsorbent dose, temperature and pH. The experimental data were analyzed by both kinetic and isotherm models. Pseudo second order kinetics was well fitted than first order kinetics with the rate constants in the range of  $1.286 \times 10^{-4}$  to  $1.653 \times 10^{-4} \text{ gm}^{-1} \text{ min}^{-1}$ . Maximum dye removal was observed at pH=3.05. Thermodynamic parameters calculated for the adsorption of Basic Violet-14 and observed that the adsorption was spontaneous and endothermic with negative  $\Delta G^0$  ranges from -1.75 to -5.03 KJ/mol and the positive  $\Delta H^0$  value ranges from 20- 26 KJ/mol. Hence the prepared TWAC was an alternate to commercial activated carbon and also effective for the removal of BV-14 from aqueous solution.

**KEYWORDS:** Tea waste activated carbon (TWAC), Basic Violet-14, isotherm, kinetics and thermodynamic studies.

## **I. INTRODUCTION**

Synthetic color dyes are playing an important role in making our life as fine looking as rainbow. Many industries such as textiles, tanneries, Printing, cosmetics & Plastics etc., are using dyes in their way of journey in the production. Due to the increase of dyes and dye based products usage in the market and their discharge cause the damage to the environment. The waste water from textile industry released into nearby land, river or stream. Even trace amount of dyes in aqueous medium is highly visible and interfere the transmission of light and upset the biological metabolism in aquatic ecosystem [1]. Since dyes are toxic and carcinogenic in nature, it is considered as an objectionable type of pollutant.

A wide range of method has been developed for the removal of synthetic dyes from wastewater to decrease their impact on the environment. The technologies involved are adsorption on inorganic or organic matters, decolourization by oxidation process, and/or by photo catalysis, microbiological or enzymatic decomposition, reverse osmosis technology and membrane separation etc. Among the physico chemical process, adsorption is considered to be effective method for waste water treatment. Activated carbon has undoubtedly been one of the most popular adsorbents for the removal of dyes from aqueous solution and is widely used in wastewater treatment applications throughout the world. It is mainly

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due to its effectiveness, versatility and high adsorption capacity for the removal of colour from dyeing and textiles [2]. But due to high operating cost, we have to find non-conventional alternative adsorbents. In this way researchers have found out a very good alternate to activated carbon from cellulosic and Lignocelluloses wastes as a starting material for the preparation of activated carbon [3, 4]. Many investigators have studied the feasibility of using inexpensive alternative materials like Orange waste [5], lemon peel [6], raw barley straw [7], egg shell [8], sawdust [9], rice husk [10], fly-ash [11, 12], Wollastonite [13,14,15] coir pith carbon [16], Pomegranate Peel [17], coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater. In the present investigation, the tea waste activated carbon prepared from used tea dust and utilized for the removal of Basic Violet-14 from aqueous solution.

## II. MATERIALS AND METHODS

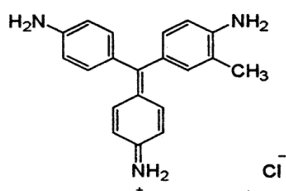
### Preparation of Tea Waste Activated Carbon (TWAC) – Adsorbent

The used tea wastes were collected from the tea shops at Kunnathur area in Erode district, Tamilnadu. The wastes were thoroughly washed with distilled water and dried. The dried sample was used to prepare the activated carbon as in the procedure given in the literature [18] with some modification. Finally the prepared tea waste activated carbon (TWAC) was grinded well and stored in air tight plastic container for further study.

### Adsorbate

The dye used for the adsorption study was Basic violet 14. Molecular formula of the dye is  $C_{20}H_{19}N_3.HCl$  with Colour Index: 42510 and molecular weight: 337.85. The molecular structure of the dye is given below.

### Molecular structure of Basic Violet – 14



A stock solution of 1000 mg l<sup>-1</sup> was prepared in double distilled water and the experimental solutions of the desired concentration were obtained by successive dilutions. All chemicals used were of analytical reagent grade (Merck /SRL,, India ). Doubly distilled water was used throughout the study.

