

## **Baggase-A Biosorbent for Basic Red-12**

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### **ABSTRACT**

*The objective of the work was to study Adsorption behavior of Baggase-a sugar industry waste for the removal of cationic dye- Basic Red-12. The equilibrium and kinetic experiments were performed in batch mode. The equilibrium data was fitted with Langmuir and Freundlich models. Several operation variables such as adsorbent dosage, contact time, initial pH, and temperature on the removal of dyes were investigated. The removal efficiency increased with increase in adsorbent dosage. The adsorption process followed pseudo second order kinetics. Thermodynamic parameters like  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  were analyzed. The processes were spontaneous for the cationic dye. These results suggest that bagasse is a potential low cost industrial waste for textile industry waste water treatment containing cationic dyes.*

**Key words:** Baggase, BasicRed-12, Kinetics, Thermodynamics, Isotherms

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### **INTRODUCTION**

In developing nations like India the conventional effluent treatment technologies are not affordable. Rapid industrial growth has brought economical revolution in all the parts of world and industrial waste water treatment is an important task due to environmental concerns. Thousands of dyes are prepared for printing and dyeing industries from coal tar based hydrocarbons such as benzene, anthracene, naphthalene, xylene, toluene etc. Dyes are used in industries like paper, textile, cosmetics, rubber, food, drug and plastics[1]. According to an estimate 10,000 different types of commercial dyes are present and  $7 \times 10^5$  tones of dyes are produced annually worldwide[2]. This is observed that aerobic biodegradation has very less color removal efficiency. Most of the treatment technologies work on biological treatment processes. Other physical and chemical methods like coagulation [3], oxidation[4], membrane separation[5] and adsorption are in practice. Adsorption is a procedure of choice due to its simplicity, efficiency and cost efficacy[6]. Activated carbon is the best adsorbent but its higher cost and difficult regeneration has encouraged many workers for the research of new adsorbents. Ionic dyes have been removed by the use of adsorbents like orange and banana peels [7], almond shells[8], corn cob [9], de-oiled soya[10], shale oil ash[11], Sugar cane bagasse [12], coir pith[13], hazelnut shells[14], rice husk[15], wheat husk[16], Baggase [17], bark [18] etc. The present work reports the results of adsorption studies of cationic dye basic red 12(BR-12), sugar industry waste bagasse after minimal chemical treatment. Thermodynamic and kinetics of the adsorption process is studied along with the mechanism of adsorption using FTIR analysis of the adsorbent.

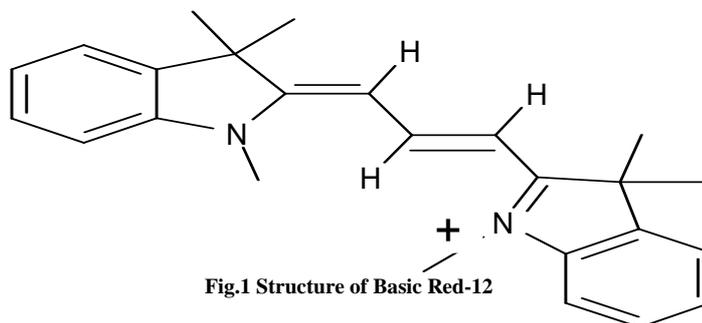
### **MATERIALS AND METHODS**

**2.1 Adsorbate** Basic Red-12, (C.I – Basic Red 12), a cationic dye, was supplied by CDH, New Delhi, India. This was used without any purification. Other reagents like hydrochloric acid, sodium hydroxide, sulphuric acid were obtained from Ranbaxy, India Ltd. The structure of basic red-12 is given in Fig. 1.

