



Thermodynamics and Instrumental Analysis of Bismarck Brown R Dye onto Activated Carbon Prepared from *Delonix Regia* Pods (Flame Tree)

A.Rajappa¹, K. Ramesh², V.Nandhakumar^{3*}, M. Pugazhenth⁴ and S.Sivajiganesan⁴

¹Department of chemistry, Sri Manakula Vinayagar Engineering College, Madagadipet, Puducherry, India.

²Department of chemistry, Arasu Engineering college, Kumbakonam, Thanjavur, India.

^{3*}&⁴ Department of chemistry, A.V.V.M Sri Pushpam college, Poondi, Thanjavur, India.

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Abstract

This work deals with the study of adsorption Bismarck Brown R dye from aqueous solution onto Carbon prepared from *Delonix regia* pods activated with Zinc chloride (DRZAC). Batch mode adsorption experiments were conducted. The characteristics of the DRZAC were determined by SEM, XRD, FTIR, BET analysis and pH_{ZPC}. Thermodynamic parameters for such as H° , S° , and G° were determined using Van't Hoff plots. Analysis of these values inferred that the adsorption was endothermic and spontaneous with increased randomness. The FTIR and XRD studies confirmed that adsorption was physisorption with partial chemisorption. The results in this study indicated that DRZAC could be employed as an adsorbent for the removal of Bismarck Brown R dye from an aqueous solution.

Keywords: Adsorption, *Delonix regia* ZnCl₂ activated carbon, Bismarck Brown R dye, Thermodynamic study, Instrumental (FTIR, XRD, SEM,) analysis.

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*Corresponding author

V. Nandhakumar

Department of chemistry, A.V.V.M
Sri Pushpam College, Thanjavur, India.
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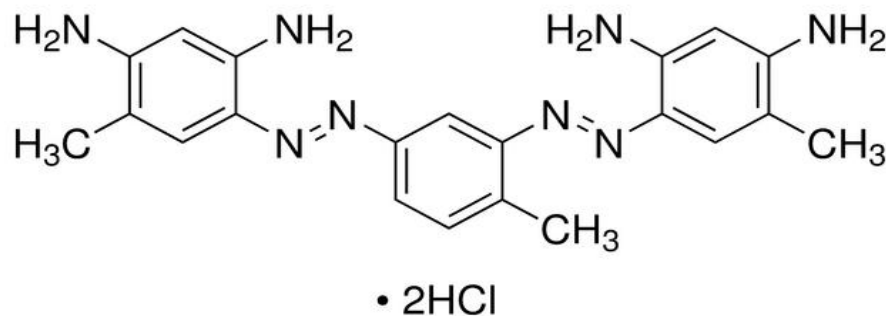
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1. Introduction

The release of dyes into wastewaters from textile, cosmetic, paper, coloring industries poses serious environmental problems. The coloration of the water by the causes inhibitory effect on photosynthesis affecting aquatic ecosystems [1]. Adsorption of Bismarck Bismarck Brown R dye from the aqueous phase is a useful tool for product control of adsorbents. Some kinds of *Delonix regia* pods have been studied as adsorbents for removal of Bismarck Brown R dye from aqueous solution [2]. Adsorption using activated carbon is most widely used method to remove dyes from aqueous solution. But its use is limited because of high cost and associated problems of regeneration, there is a constant search for cheaper substitutes. Many efforts have been made to use low cost agro waste materials in substitute for commercial activated carbon. Some agro waste materials studied for their capacity to remove dyes from aqueous solutions are coir pith [3], Cocoa shell [1] etc.

Azo dyes are divided according to the presence of azo bonds ($-N=N-$) in the molecule; these include mono azo, diazo, triazo etc [4]. Azo dyes resist the effect of oxidation agents and light, thus they cannot be completely treated by conventional methods of anaerobic digestion [5]. It is necessary to find an effective method for the treatment of Bismarck Brown R. The degradation of Bismarck brown R dye in the presence of aqueous zinc oxide suspension has been reported [6]. The adsorption technique proved to be an effective and attractive process for removing dyes from aqueous solutions in terms of initial cost, ease of operation, insensitivity to toxic substance, high efficiency, easy recovery and simplicity of design [7].