### Batch Adsorption Experiments

Absorbance of 10 mg l<sup>-1</sup> was determined at different wavelengths using UV visible spectrophotometer to obtain a plot of absorbance versus wavelength. The wavelength corresponding to the maximum absorbance ( $\lambda_{max}$ =540 nm) as determined from the plot was noted. This wavelength was used for measuring the absorbance of residual concentration of Basic violet-14. The efficiency of an adsorbent was evaluated by conducting batch mode experiments. The experiment was carried out by using 100mg adsorbent with 100ml of dye solution varies from 25 mg l<sup>-1</sup> to 100 mg l<sup>-1</sup> concentration at 180 rpm speed on an REMI made orbital shaker. The mixture was withdrawn at specified intervals and centrifuged by electrical centrifuge at 5000 rpm for about 15 minutes. The unadsorbed supernatant liquid was analyzed for the residual dye concentration using Elico make Spectrophotometer at the wavelength 540 nm. The pH of solutions was adjusted using 1M HCl and 1M NaOH. The P<sup>H</sup> meter was used to adjust the pH of dye solution as per the requirement. The effect of temperature was also studied at 30° C, 40° C and 50° C. All experiments were carried out in duplicate for accuracy.

### Adsorption Isotherm

The adsorption isotherms generally used for the design of adsorption system. The Langmuir and Freundlich equations are commonly used for describing the adsorption isotherms. The linear equation of Langmuir and Freundlich are represented as following Equations (1) and (2), respectively.

$$C_e/Q_e = (C_e/Q^0) + (1/Q^0 b) \quad \longrightarrow \quad (1)$$

$$\log Q_e = 1/n \log C_e + \log K \quad \longrightarrow \quad (2)$$

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Where  $Q_e$  and  $C_e$  have the usual meanings and  $Q^0$  and  $b$  are the Langmuir constants, indicating that the adsorption capacity and energy of adsorption respectively.  $K$  and  $n$  are the empirical constants of the Freundlich isotherm measuring the adsorption capacity and intensity of adsorption respectively.

## Thermodynamic Analysis

The standard free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) were calculated from the variation of the thermodynamic equilibrium constant  $K_0$ . The  $K_0$  for the adsorption process and the thermodynamic parameters were calculated using the following equations,

$$K_0 = C_{\text{solid}} / C_{\text{liquid}} \longrightarrow (3)$$

$$\ln K_0 = (\Delta S^0/R) - (\Delta H^0/RT) \longrightarrow (4)$$

$$\Delta G^0 = -RT \ln K_0 \longrightarrow (5)$$

$\Delta H^0$  and  $\Delta S^0$  were determined from the slope and intercept of the plot of  $\ln K_0$  versus  $1/T$  respectively.

## III. RESULTS AND DISCUSSION

### Effect of Initial Dye Concentration

The experimental results of adsorptions of Basic violet – 14 onto surface modified TWAC at various initial concentrations (25, 50, 75 and 100 ppm) with contact time are shown in the Fig.1 and Fig.2. The percentage of adsorption decreased with increase in initial dye concentration, but at the same time, the actual amount of dyes adsorbed per unit mass of carbon increased with increase in dye concentration. The amount of dye adsorbed was increased from 33.93mg/g to 73.21mg/g for basic violet - 14. This shows that the adsorption is highly dependent on initial concentration of dye. It is because that at lower concentration, the ratio of the initial number of dye molecules to the available surface area is low whereas at high concentration the available sites of adsorption becomes lesser and hence the percentage removal of dye gets decreased with increase in initial concentration.