#### **2.2 Preparation of Biosorbent**

Bagasse (BG) was collected from Rana sugar mills, Dhilwan (Punjab). This was then dried under sunlight and crushed to a fine powder to get the size of fiber between  $<0.5$ mm. 5.0 g of BG was refluxed with 100 ml of 1%

(w/v) HCHO for four hours at 323K. The BG after cooling was filtered by using Buchner funnel and vacuum pump, washed with deionized water till washings had no color and its UV-Vis absorbance (200-780 nm) was equal to zero, conductivity and pH remained constant. The material was then completely dried in an oven at 353 K for 24 h. The material was then stored in an air tight containers till further use.



### 1.3 Analysis of Adsorbent

The biosorbent was characterized using FTIR; XRD and SEM. FTIR spectra were obtained using FTIR 1600, Perkin Elmer. XRD of biomass was carried out with X pert Pro X-ray diffractometer. SEM was carried out by using Philips scanning electron microscope.

The surface area of BG was determined by BET method and the calculated surface area was 39.32 m<sup>2</sup>/g. The concentration of basic red – 12 before and after biosorption was determined using UV-visible spectrophotometer (Shimadzu 2101 PC) at  $\lambda_{max}$  = 469 nm. A stock solution of 500 ppm was prepared by dissolving required amount of basic red-12 in distilled water and further dilutions were carried out to get a particular concentration. An incubator shaker was used for carrying out experiments at 303 K, 313 K and 323 K. The experiments were conducted by taking 50 ml of dye solution in Erlenmeyer flask and adding required amount of BG in that. The pH of different solutions was adjusted with 0.1 N HCl and 0.1 N NaOH using microprocessor based pH meter by Toshnival India. The BG dose was varied from 2.5 g /L to 20.0 g /L. The solutions were kept in incubator shaker at 303 K. After attainment of equilibrium the aqueous phase was analyzed for residual dye concentration. It was observed that  $\lambda_{max}$  remained unchanged in pH range 2.0-9.0 suggesting negligible structural changes in the said pH range for basic red -12.

From the absorbance data  $q_e$  (mg/g) was determined using following equation

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where  $C_0$  is initial dye concentration,  $C_e$  is final dye concentration and V is volume of dye in liters and W is mass of biosorbent in g. Duplicate experiments were performed to get concordant results. The results showed variation in the range  $\pm 5\%$ . The Kinetics of dye was studied by using 250 ppm dye concentration. The samples were withdrawn at regular intervals and residual concentration was analyzed after centrifugation. Freundlich and Langmuir isotherms were studied by using 50 ml of dye solution with in concentration range 100 ppm to 500 ppm. After the attainment of equilibrium the residual dye concentration was analyzed spectrophotometrically.

## RESULTS AND DISCUSSION

### 3.1 Characterization of biosorbent

FTIR spectra were carried out by encapsulating 0.5 mg of finely ground biomass was with 400 mg of KBr to get a translucent disk. FTIR spectra (Fig 2) of BG display a number of absorption peaks indicating complex nature of biomass. A broad absorption peak at 3402 cm<sup>-1</sup> is indicative of bonded hydroxyl group. A peak observed at 1652.9 cm<sup>-1</sup> can be assigned to >C=O group. A peak at 1541.5 cm<sup>-1</sup> indicates secondary amino group. The peak at 2925.6 cm<sup>-1</sup> may be due to C-H stretching vibrations. The XRD spectra revealed small peaks at  $2\theta = 20.89^\circ$ ,  $28.00^\circ$  and  $50.21^\circ$  with d spacing 4.25Å, 3.18Å and 1.81Å respectively.