Structure of Bismarck Brown R Dye:



The present research is to remove Bismarck Brown R dye from aqueous solution using activated carbon prepared from *Delonix regia* pods (Flame tree).

2. Materials and methods

2.1 Materials:

All the chemicals used for this experiment are of analytical grade. Activated Carbon was prepared from *Delonix Regia* pods. Bismarck brown R a cationic dye purchased from Merck Company. Xray Diffraction studies of the DRZAC were carried out using D8 Focus powder XRD, company Bruker, make Germany. The FTIR spectra were measured within the range of $400-4000\text{cm}^{-1}$ in a FT- spectrometer, Make-Perkin Elmer, Model- Spectrem one, Version-5.0.1.

2.2 Preparation of Dye Solution:

Bismarck brown R dye was used without further purification. The dye stock solution was prepared by dissolving appropriate amount of accurately weighed dye in double distilled water to a concentration of 500 mg/L. The experimental solutions were prepared by proper dilution.

2.3 Preparation of Adsorbent:

Delonix Regia pods were collected in the region of Kumbakonam, Thanjavur District. *Delonix Regia* pods repeatedly washed with distilled water to remove dirt, dust and impurities. The washed materials were then dried in sunlight for a month. The dried shells were chopped into small chips. Chemical activation of the *Delonix Regia* pods was carried out with ZnCl_2 solution. 20g of dried *Delonix Regia* pods were well mixed with 20ml desired concentration of (20%, 40%) of ZnCl_2 1:1 w/v solution. The slurry was kept in an air oven at 100°C for 24 hours. The resulting product was then subjected to carbonization and activation process in a muffle furnace at 400°C for 1 hour. Then the sample was cooled and subsequently washed with 0.05M HCl and then with deionized water for several times. It was ground and sieved. The particle size ranged between 110 μm & 90 μm were taken and kept in a desiccator for further use.

2.4 Physical Characterization of DRZAC

The properties of DRZAC were given in Table 1. The total surface areas were calculated using the BET equation [8].

Table 1: Physico-chemical characteristics of DRZAC

S.No	Properties	DRZAC Values
1.	pH zpc	6.0
2.	Particle size, mm	90-110
3.	Surface area (BET), m^2/g	916.1234
4.	Pore volume, cm^3/g	0.3986
5.	Pore size (Pore width), nm	2.7174
6.	Bulk density, g/mL	0.52
7.	Fixed Carbon, %	71.11
8.	Moisture content, %	4.36

2.5 Determination of point of zero charge:

20 mg of the DRZAC was added to 50ml of 50 ppm Bismarck brown R dye solution taken in 250 ml of Iodine flask. The initial pH values of the solutions were adjusted to 2.0 to 10.0 by adding either 0.1M HCl or 0.1M NaOH. The mixtures were allowed to equilibrate for 24 hrs with periodic shaking. The pH values of the supernatant liquid were determined. A plot of the initial pH versus final pH was drawn. From the horizontal portion, the pH zpc was evaluated which is shown in figure 1 [9].