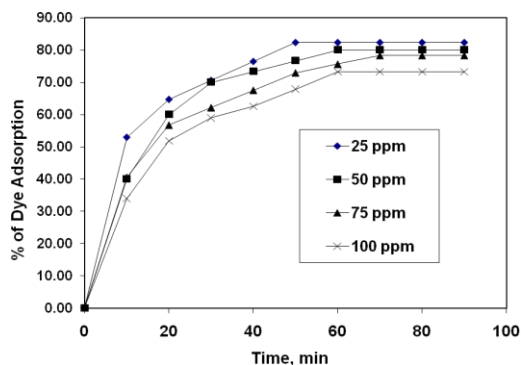


Fig 1: Effect of initial dye concentration on percentage removal of BV-14

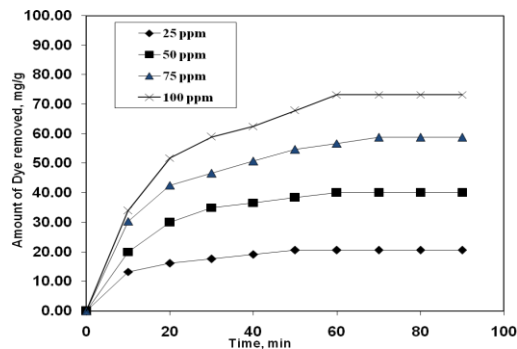


Fig 2: Effect of initial dye concentration on the amount of removal of BV-14

### Effect of pH

The pH is one of the most important factor controlling the adsorption of dye onto the adsorbent. The experiments were carried out at different pH (3-11) shows that there was a change in percentage removal of dye with change in pH. Fig. 3 clearly shows that at lower pH (acidic pH = 3.05), the percentage of dye removal was maximum and at higher pH (alkaline pH = 11.14) it was minimum.

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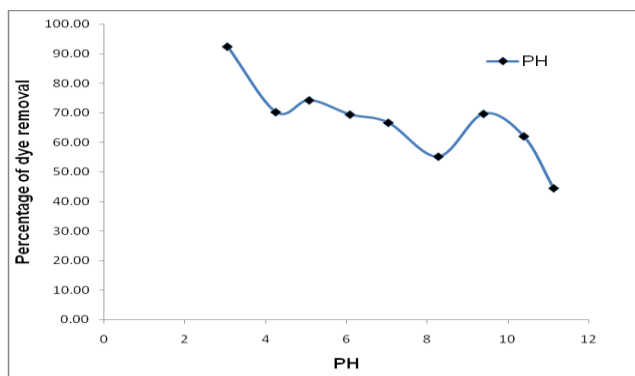


Fig 3: Effect of pH on the percentage removal of BV-14

## Effect of Temperature

The adsorption capacity of the TWAC was increased with increase in temperature of the system from 30 - 50°C. The increase in the equilibrium adsorption capacity of BV -14 dye indicates that the high temperature favours the dye removal. The percentage and the amount of BV-14 removal were increased from 80.00 to 83.33% and 40 mg/g to 41.67 mg/g respectively. This was shown in the Fig.4 and Fig.5. From the above results it is clear that adsorption equilibrium is a temperature dependent process. This effect may be due to the fact that at higher temperature, there was an increase in the movement of the solute occurs. Similar results were also reported by other researchers<sup>9-10</sup>.

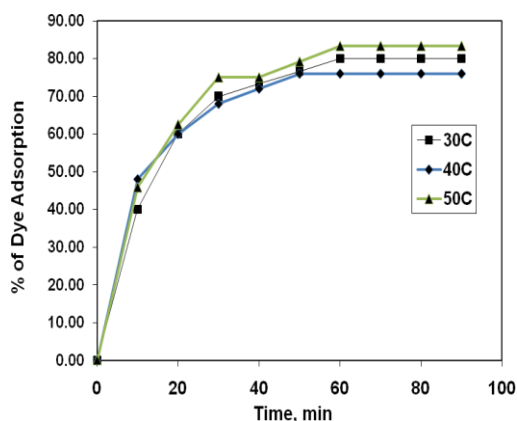


Fig 5: Effect of temperature on the Percentage removal of BV-14

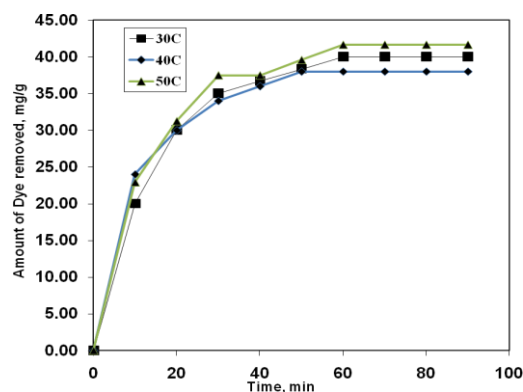


Fig 4: Effect of temperature on the amount of BV-14 removal

## Adsorption Kinetics Study

The prediction of the adsorption kinetics of dye from aqueous system is very important to design a suitable treatment system. The following kinetic equations have been studied to analyze the adsorption kinetics of Basic Violet-14 dye onto TWAC.