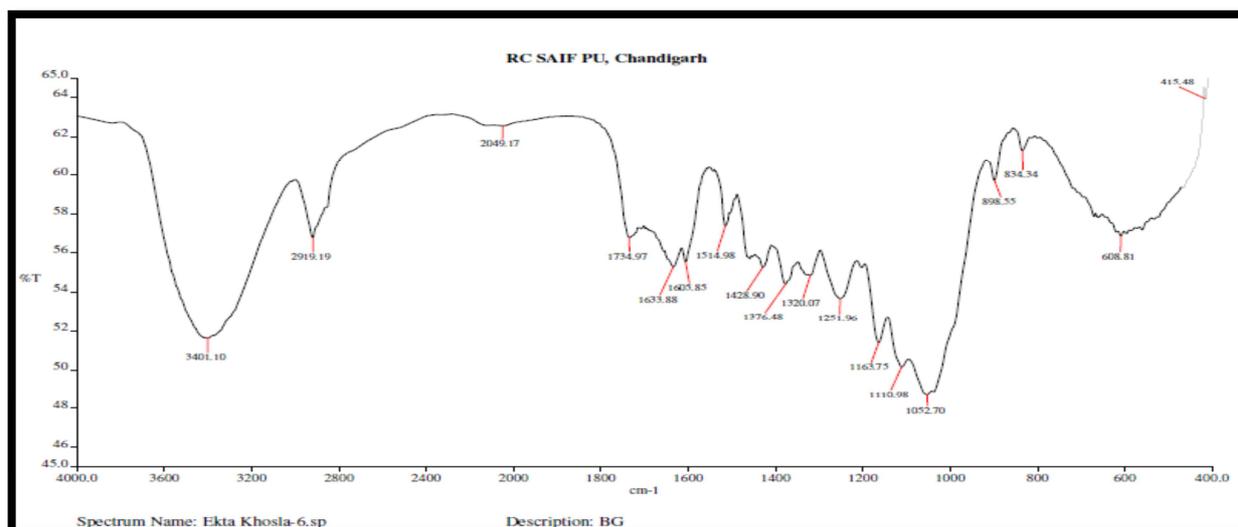


Fig.2 FTIR spectra of BG

While the main peak is observed at  $2\theta = 26.68^\circ$  indicating crystalline nature of biosorbent with d spacing  $3.34^\circ\text{A}$  (Fig. 3), SEM (Fig. 4) revealed that the surface of biosorbent is rough and almost non compact in nature. It has considerable number of pores for dye to be trapped.