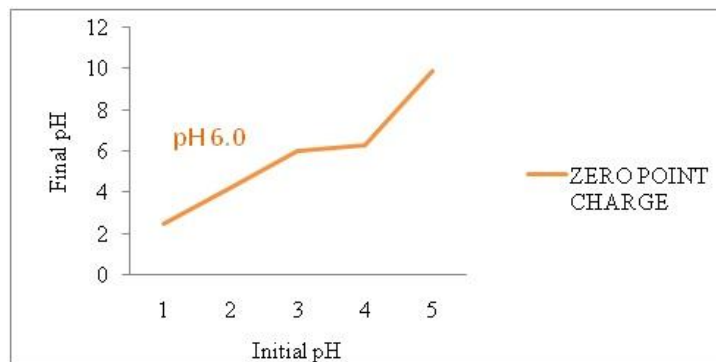


Figure 1: point of zero charge

2.6 Adsorption Experiments:

20mg of DRZAC was interacted with 50ml known concentration of Bismarck brown R dye solution in a Iodine flask at predetermined temperatures. The mixtures were agitated in a mechanical shaker at 180 rpm continuously for predetermined time intervals. It was then centrifuged. The concentration of dye in the centrifugate was determined using Systronics Double Beam UV-visible Spectrophotometer: 2202 at 470 nm. The amount adsorbed at equilibrium, q_e (mg/g), was calculated as follows:

$$q_e = (C_0 - C_e) / V / W$$

Where, C_0 and C_e (mg/L) are the liquid-phase concentrations of BBR dye at the initial stage and the equilibrium respectively. V (L) is the volume of the Bismarck brown R dye solution and W (g) is the weight of the adsorbent used. The percentage dye removal was calculated as:

$$\text{Percentage of removal} = (C_0 - C_e) / 100 / C_0$$

2.7 Effect of temperature:

To observe the effect of temperature on the adsorption capacity, experiments are carried out at three different temperature (30, 40 and 50°C) using 20mg of DRZAC per 50 ml 50 ppm of the solution. The experiment was carried out in a constant temperature water bath. It was seen that as the temperature was increased, the dye removal was also increased [10].

3. Results and Discussion

3.1 Effect of Contact time and initial concentration:

The effect of contact time on percentage removal of dye for different initial concentration have been shown in figure 2. Adsorption of dye from the solution increases with the time and finally attains equilibrium in 80,100 and 120 minutes for the initial concentrations of adsorbates 50,100 and 150 mg/L respectively. The percentage of removal increased with the increase in contact time and decreased with the increase of initial concentration of the dye. However the amount of dye adsorbed on the adsorbent increased with the increase of initial concentration of the dye solution [11]. Which is depicted in figure 3 and given in table 2.

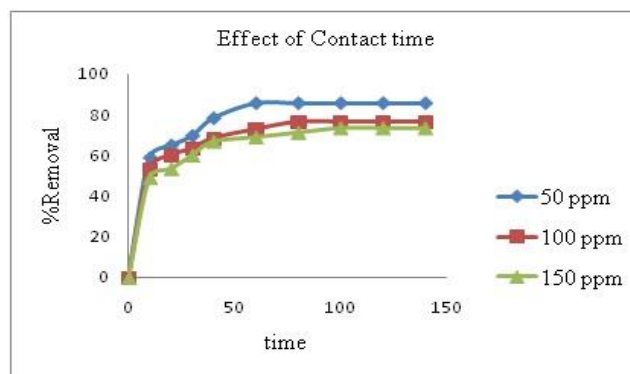


Figure 2: Effect of Contact time and initial concentration

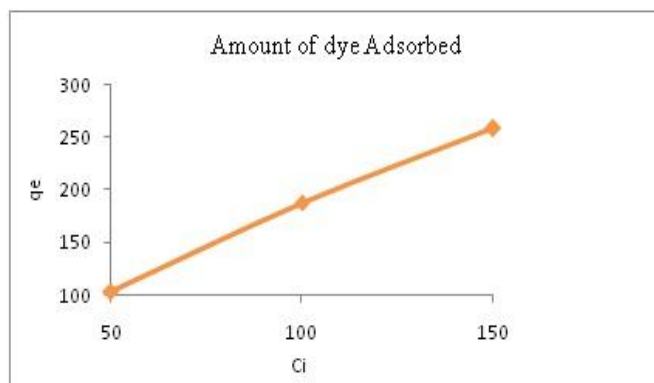


Figure 3: Amount of dye adsorbed at equilibrium

Table 2: Percentage of removal of dye and amount of dye adsorbed

Ci (mg/L)	% of Removal of dye At equilibrium	Adsorption capacity at equilibrium (mg/g)
50	85.34	104.17
100	76.33	187.50
150	73.33	258.33

