

REMOVAL OF REACTIVE BLACK 5 DYE FROM WATER BY ADSORPTION ONTO CARBON ADSORBENT PREPARED FROM A NATURAL BIO WASTE *BAUHINIA RACEMOSA* FRUIT PODS

S. UMA DEVI* AND P. PRABHAKAR¹

*Department of chemistry, Sri GVG Visalakshi College for Women, Udumalpet, Tamil Nadu, India

¹Department of chemistry, Arulmigu Palaniandavar College of Arts and Culture, Palani, Tamil Nadu, India

(Received 18 November, 2019; accepted 24 January, 2020)

ABSTRACT

The adsorption of Remazol Black 5 (RB 5) dye onto chemically activated carbon adsorbent prepared from fruit pods of *Bauhinia Racemosa* was carried out by adsorption technique. Batch adsorption experiments were performed to find out the effect of adsorbent dose, pH and temperature on the removal of RB 5 dye from aqueous solution. The results revealed that percentage removal of the dye was 60 -70 % at pH 6.8 with contact time of 120 minutes. The optimum dosage amount of adsorbent was 0.05g / 100 mL. Acidic pH was suitable for the adsorption of RB 5 dye. The equilibrium adsorption behavior was measured by applying Langmuir and Freundlich adsorption isotherm models. The FE-SEM images of the adsorbent clearly indicate the existence of large number of pores on the external surface of the adsorbent provide binding sites for the adsorption of dye molecules.

KEY WORDS: Adsorption, Remazol Black 5, *Bauhinia Racemosa*, Adsorption isotherms

INTRODUCTION

Environmental pollution is one of the greatest problems that the world is facing today. All kinds of industries contribute various forms of pollutants to the environment. These pollutants can kill animals and plants, affect human lives and health, imbalance ecosystems, degrade water, air quality and soil (Kudesia, 2015). Large quantities of water are required for textile processing, dyeing and printing. The waste water released from these industries contains huge amount of dyes, number of chemicals and other materials which are unsuitable for further use and can cause environmental problems. Since dyes possess complex aromatic molecular structure and high stability to heat and light, they remain in the environment and resist biodegradation (Ventura and Martin, 2013).

Many dyes and their degradation products are carcinogenic and mutagenic. Textile dyes can also cause allergies such as contact dermatitis, respiratory diseases, skin irritation and irritation to

mucous membrane (Gupta and Suhas, 2009). A number of conventional physical, chemical and biological treatment methods are used for waste water treatment and they vary in their environmental impact, effectiveness and cost. (Mahajan, 2004).

Adsorption is an effective technique and carbonaceous materials that exhibit high degree of porosity, large surface area and good mechanical properties are used as adsorbents to remove toxic, non-biodegradable substances from waste waters.

Adsorption using Commercial activated carbon as adsorbent is a powerful technology for dye removal from aqueous effluent due to its huge surface area and outstanding adsorption capacity. But its high regeneration cost has led to search for more suitable, efficient and cheaper natural adsorbents particularly from the waste material (Bharthi and Ramesh, 2013). Natural materials or the waste / agricultural by-products, industrial by-products or synthetically prepared materials which cost less can be used as such or used after some

minor chemical treatment as adsorbents. They are generally called low-cost adsorbents and they also act as substitutes for activated carbon (Gupta *et al.*, 2009).

In view of the above facts the present work is aimed to study the removal of Remazol Black-5 (RB5) dye from aqueous solution and also from dyeing industrial effluent by adsorption technique using a low cost, eco- friendly carbon adsorbent prepared from the fruit pods of naturally occurring biomass *Bauhinia racemosa* using H_3PO_4 was carried out.

MATERIALS AND METHODS

Preparation of Adsorbent

The low cost activated carbon adsorbents used in this research study was prepared from the fruit pods of *Bauhinia racemosa*. The fruit pods of *Bauhinia racemosa* were collected and cut into small pieces, dried in sunlight for 10 days and further dried in hot air oven at 80 °C for 24 hours. The completely dried material was powdered well and chemically activated by treating it with 60% phosphoric acid with constant stirring and kept for 24 hours at room temperature. It was then activated at 700 °C in muffle furnace for 30 minutes. The carbonized material thus obtained was washed well with plenty of water several times to remove excess of acid present and then dried at 110 °C–120 °C in a hot air oven for 24 hours. The adsorbent thus obtained was ground well and sieved through a 383 K to 393 K mesh and kept in air tight containers for further use (Umadevi and Renuga Devi, 2018). The adsorbent material is abbreviated as BR-PAC.

