

# Adsorption of Basic Blue 12 From Cocoa (*Theobroma Cacao*) Shell Activated Carbon-Equilibrium Isotherm Analyses



## Chemistry

**KEYWORDS :** adsorption, cocoa shell, dyes, isotherm

Dr.S.Mylsamy

Professor, Department of Chemistry, Shree Venkateshwara Hi-Tech Engg. College, Gobi, Erode-638 455, India.

### ABSTRACT

The ability of cocoa shell activated carbon (CSAC) was used to remove Basic blue 12 (BB12) dye from aqueous solution by adsorption have been studied. Equilibrium isotherms for the adsorption of BB14 onto CSAC were measured experimentally. Results were analyzed by Langmuir, Freundlich, Tempkin and Harkin's-Jura isotherm equations using a linearised correlation coefficient. The Langmuir isotherm gave the best correlation for the adsorption of BB12 onto CSAC. Thermodynamic parameters such as  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were evaluated. The positive enthalpy shows that the adsorption process was endothermic in nature. The results show that CSAC holds a great potential in removal of BB12 dye from industrial wastewater.

### 1. INTRODUCTION

Synthetic dyes are used extensively in dyeing and printing processes. Textile and dyeing industry effluents can create serious environmental pollution problems when they are discharged into water bodies [1]. The colored wastewater discharge into environmental water bodies interferes with transmission of sunlight into streams, therefore, reduces photosynthetic activity. In addition, some dyes are either toxic or mutagenic and carcinogenic adverse effect of dyes on environment and human such as skin, lung and other respiratory disorders are also reported [2]. Several techniques have been developed to treat dye effluents such as microbial degradation, chemical oxidation, membrane separation, electrochemical treatment, adsorption and reverse osmosis [3]. Among these techniques, adsorption is generally preferred due to easy handling, high efficiency, low energy input and availability of different adsorbents. The most commonly used adsorbent for dye removal was activated carbon [4].

### 2. MATERIALS AND METHODS

#### 2.1 Adsorbent preparation

Cocoa shell, an agro-waste collected from local agricultural field was air-dried and allowed to chemical activation, by the addition of 50% sulfuric acid with constant stirring (w/v). The resulting black product obtained was kept in muffle furnace maintained at 550°C for 7 hours. The carbon obtained was washed with double distilled water and soaked in 10% sodium bicarbonate solution and allowed to stand overnight to remove the residual acid from pores of the carbon. The material was washed with distilled water, until the pH of the adsorbent reached 7.0. Then it was dried in a hot air oven at 100±5 °C for 12 hours. The dried material was ground and sieved to get the particle size of 150µm and stored in an airtight container. The physico-chemical characteristics of CSAC were studied as per the standard testing methods and reported in our earlier paper [7].

#### 2.2 Adsorbate preparation

Stock solution of Basic blue 12 (Molecular formula: C<sub>20</sub>H<sub>20</sub>CIN<sub>3</sub>O, M.W.: 353.84, C.I. no.51180, CAS: 2381-85-3) was prepared by dissolving 1gm of dye in 1000ml of double distilled water to give the concentration of 1000mg/L. The stock solutions were diluted with known initial concentrations say 20, 40, 60 and 80mg/L in accurate proportions.

#### 2.3 Adsorption experiments

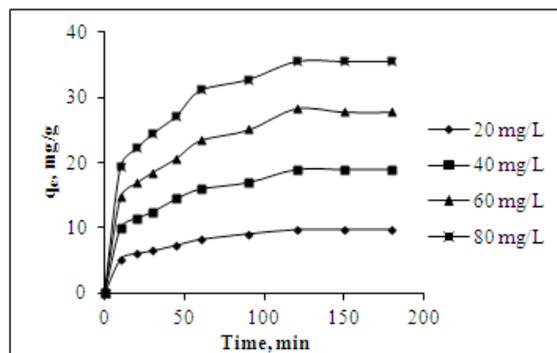
Adsorption experiments were carried out in temperature controlled orbital shaker at a constant speed of 125rpm using 250mL conical flasks containing 100mg of activated carbon with 50mL of dye solution at 35°C. All the experiments were carried out at pH of 7±0.5. After agitating the flasks for predetermined time intervals, samples were withdrawn from the flasks and the adsorbents were separated from the solution by centrifugation (REMI make) at 2000rpm for 10 minutes.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of agitation time and initial concentration