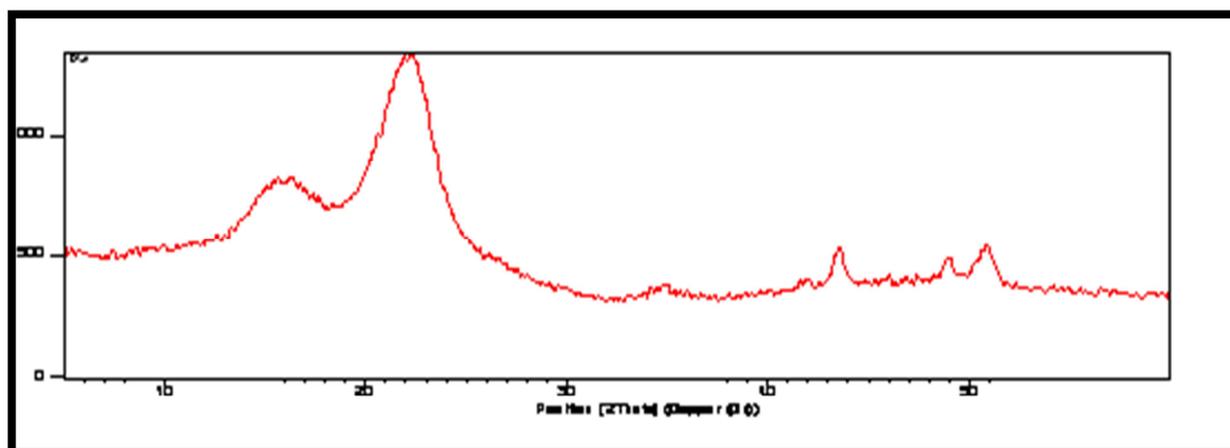


Fig.3 XRD spectra of BG

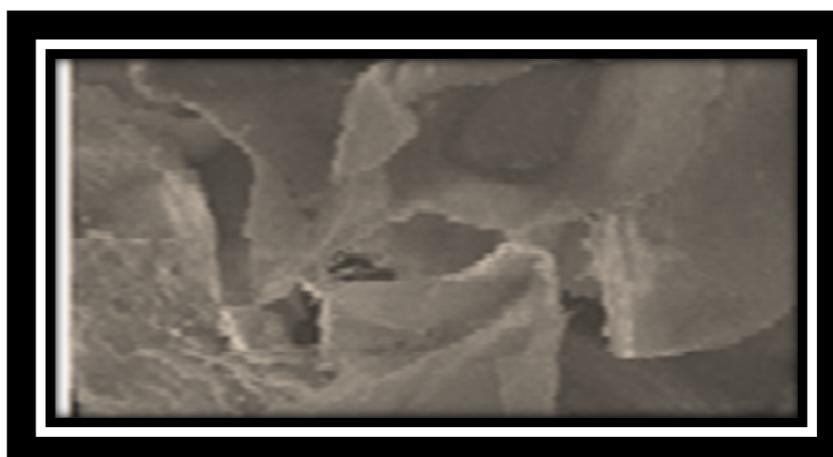


Fig.3 SEM of BG (15KV, 1800x)

### 3.2 Effect of pH

Biosorption of dye on BG is influenced by pH of the aqueous phase. The effect of pH on percentage removal of dye is shown in Fig 5, enhanced adsorption took place in pH range 6-9. This may be attributed to the fact that basic red 12 is a cationic dye and the adsorption is primarily due to surface charge of the adsorbent. At pH less than 6.0 the secondary amino group is protonated and carries positive charge which repels the cationic dye on the surface. At high pH the surface is deprotonated thus the dye and adsorbent attracts each other electrostatically. In the present study the initial pH of the dye solution was 6.3 thus not much changes were required in pH for this treatment. Moreover the dye was desorbed with suitable techniques and was recovered without degradation after the process. When the pH was reduced to 2.0 the protons compete with cationic dye for adsorption to the binding sites of adsorbent hence the dye was desorbed by using 5% v/v HCl.

### 3.3 Variation in biosorbent dosage.

As the biosorbent dosage increases, the adsorption sites available for the dye molecules also increases. Thus better biosorption takes place. In the present study, the biosorbent dose was varied between from 2.5g/L to 20 g/L in 250 ppm dye solution. the adsorption increases with the increase in biosorbent dosage due to availability of more active sites for dye adsorption. However it was seen that efficiency did not increase linearly with increase in adsorbent dosage thus the adsorbent dosage was fixed conveniently at 12.5g/L. The decolorisation of dye by a biomass involves several complex mechanisms like chelation, complexation, ion exchange and surface accumulation etc. The dye can interact on biosorbent in different manners and the most important mechanism is ion exchange, thus ion exchange by the biosorbent increases with the increase of biosorbent dose.