The parameters pH, moisture content, ash content, specific gravity, Methylene blue adsorption, acid soluble matter and water soluble matter of the prepared adsorbent were determined by following standard ISI 1989 procedures. The BET surface area of the adsorbent was determined using BET (Brunauer, Emmett and Teller) analyzer (1994-2012, Quantachrome Instruments Version 3.0) at Chemistry research centre, Bangalore Institute of Technology, Bangalore, India (Table 1).

Preparation of Adsorbate

The dye Remazol Black 5 (RB5) used in the present study were procured commercially from SD-Fine chemicals, Mumbai and used without further purification. All the chemicals used in this study

Table 1. Characteristics of Activated Carbon

S.No	Parameters	BR-PAC
1	pH	6.9
2	Moisture content (%)	1.81±0.05
3	Ash content (%)	2.94±0.04
4	Specific gravity	1.32
7	Methylene blue adsorption (mg/g)	363
8	(pHzpc)	6.3
9	Acid soluble matter (%)	1.70
10	Water soluble matter (%)	1.62
11	BET Surface area (m ² /g)	1083.44
12	Pore volume(cm ³ /g)	1.113

were of analytical grade. The chemical structure of the dye used in this study is shown in (Fig. 1). The stock solutions were prepared by dissolving 1g of dye in 1000 mL of distilled water.

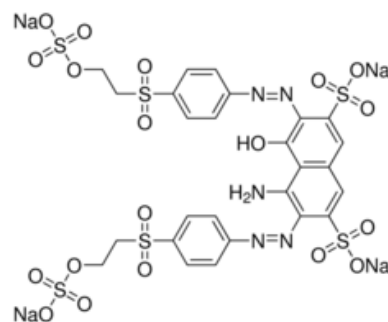


Fig. 1. Remazol black 5 (RB5)

Batch Adsorption Experiments

Batch adsorption studies were carried out to study the adsorption capacity of the adsorbent BR-PAC. These experiments are simple and very effective for assessing the basic parameters affecting the adsorption process. Different initial concentration (30, 50, 70 and 100 mg/L) of dye solutions (100 mL) were taken in Pyrex bottles having 50 mg BR-PAC adsorbent. Then the adsorbent and adsorbate mixture was agitated at 120 rpm speed on a horizontal electrical bench shaker for 120 minutes at three different temperatures (303 K, 313 K and 323 K). The adsorbate was separated from the adsorbent by centrifugation and the residual dye concentrations were measured using spectrophotometer at 597nm for RB 5 dye solution.

The influence of pH and the influence of adsorbent dosage on dye adsorption were studied by changing the pH of the dye solution (2 to 10) and adsorbent dose (25, 50, 75 and 100 mg) of the adsorbent using 50 mL dye solution of dye

concentration 100 mg/L. The surface morphology of the adsorbent BR-PAC before and after adsorption of the dye was observed using Field Emission Scanning Electron Microscope (Model: MIRA3 TESCAN).

RESULTS AND DISCUSSION

Effect of Temperature

The dye removal efficiency of BR-PAC adsorbent increased from 53.7 to 89.2 % as the temperature was raised from 303 K to 323 K at a fixed dosage of 0.05g and dye Concentration 100 mg/L. The results are given in Fig. 2. The percentage removal of RB 5 was higher at higher temperatures. This is due to rise in temperature may impel swelling effect within the internal surface of the adsorbent and enhance the movement of dye molecules inside the pores of the adsorbent (Lin Liu *et al.*, 2015).