To study the effect of dyes initial concentration and contact

time on adsorption uptake, BB12 solution with initial concentrations 20-80mg/L were agitated with 100mg of CSAC. The experimental results of adsorption of BB12 onto CSAC at various initial concentrations are shown in Fig. 1. The adsorption at different dye concentrations was rapid at the initial stages and then gradually decreases with the progress of adsorption until the equilibrium was reached. The rapid adsorption at the initial contact time can be attributed to the availability of the positively charged surface of activated carbon. As shown in Fig. 1, the contact time needed for BB12 solution to reach equilibrium was 120mins. The results indicated that there was no change in the sorption capacity after 120mins; therefore 180mins was fixed as the agitation time for isotherm studies. The adsorption capacity at equilibrium ( $q_e$ ) increased from 5.22 to 35.56mg/g with an increase in the initial concentrations from 20 – 80mg/L.



**Fig. 1 Effect of agitation time on adsorption: Initial concentration variation**

#### 3.2 Adsorption isotherm

To optimize the design of an adsorption system for the adsorption of dye wastewater, it is important to establish the most appropriate correlation for the equilibrium curves. Langmuir, Freundlich, Tempkin and Harkin's-Jura isotherm models were used to describe the equilibrium characteristics of adsorption.

##### 3.2.1 Langmuir isotherm

The basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a dye molecule occupied a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond no further sorption can take place [8]. The linear form of Langmuir model is represented by equation

$$\frac{C_e}{q_e} = \frac{1}{b} Q_0 + \frac{C_e}{Q_0} \quad (3)$$

where,  $C_e$  is equilibrium constant of dye (mg/L),  $q_e$  is amount of dye adsorbed at equilibrium (mg/g),  $Q_0$  is Langmuir constant related to adsorption capacity (mg/g),  $b$  is Langmuir constant related to energy of

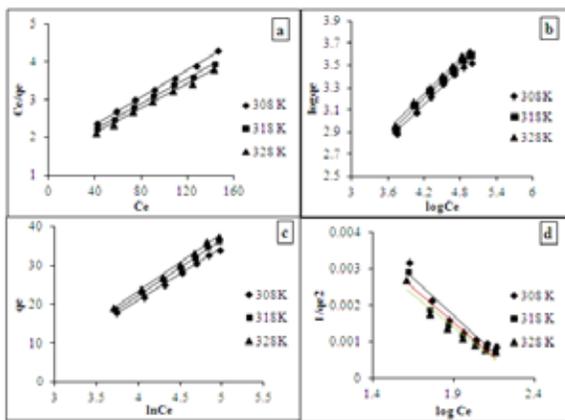


Fig. 2 Adsorption isotherm plots

(a) Langmuir plot (b) Freundlich plot (c) Tempkin plot (d)Harkin's -Jura plot adsorption capacity (L/mg). The linear plot of Ce/qe versus Ce for 308K, 318K and 328K was shown in Fig. 2(a). The constants Q0 and b can be calculated from slope and intercept of the plot and the values are tabulated in Table-1. The shape of the Langmuir isotherm was investigated by the dimensionless constant separation term (RL) to determine high affinity adsorption. RL is calculated as follows

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where, Co is the initial dye concentration(mg/L). RL indicates the type of isotherm to be irreversible (RL= 0), favorable (0 < RL< 1), linear (RL = 1) (or) unfavorable (RL > 1). In the present investigation, the RL values were less than one which shows the adsorption process was favorable.