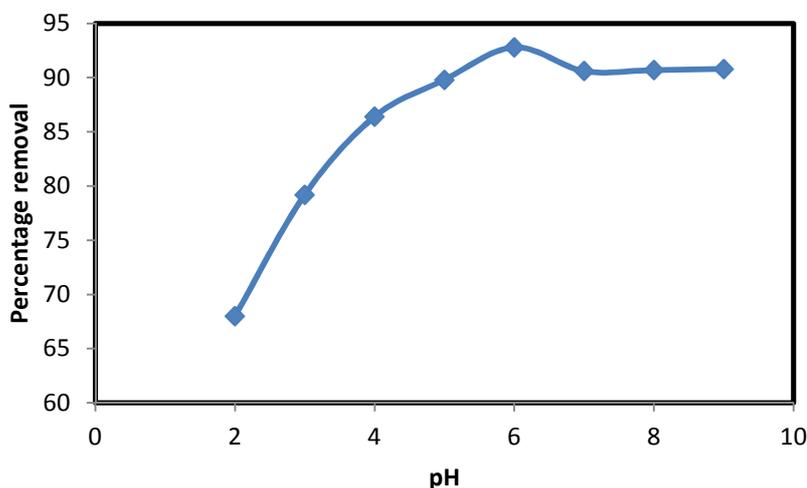


Fig.5 Effect of pH on adsorption of BR-12 on BG

### 3.4 Adsorption isotherm study.

The Freundlich and Langmuir isotherm models have been successfully applied to the above system at various temperatures 303 K, 313 K and 323 K and thermodynamic parameters calculated accordingly. For the equilibrium concentration of adsorbate ( $C_e$ ) and amount of dye adsorbed at equilibrium ( $q_e$ ), the following linear forms of Langmuir and Freundlich isotherms were studied.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where  $Q_0$  (mg/g) and  $b$  (L/mg) are Langmuir constants related to maximum adsorption capacity and equilibrium constant related to binding energy respectively, while  $K_F$  and  $n$  are Freundlich constants related to adsorption capacity and sorption intensity. The Freundlich isotherms fitted well suggesting that on the heterogeneous surface, several sites with different adsorption energies are involved. The Langmuir isotherm also fitted well suggesting that adsorption takes place at specific homogenous site forming monolayer and once a dye molecule occupies the site no further adsorption can take place at that site. The applicability of both isotherms suggest heterogeneous surface with homogenous functional groups. The intercepts and slopes were used to determine the values of Freundlich and Langmuir parameters as indicated in Table 1 and the isotherms are shown in Figs. 6 (a) and 6(b) respectively.

To investigate the favorability of a process the dimensionless separation factor  $R_L$  was also calculated and found to be less than 1.

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

Where  $b$  is Langmuir constant and  $C_0$  is optimum initial concentration of the dye. The values of  $R_L$  were 0.1283, 0.1667 and 0.2907 respectively at 303 K, 313 K and 323 K respectively indicating that the adsorption of basic red - 12 over BG process is favorable.

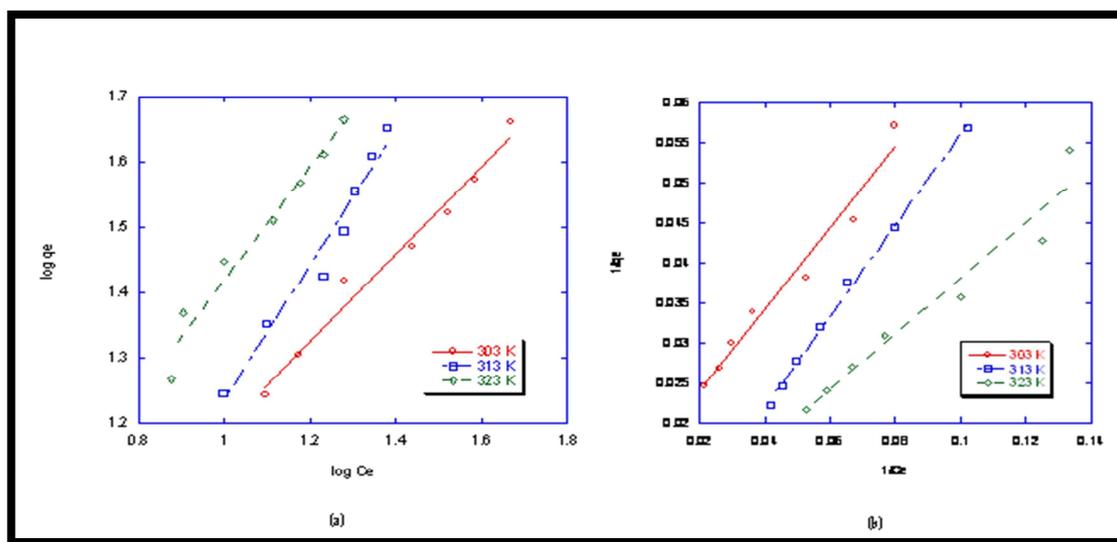


Fig 6.(a) Freundlich adsorption isotherm (b) Langmuir adsorption isotherm

### 3.5 Kinetics of biosorption.

The kinetic data of biosorption gives a useful data regarding the efficiency and feasibility of ongoing operations. The kinetic data can be evaluated using different types of mathematical models. Adsorption rate constant study was carried out with the famous Lagergran rate equation (Eq.5).