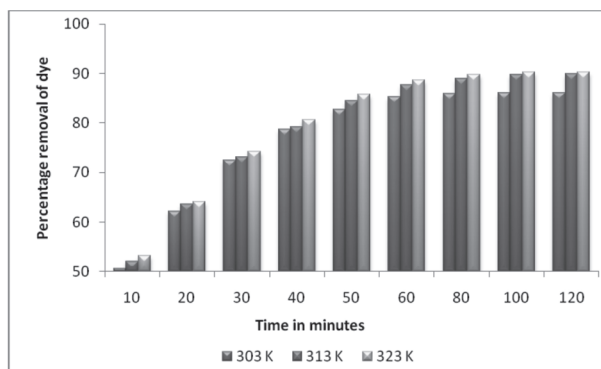


Fig. 2. Adsorption of RB5 Dye from Aqueous solution with Temperature variation

Effect of Adsorbent Dose

The dye removal efficiency of the adsorbent increased from 55.58 to 99.56 % with the increase in dosage of adsorbent material from 25 to 100 mg per 50 mL of dye solution. This is caused by increased

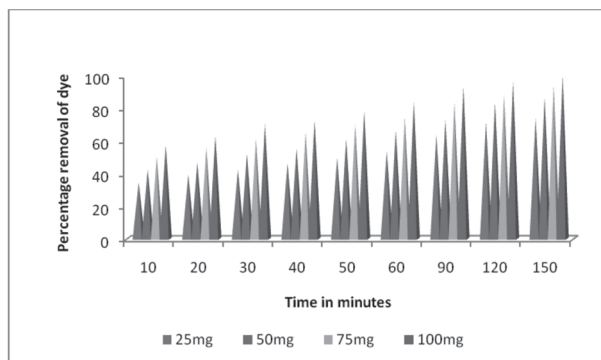
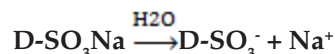


Fig. 3. Adsorption of RB5 Dye from Aqueous Solution with Adsorbent Dosage Variation

surface area and more number of adsorption sites obtained on the surface of the adsorbent (Fig. 3).

Effect of pH

The percentage removal of dye using BR-PAC adsorbent decreased from 98.88 to 87.96% with the increase in pH of the dye solution from 2.0 to 10 in 120 minutes of agitation time (using 0.1 M NaOH / HCl). In the aqueous solution the sulphonic acid group of anionic dye (D-SO₃Na) is dissociated and converted to anionic dye ion (Mall *et al.*, 2006; Sivakumar *et al.*, 2014).



At higher pH the electrostatic repulsion between the negatively charged surface of adsorbent and the anionic dye ions (RB5) causes considerable drop in the removal of dyes from aqueous dye solutions (Fig.4).

Adsorption Isotherms

In the current study the adsorption capacities of the adsorbent for the removal of RB5 dye from aqueous solution was obtained by demonstrating the experimental data with Langmuir and Freundlich adsorption isotherm models.

Langmuir Adsorption Isotherm

Irvin Langmuir developed Langmuir adsorption isotherm to illustrate the surface coverage of the adsorbate on a solid adsorbent surface. Langmuir adsorption isotherm model describes monolayer coverage of the adsorbate over a homogeneous adsorbent surface with energetically equivalent adsorption sites (Aparna Roy *et al.*, 2013). Moreover it is considered that the existence of adsorbed molecules at one site will not affect the adsorption of molecules at neighboring site (Valliammai *et al.*, 2013; Renugadevi *et al.*, 2009a). The linear form

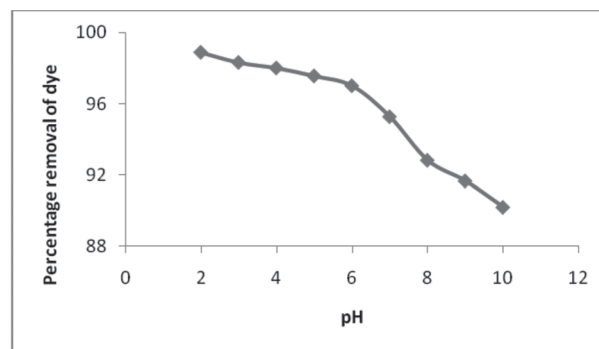


Fig. 4. Effect of pH for the adsorption of RB5 dye from aqueous solution

Langmuir adsorption equation is generally expressed as (Langmuir, 1916).