**3.2.2 Freundlich isotherm**

Freundlich isotherm is driven by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface [9].

Table-1 Results of various isotherm plots

Temperature, K	308	318	328
Langmuir			
Q0 (mg /g)	55.55	58.82	62.5
b x 10-3 (L/mg)	11.1	10.9	10.8
RL	0.4443	0.4482	0.4477
r2	0.998	0.996	0.996
Freundlich			
n	1.88	1.85	1.87
kf (mg/g)	2.5	2.55	2.75
r2	0.991	0.994	0.993
Tempkin			
α(L/mol)	0.09	0.08	0.09
β	13.46	14.45	14.76
b	190	184	185
r2	0.997	0.996	0.996
Harkin's-Jura			
A	250	333	333
B	2.25	2.66	2.67
r2	0.933	0.930	0.933

**3.2.3 Tempkin isotherm**

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that; (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [10]. Tempkin isotherm model is represented by the equation

$$q_e = \frac{RT}{b} \ln AC_e \quad (6)$$

The linear form of Tempkin equation is

$$q_e = \beta h \alpha + \beta h C_e \quad (7)$$

where,

$$\beta = \frac{RT}{b} \quad (8)$$

T is the absolute temperature in Kelvin, R is the universal gas constant, 8.314 J/(molK), b is the Tempkin constant related to heat of sorption (J/mg) and A the equilibrium constant corresponding to the maximum binding energy (L/g)

The Tempkin constants α and b are calculated from the slope and intercept of qe versus lnCe (Fig. 3(c)) and parameters are given in the Table-1.

**3.2.4 Harkin's - Jura isotherm**

Harkin's - Jura isotherm assumes the presence of multilayer adsorption with the existence of heterogeneous pore distribution [11]. The Harkin's-Jura isotherm is expressed as

$$\frac{1}{q_e^2} = \frac{B}{A} - \frac{1}{A} \log C_e \quad (9)$$

where, Ce is the equilibrium concentration of the dye in solution (mg/L), qe is the amount of dye adsorbed onto the adsorbent (mg/g), A and B are the isotherm constants. The plot of 1/qe<sup>2</sup> versus logCe gives a linear plot(Fig.3(d)) and the isotherm constants and correlation coefficients are given in Table -1.

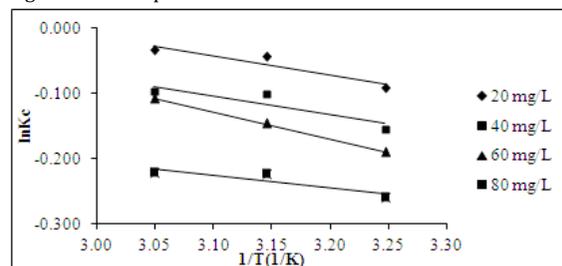
**3.3 Adsorption Thermodynamics**

The thermodynamic parameters like ΔH°, ΔS° and ΔG° of adsorption were measured based on van't Hoff's relationship

$$\ln k_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where, kc is the Langmuir equilibrium constant, ΔH° and ΔS° are the standard enthalpy and entropy changes of adsorption respectively. The ΔH° and ΔS° values can be calculated from the slope and intercept of a plot of ln kc versus 1/T.

Fig. 3 van't Hoff plot



The free energy of adsorption ΔG° (KJ/mol) is calculated from the following equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

van't Hoff plot for the adsorption process is given in Fig. 3 and the results are presented in Table-2.