3.2 Effect of pH:

Figure 4 shows the effect of pH on the adsorption of BBR dye onto DRZAC. It is found that percentage of removal of dye from aqueous solution increases with the increase of pH of the solution. This may be due to two reasons, one reason is accumulation of H^+ ion on the surface of the adsorbent at lower pH may exert repulsive force towards the cationic dye approaching the adsorbent. As the pH of the solution increases up to 7, the accumulated H^+ ion on the surface decreases and hence the repulsive force exerted on the approaching cationic dye decreases which facilitates the increase of percentage removal of the dye solution. Increase of pH from 7 to 14 may increase the accumulation of OH^- ion on the surface of the adsorbent which attracts the cationic dye, thus the smaller OH^- ions are gradually replaced by larger dye ions. This effect becomes more pronounced as the pH increases from 7 to 14. The second reason is increase of pH beyond 7 may precipitate the cationic dye. In order to understand this possibility, experiments were carried out with and without adsorbent at alkaline pH. It is found that the concentration of dye solution remains constant in alkaline solutions having no adsorbent, but the concentrations of dye were found to decrease in alkaline solutions having the adsorbents. Thus the possibility of dye removal due to precipitation was not happened. However, the other adsorption experiments were carried out at neutral pH only.

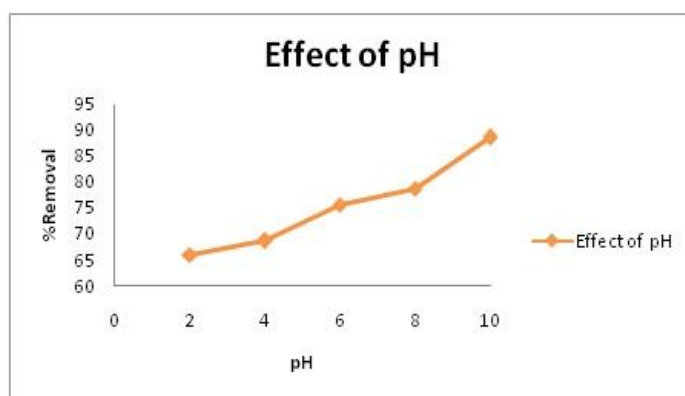


Figure 4: Effect of pH

4. Thermodynamic studies

Thermodynamic parameters like H° , S° and G° were measured based on van't Hoff's plot.

$$G = -RT \ln K_L \quad (\text{Gibbs Equation})$$

$$\ln K_L = -\frac{H^\circ}{RT} + \frac{S^\circ}{R} \quad (\text{Van't Hoff equation})$$

Where, K_L is the equilibrium constant, H° and S° are the standard enthalpy and entropy changes of adsorption respectively and the values of H° and S° are calculated from the slopes and intercepts of the linear plot of $\ln K_L$ vs $1/T$. The free energy of specific adsorption G° (kJ/mol) is calculated from the following expression

$$G^\circ = H^\circ - T S^\circ$$

The thermodynamical parameters calculated from van't hoff plot are given in table 3. Negative standard free energy of adsorption indicates that the adsorption process is favourable and spontaneous in nature. The endothermic nature of adsorption is confirmed by the positive H° values. The bonding between BBR dye and DRZAC surface is very weak, since H° values are found to be in between 32.26 to 16.10 kJ/mol. Positive values of S° suggested good randomness of the adsorption process [12].