$$\frac{C_e}{q_e} = \frac{1}{Q_m k_L} + \frac{1}{Q_m} C_e$$

where

C_e is the concentration of dye solution at equilibrium (mg/L)

q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g)

Q_m is theoretical monolayer adsorption capacity (mg/g) and

k_L is Langmuir equilibrium constant (l/mg) related to the affinity of the binding sites

The plots of C_e/q_e versus C_e at different temperatures were found to be linear indicating the applicability of Langmuir isotherm model (Fig.5). The correlation coefficient values (R^2) close to unity suggest the monolayer coverage of the dye molecules on the surface of the adsorbent (BR-PAC). The parameters Q_m and k_L have been calculated from the slope and intercept of the plots (C_e/q_e versus C_e) and the results are presented in Table 2.

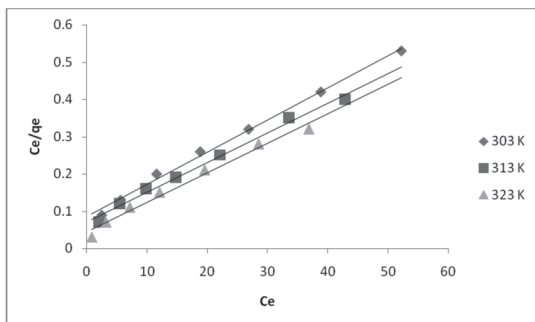


Fig. 5. Langmuir Isotherm Plots for Adsorption of RB5

The necessary characteristics of the Langmuir isotherm can be articulated by a dimensionless constant called equilibrium parameter (or separation factor) R_L which can be explained using the equation

$$R_L = 1 / (1 + k_L C_0)$$

where

C_0 is the initial concentration (mg/L)

k_L is the Langmuir constant

The R_L values ($R_L > 1$ Unfavourable, $R_L = 1$ Linear, $R_L < 1$ Favorable and $R_L = 0$ irreversible) signifies whether the studied adsorption process is favorable or unfavorable (Sumanjit Kaur *et al.*, 2013; and Parimalam *et al.*, 2012).

From Table 2 it was found that R_L values for the removal of dye (RB 5) lies in the range 0.0431 to 0.3650 indicates the favorable uptake of dye onto BR-PAC adsorbent.

Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm model assumes adsorption of dye molecules on a heterogeneous adsorbent surface (Aparna Roy *et al.*, 2013; Mona Shouman, 2012 and Lin Liu *et al.*, 2015). The linear form of Freundlich equation is given by

$$\log q_e = \log (K_f) + 1/n \log C_e$$

where

C_e is the concentration of dye solution at equilibrium (mg/L)

q_e is the amount of dye adsorbed per unit mass of adsorbent (mg/g)

K_f is Freunlich constant (Adsorption capacity mg/g)

n is the heterogeneity factor (Adsorption intensity)

The Freundlich adsorption isotherm plots obtained ($\log q_e$ versus $\log C_e$) were linear which confirms the successfulness of Freundlich adsorption isotherm for the removal of dye (RB5) from aqueous solution using the adsorbent BR-PAC. The value of 'n' is calculated from the slope and K_f value from the intercept of the linear plots and revealed in Fig. 6.

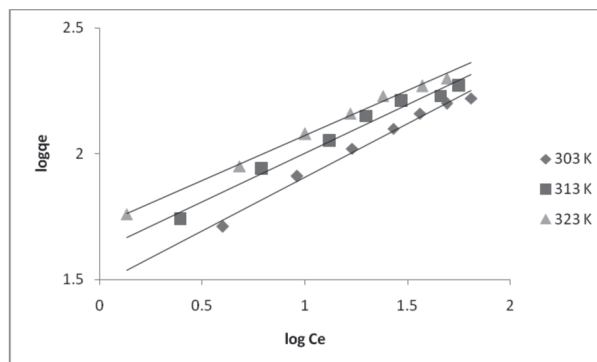


Fig. 6. Freundlich Isotherm Plots for Adsorption of RB5

The greater K_f values obtained showed the higher adsorption capacity of the adsorbents used in this study. The values of 'n' greater than unity revealed stronger adsorption intensity and the adsorption process was favourable (Lin Liu *et al.*, 2015, Ayesha Wasti and Ali Awan, 2016). From Table 3 it was found that 'n' values were greater than unity (2.03 to 5.10) representing the effective adsorption of the dye onto the adsorbent BR-PAC. The high correlation coefficient (R^2) confirms the validity of Freundlich adsorption isotherm with the experimental data.