$$\log(q_e - q_t) = \log q_e - \left( \frac{k_1}{2.303} \right) t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

The time versus  $\log (q_e - q_t)$  plots revealed correlation coefficient greater  $R^2$  than 0.97. The slope of the plot gave the value of rate constant and it was found to be  $2.9307 \times 10^{-2} \text{ min}^{-1}$ . Pseudo second order rate equation (Eq.6) was also applied on the data and  $R^2$  was found close to unity; the value of rate constant was calculated to be  $9.882 \times 10^{-5} \text{ g/mg min}$  so pseudo first order kinetics seems to be more realistic.

### 3.6 Thermodynamic studies.

The changes in the reaction that can be expected during the process require the brief idea of the thermodynamic parameters which were also calculated from the above data

$$\Delta G^\circ = -RT \ln b \tag{8}$$

$$\Delta H^\circ = -R \left( \frac{T_2 T_1}{T_2 - T_1} \right) \ln \left( \frac{b_2}{b_1} \right) \tag{9}$$

$$\Delta S^{\circ} = \frac{\Delta H^{\circ} - \Delta G^{\circ}}{T} \quad (10)$$

The Gibbs free energy,  $\Delta G^{\circ}$  was found to be negative at all temperatures, indicating spontaneous process at all the temperatures while enthalpy  $\Delta H^{\circ}$ , was positive suggesting endothermic nature of the process. The positive value of entropy,  $\Delta S^{\circ}$  suggests favorable randomness factor though its value is small. The thermodynamic parameters were calculated using following equations and the values of parameters are listed in Table2.

Where  $b$ ,  $b_1$ ,  $b_2$  are Langmuir constants at 303 K, 313 K and 323 K respectively.

**Table 1. Isotherm Parameters for Adsorption Process**

Temperature (K)	$K_F$	$n$	$Q_0$ (mg/g)	$B$ (L/mg) $\times 10^{-2}$
303	3.6837	1.5582	72.48	2.7156
313	3.5906	1.1565	138.72	1.1199
323	1.0712	0.9335	295.85	0.9761

**Table 2. Thermodynamic Parameters for Adsorption Process**

Temperature (K)	$\Delta G^{\circ}$ (KJ mol <sup>-1</sup> )	$\Delta H^{\circ}$ (KJ mol <sup>-1</sup> )	$\Delta S^{\circ}$ (JK <sup>-1</sup> mol <sup>-1</sup> )
303	-17.329	+7.671	+82.805
313	-15.773		
323	-15.725		

## CONCLUSION

This study shows that BG can be successfully used for the basic dye removal from the aqueous solution. This adsorbent was found to be useful and valuable mean for controlling water pollution due to dyes. The following conclusions can be drawn from this study:

- (i) The batch adsorption experiments show that the adsorption of basic dyes over BG is dependent on pH, amount of adsorbent, concentration, contact time, and temperature, and almost 92.5% could be accomplished at low concentrations, whereas at higher concentrations, the adsorption was slightly decreased to 90% for BG.
- (ii) The thermodynamic parameters obtained in both cases confirm the feasibility of the process at each concentration.
- (iii) The results of kinetic experiments show that the process followed pseudo first order kinetics and proceeds via film diffusion at higher and lower concentrations.
- (iv) The BG is inexpensive and can be used as excellent adsorbents for basic dyes.

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