### Pseudo-First Order Kinetics

The first order equation is the simplest one and is the most widely used for the adsorption of a solute from a liquid solution. The rate equation expression is given below

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \quad (6) \longrightarrow$$

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where  $q_e$  and  $q_t$  are the amounts of dye adsorbed at equilibrium and time  $t$  (min),  $k_1$  is the rate constant ( $\text{min}^{-1}$ ). Linear plot of  $\log (q_e - q_t)$  versus  $t$  gives the value of  $k_1$  and  $q_e$ . The adsorption data fitted poorly with pseudo-first order kinetic model. Hence the adsorption was not more fit to first order rate expression. This was shown in Fig.6.

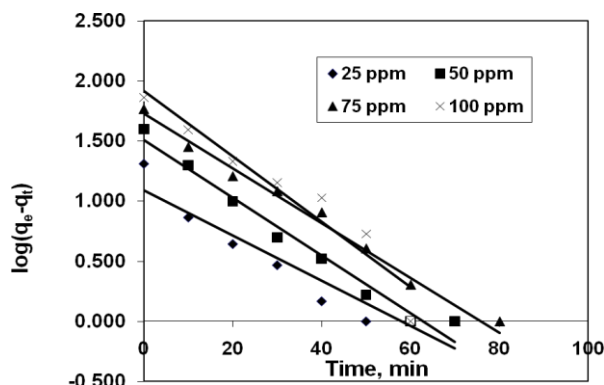


Fig 6: Pseudo first order plot for the adsorption of BV- 14 onto TWAC at 30°C (adsorbent dose = 100mg)

## Pseudo Second Order Kinetics

Adsorption of dyes on porous TWAC material has been observed that evolution of the adsorbed amount with time follows second order law

$$t/q_t = (1/k_2 q_e^2) + (1/q_e * t) \longrightarrow (7)$$

The values of  $k_2$  and  $q_e$  can be calculated from the plot of  $t/q_t$  versus  $t$ . The  $k_2$  is the second order rate constant ( $\text{g/mg min}$ ) and  $q_e$  is the equilibrium adsorption capacity ( $\text{mg/g}$ ). The correlation co-efficient ( $r^2$ ) values are greater than 0.99. This result shows that the adsorption of BV-14 dye onto TWAC follows the second order kinetics which describes the adsorption much better than pseudo-first order kinetics. Fig.7 shows the second order plot for the adsorption of BV14 onto TWAC. The calculated kinetic parameters were given in the **Table 1**.

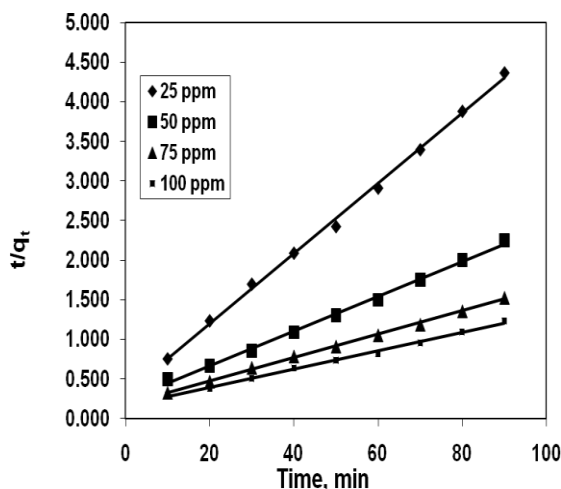


Fig 7: Pseudo Second order plot for the adsorption of BV- 14 onto TWAC at 30°C (adsorbent dose = 100mg)