FE-SEM Analysis

The surface morphology of BR-PAC adsorbent

Table 2. Langmuir Adsorption Isotherm Parameters

Temperature (K)	C_0 (mg/L)	Q_m (mg/g)	k_L (l/mg)	R_L	R^2
303	30	250.00	0.058	0.3650	0.9950
	50			0.2564	
	70			0.1976	
	90			0.1608	
	110			0.1355	
	130			0.1171	
	150			0.1031	
313	30	263.16	0.0976	0.2545	0.9884
	50			0.1701	
	70			0.1277	
	90			0.1022	
	110			0.0852	
	130			0.0731	
	150			0.0639	
323	30	285.71	0.1481	0.1837	0.9895
	50			0.1190	
	70			0.0880	
	90			0.0698	
	110			0.0578	
	130			0.0494	
	150			0.0431	

Table 3. Freundlich Adsorption Isotherm Parameters

Temperature (K)	K_f (mg/g)	n	Correlation coefficient (R^2)
303	30.3389	2.3529	0.9860
313	41.3047	2.5974	0.9814
323	52.1195	2.8169	0.9956

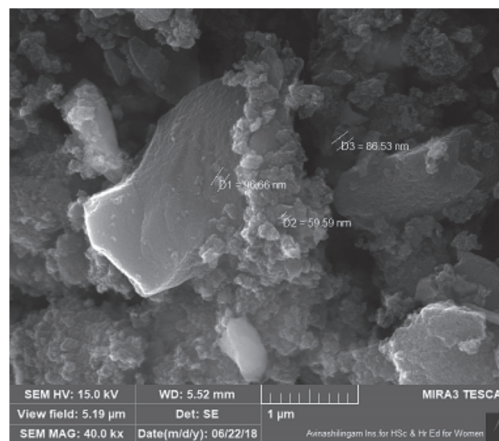
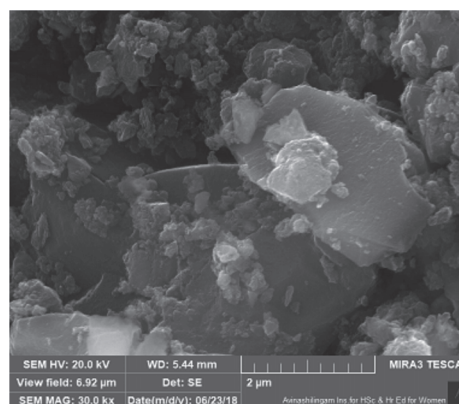
before and after adsorption of the dye has been visualized using Field Emission Scanning Electron Microscope (FESEM). The FESEM images of the adsorbent BR-PAC and RB5 dye loaded BR-PAC adsorbent clearly designate the existence of large number of pores on the exterior surface of the adsorbent afford suitable binding sites for the adsorption of the dye molecules (Fig. 7 and 8).

FT-IR Spectral Analysis

The FT-IR spectrum of the adsorbent BR-PAC was shown in Fig. 9. The peaks exist in infrared spectrum gives significant information about the various surface functional groups present on the surface of the adsorbent.

The regions of the spectrum for various functional groups present are shown below (Sharma, 2012)

The peak obtained at 3724.54 and 3657.04 cm^{-1} corresponds to free O-H group.

**Fig. 7.** FE-SEM Image of BR-PAC**Fig. 8.** FE-SEM Image of RB 5 loaded BR-PAC

Peak detected at 2978.09 cm^{-1} was due to O-H stretching of carboxylic acid.

The peak at 2891.30 cm^{-1} corresponds to N-H stretching of $-\text{NH}_2$ group.

Peak at 2303.01 cm^{-1} corresponds to the presence of $-\text{C}=\text{O}$ group.