Table-2 Thermodynamic parameters

Conc., mg/L	$\Delta H^{\circ}$ kJ/mol	$\Delta S^{\circ}$ J/ molK	$\Delta G^{\circ}$ ( kJ/mol)		
			308K	318K	328K
20	2.44	7.20	-2.22	-2.29	-2.36
40	2.39	6.56	-2.02	-2.08	-2.15
60	3.44	9.61	-2.96	-3.05	-3.15
80	1.62	3.17	-0.97	-1.01	-1.04

The positive enthalpy ( $\Delta H^{\circ}$ ) proves the adsorption process was endothermic in nature. The value of  $\Delta H^{\circ}$  are within the range of 1 to 93 kJ/mol indicating the physisorption is much more favorable for the adsorption of BB12 onto CSAC. Entropy has been defined as degree disorder of the system. Positive values of  $\Delta S^{\circ}$  suggested good affinity of the dye towards the adsorbent and the adsorption was spontaneous in nature [12]. Negative value of  $\Delta G^{\circ}$  indicated the adsorption process was feasible and spontaneous in nature. The decrease in the negative value of  $\Delta G^{\circ}$  with an increase in temperature indicates that the adsorption process of BB12 on CSAC becomes more favorable at higher temperatures [13].

### 3.4 DESORPTION STUDIES

Desorption studies help to elucidate the mechanism of adsorption and recovery of the adsorbate and adsorbent. The regeneration of the adsorbent may make the treatment process economical. Neutral pH water, sodium hydroxide (1M), sulphuric acid (1M) and 50% acetic acid (v/v) were used for desorption of BB12 dye by CSAC.

### 4. CONCLUSIONS

In this study, activated carbon prepared from cocoa shell, an agro waste was tested for removing BB12 from aqueous solution. The batch study parameters were found to be effective on the adsorption efficiency of BB12 onto CSAC. The experimental data obtained isotherm studies well fitted the Langmuir isotherm model with good correlation coefficient. The positive enthalpy proves that the adsorption of BB12 onto CSAC was endothermic in nature. Desorption studies and thermodynamic studies confirm physisorption mechanism. Results indicated that CSAC could be employed as a low cost alternative for BB12 dye removal from aqueous solution.

## REFERENCE

- [1] Sumanjith, Tejinder Pal Singh Walia and Ishu Kansal. (2008), "Removal of Rhodamine-B by adsorption on Walnut shell Charcoal." *Journal of Surface Science Technology*, 24(3-4), 179-193. | [2] Md. Tamez Uddin, Md. Rakanuzzaman, Md. Maksudur Rahman Khan and Md. Akhtarul Islam. (2009), "Jackfruit (*Artocarpus heterophyllus*) leaf powder: An effective adsorbent for removal of methylene blue from aqueous." *Indian Journal of Chemical Technology*, 16, 142-149. | [3] Yi Liua, JintaoWanga, Yian Zhenga and Ai QinWanga. (2012), "Adsorption of methylene blue by kapok fiber treated by sodium chlorite optimized with response surface methodology." *Chemical Engineering Journal*, ELSEVIER, 184, 248-255. | [4] Vasanth Kumar, K. (2006), "Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon." *Journal of Hazardous Materials*, ELSEVIER, B137, 1534-1544. | [5] Gre'gorio Crini. (2005). "Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment." *Progress in Polymer Science*. ELSEVIER, 30, 38-70. | [6] Upendra Kumar. (2006). "Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review." *Scientific Research and Essay*, 1(2), 33-37. | [7] Mylsamy Shanker and Theivarasu Chinnigounder. (2012). "Adsorption of Reactive Dye Using Low Cost Adsorbent: Cocoa (*Theobroma Cacao*) Shell." *World Journal of Applied Environmental Chemistry*, 1(1), 22-29. | [8] Vaishnav Vinod, Daga Kailash, Chandra Suresh and Lal Madan. (2012). "Adsorption Studies of Zn (II) ions from Wastewater using Calotropis procera as an Adsorbent." *Research Journal of Recent Sciences*, 1, 160-165. | [9] Zhe XU, Jian-guo CAI and Bing-cai PAN. (2013). "Mathematically modeling fixed-bed adsorption in aqueous systems." *Journal of Zhejiang University-SCIENCE A (Applied Physics & Engineering)*, 14(3), 155-176. |