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Table 1: Kinetic parameters for adsorption of BV-14 onto TWAC

Parameters	Initial dye concentration,mg/L (qt)				Temperature , °C		
	25	50	75	100	30°C	40°C	50°C
$q_e$ exp (mg/g)	20.59	40.00	58.78	73.21	40.00	38.00	41.67
Pseudo first order kinetics							
$K_1 * 10^{-2}$ (min <sup>-1</sup> )	5.9878	5.5272	5.0666	6.2181	6.2181	7.1393	5.7575
$q_e$ cal (mg/g)	16.98	32.43	53.70	82.60	37.33	33.57	34.99
$r^2$	0.972	0.975	0.984	0.928	0.995	0.991	0.963
Pseudo second order kinetics							
$K_2 * 10^{-4}$ (g/mg min <sup>-1</sup> )	2.811874	16.54082	39.61519	73.6087	1.285959	1.568627	1.652893
h	9.832841691	14.30615	15.72327	16.26016	6.802721	9.803922	8
$q_e$ cal (mg/g)	53.47594	107.5269	158.7302	212.766	43.47826	40.00	45.45455
$r^2$	0.9997	0.9995	0.9991	0.999	0.99	0.995	0.993

## Adsorption Isotherm Models

The adsorption isotherms are generally used for designing the adsorption system. For that we use linear equations of Langmuir and Freundlich. The linear equation of Langmuir is given below.

$$C_e/q_e = (C_e/Q_0) + (1/Q_0 b) \longrightarrow (8)$$

Where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $Q_0$  and  $b_L$  are constants related to monolayer adsorption capacity and energy of adsorption (L/mg). Plotting  $C_e/q_e$  against  $C_e$  gave a straight line with slope  $1/Q_0$  and intercept with  $b$  indicating the adsorption of BV- 14 dye onto TWAC.

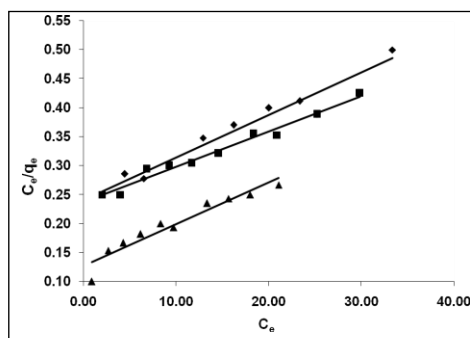


Fig 8: Langmuir adsorption isotherm plot for the adsorption of BV- 14 onto TWAC at 30°C  
(adsorbent dose = 100mg; time = 90 min)

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The Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of active sites onto the surface, since the Langmuir model assumes that the surface is homogeneous. Fig.8 shows the Langmuir isotherm for the adsorption of BV-14 onto TWAC.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems, in which it is characterized by the heterogeneity factor  $1/n$ . Hence linearised form of Freundlich equation can be written as

$$\log Q_e = 1/n \log C_e + \log K \quad \longrightarrow \quad (9)$$

Where  $K$  is the measure of adsorption capacity,  $n$  is the adsorption intensity and these values are calculated from intercept and slope of a linear plot of  $\log q_e$  versus  $\log C_e$  (Fig.9). The value of  $1/n$  is below one for the BV-14 dyes indicating that the adsorption of BV-14 dyes onto TWAC is favourable and also fits with the experimental data with correlation coefficient ( $r^2$ ) value. The calculated values are given in Table-2.