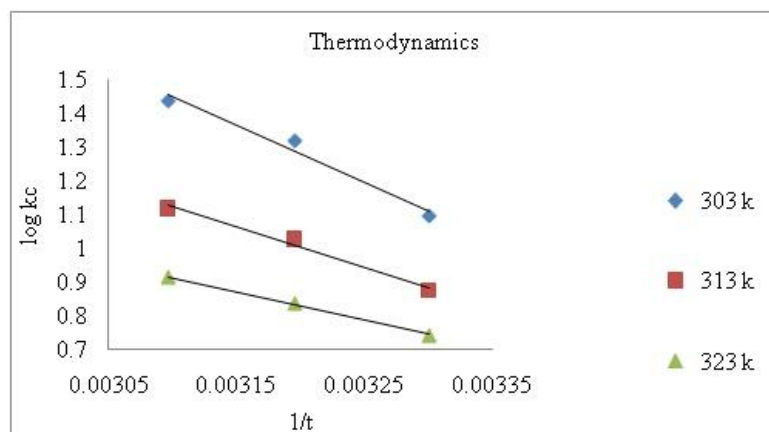


Figure 5: Thermodynamics

Table 3: Thermodynamics parameters for the adsorption of BBR dye onto DRZAC

Ci mg/L	G° kJ/mol			H° kJ/mol	S° kJ/mol
	303K	313K	323K		
50	-6.21	-7.49	-8.76	32.26	0.127
100	-5.01	-5.01	-6.85	22.86	0.092
150	-4.20	-4.20	-5.54	16.10	0.067

5. Instrumental Analysis

5.1 XRD Study:

The XRD pictures were taken before and after adsorption. New two peaks were formed in between the $2-\theta$ values of 27 and 30 after adsorption.. This may be due to formation of new chemical bonds. This results lead to conclude that physisorption with partial chemisorption.

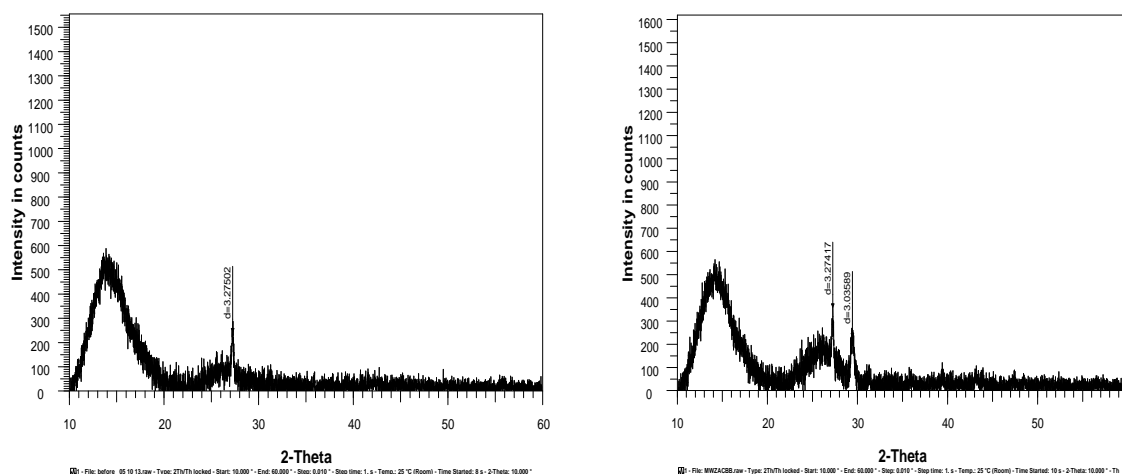


Figure 6: XRD Pattern of DRZAC Before and after adsorption of BBR dye

5.2 FTIR Study:

Fourier transform infrared spectroscopy (FTIR) was used to determine the functional group on the DRZAC surface. It is noticed that six new peaks were formed after adsorption which may be due to formation new chemical bonds. This results confirm that physisorption with partial chemisorption.