The peak at 1577.77 cm^{-1} corresponds to N-H bending of $-\text{NH}_2$ group

The peak obtained at 1379.10 cm^{-1} corresponds to O-H bending of $-\text{COOH}$ group

Peaks at 1238.30 cm^{-1} , 1153.43 cm^{-1} and 1076.28

cm^{-1} are attributed to the C-H vibration modes of alcohol, ether and ester groups (Valliammai *et al.*, 2013).

The existence of various functional groups - COOH , $-\text{C}=\text{O}$ and $-\text{OH}$ on the adsorbent BR-PAC was confirmed by FTIR spectrum. The possibility of the formation of hydrogen bonds between the surface functional groups of the adsorbent with the adsorbate dye molecule may be responsible for the adsorption of RB5 dye onto BR-PAC adsorbent Fig.10 (Aparna Roy *et al.*, 2013).

CONCLUSION

The following conclusion may be drawn from the present investigation.

1. The activated carbon prepared from *Bauhinia racemosa* fruit pods by phosphoric acid activation process acts as good adsorbent for the removal of Reactive Black 5 dye from its aqueous solution.
2. Adsorption process is dependent on pH and temperature.
3. Both Langmuir and Freundlich adsorption isotherm models describe the equilibrium adsorption isotherm data with high R^2 values. The maximum monolayer adsorption capacity of the adsorbent at 50 °C is 285.71 mg/g.
4. Absolute removal of the RB 5 dye from aqueous solution can be attained using proper dosage of the adsorbent and pH
5. Physical forces such as hydrogen bonding and Van der Waals forces are responsible for binding of RB 5 dye with BR-PAC adsorbent.

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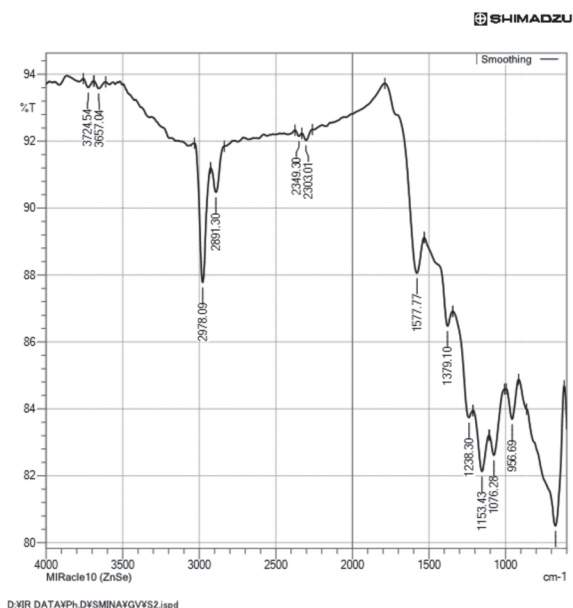


Fig. 9. The FT-IR spectrum of BR-PAC

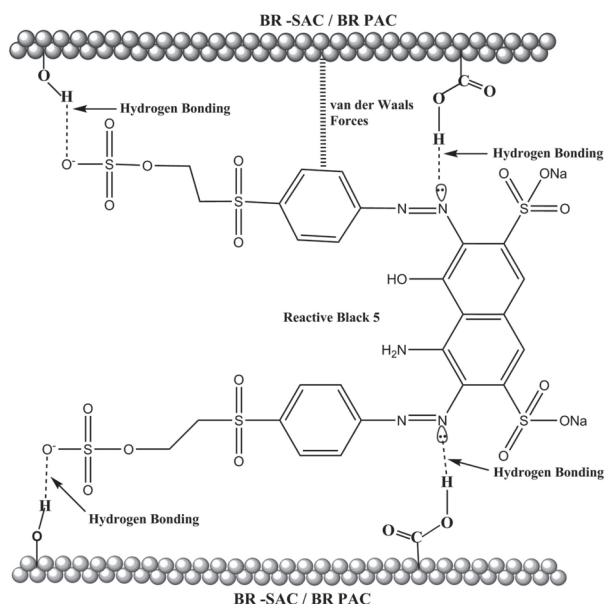


Fig. 10. Adsorption Means of RB 5 onto BR-PAC

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