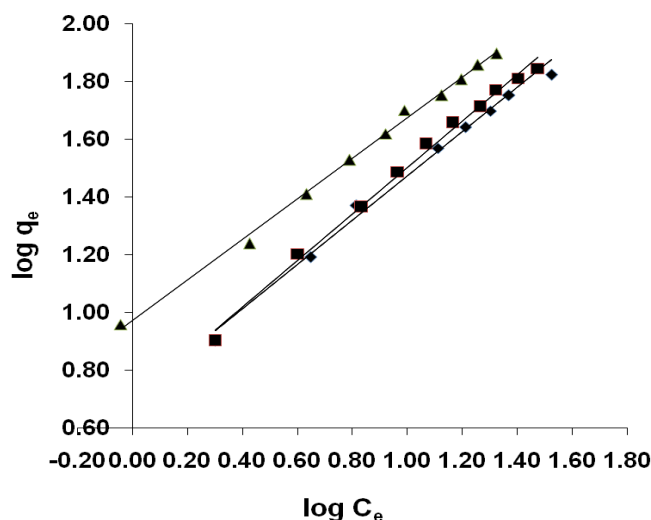


Fig 9: Freundlich adsorption isotherm plot for the adsorption of BV- 14 onto TWAC at 30°C (adsorbent dose = 100mg; time = 90 min)

Table 2: Isotherm parameters for adsorption of BV-14 onto TWAC

Statistical parameters / Constants	Isotherms	Temperature , °C		
		30°C	40°C	50°C
$r^2$	Freundlich	0.989	0.993	0.996
$K_f$		5.081	4.966	9.354
$n$		1.300	1.240	1.422
$r^2$	Langmuir	0.955	0.977	0.919
$Q_0$		142.86	166.67	142.86
$b$		0.0292	0.0253	0.0556



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## Thermodynamic Parameters

Thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) of adsorption were calculated from the binding constant which obtained from Langmuir equation using the following relations,

$$\Delta G^\circ = -RT \ln K \longrightarrow (10)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \longrightarrow (11)$$

The  $\Delta H^\circ$  values were calculated from the slopes of linear variation of  $\ln K$  versus  $1/T$ . The negative value of  $\Delta G^\circ$  indicates the high affinity of dye to the surface of TWAC and the adsorption was favourable and spontaneous in nature. The spontaneity of the process was further supported by the positive value of  $\Delta S^\circ$  ( $94 \text{ JK}^{-1} \text{ mol}^{-1}$ ). The endothermic process of adsorption was supported by positive value of  $\Delta H^\circ$ . The bonding between BV-14 dye and prepared TWAC surface is strong, since  $\Delta H^\circ$  value was found to be 20 KJ/mole to 26 KJ/mole for BV-14. The calculated thermodynamic parameters were given in **Table-3**.

**Table 3: Equilibrium constants and thermodynamic parameters for adsorption of BV-14 onto TWAC**

Initial BV 14 Concentration Mg/l	$K_0$			$\Delta G^\circ$ (kJ mol <sup>-1</sup> )			$-\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> )
	303K	313K	323K	303K	313K	323K		
20	3.50	4.00	6.50	-3.16	-3.61	-5.03	-25	92
40	3.33	3.33	5.50	-3.03	-3.13	-4.58	-20	76
60	2.70	3.11	5.17	-2.50	-2.95	-4.41	-26	94
80	2.43	2.83	4.11	-2.24	-2.71	-3.80	-21	77
100	2.00	2.35	3.75	-1.75	-2.23	-3.55	-25	89

## IV. CONCLUSION

In the present study, the investigation was made with prepared low cost, non-conventional TWAC as an adsorbent for the removal of Basic Violet-14 from aqueous solution. The investigation results showed that there was an increase of dye removal with increase in temperature from 30°C to 50°C indicates that the adsorption was endothermic in nature which was supported by positive  $\Delta H^\circ$  values. Also the data obtained from adsorption isotherms were well fitted with Freundlich than the Langmuir Isotherm models by a linear straight line and the parameters suggested that the adsorption of BV-14 onto TWAC follows the monolayer adsorption. The kinetic studies showed that the adsorption of BV-14 onto TWAC followed pseudo second order kinetics and also suggests the monolayer coverage of the dye molecule. The adsorption of BV14 onto TWAC was more favourable at acidic pH rather than the alkaline pH. Thermodynamic parameters calculated for the adsorption of Basic Violet-14 was spontaneous and endothermic with negative  $\Delta G^\circ$  ranges from -1.75 to -5.03 KJ/mol and the positive  $\Delta H^\circ$  value ranges from 20- 26 KJ/mol. Hence the prepared TWAC is an alternate to commercial activated carbon and also effective for the removal of BV-14 from aqueous solution.

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