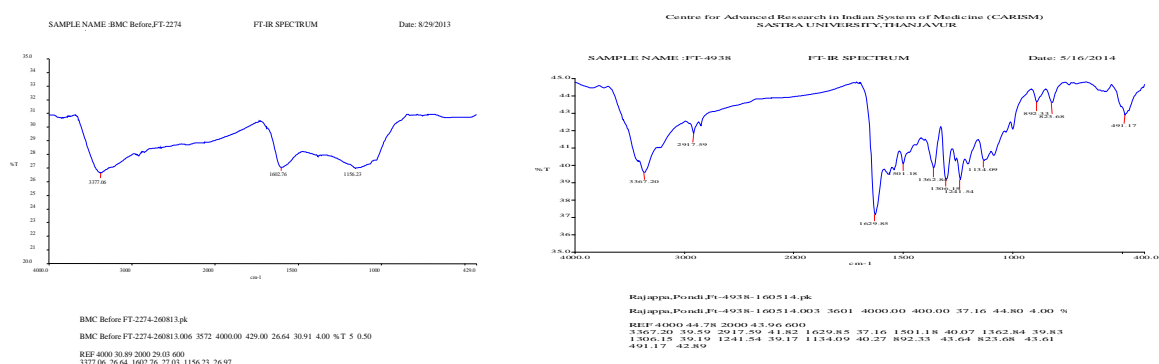


Figure 7: FTIR Spectrum of DRZAC Before and After adsorption of BBR dye

5.3 SEM Analysis:

The surface morphology of the DRZAC carbon was examined using scanning electron microscopy (SEM), the corresponding SEM Micrographs being obtained using at an accelerating voltage of 15kv at 2500x and 3.0kv at 1500 x magnifications (Figure 8). At such magnification, the activated carbon particle showed rough areas of surface on which micro pores and macro pores were clearly identifiable.

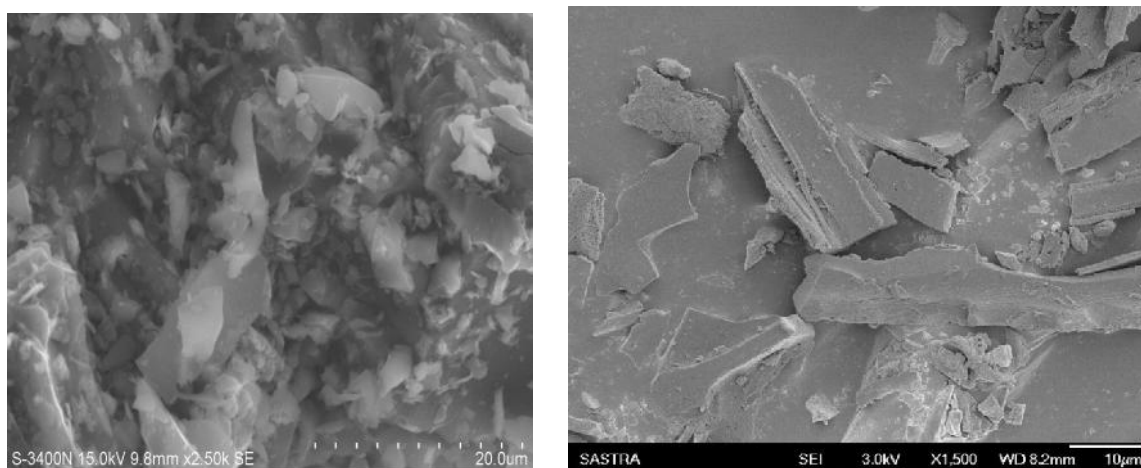


Figure 8: SEM micrograph of DRZAC before and after adsorption of BBR dye

6. Conclusion

This study shows that DRZAC can be used effectively for the removal of BBR dye from aqueous solution. The adsorption of BBR dye onto DRZAC increased with the increasing of initial concentration of dye. Thermodynamics parameters such as H^0 , S^0 , G^0 values inferred that the adsorption was spontaneous, endothermic and physical nature. The instrumental analysis FTIR, XRD studies gives an idea that adsorption was physisorption with partial chemisorption. SEM pictures described the porosity of DRZAC.

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