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Bengal Gram Seed Husk an Adsorbent for Removal of Reactive Blue 25 Dye from Aqueous Solution

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Dyes are carcinogenic and toxic chemicals that affect aquatic life and human beings even at lower concentrations. Treatment of industrial effluents containing dyestuffs is therefore important for wastewater treatment engineers. In this study, batch adsorption experiments were conducted to study the adsorption of Reactive Blue 25 dye from aqueous solution using agricultural solid waste *e.g.*, Bengal gram seed husk. The operating parameters are initial solution pH, initial dye concentration, adsorbent dosage and adsorbent-adsorbate contact time affecting dye adsorption were investigated. Experimental data were fitted to Langmuir and Freundlich isotherm models. Lagergren's kinetic models were used to explain the adsorption kinetics and predict the theoretical adsorption capacity of adsorbent.

Keywords: Adsorption, Bengal gram, Isotherms, Kinetics, Reactive Blue dye, Langmuir, Freundlich.

INTRODUCTION

The pollutants in the industrial effluents depend upon the type of the industry. The discharges of industries such as textile, food processing, leather, pulp and paper, *etc*. mainly contain unexhausted dyestuffs which are carcinogenic, toxic in nature and non-biodegradable. The discharge of effluents containing unexhausted dyestuffs without prior treatment into water bodies affects the aquatic life as well human beings [1,2]. The treatment of industrial effluents containing dyestuffs is hence important for wastewater treatment engineers.

Among various wastewater treatment processes, adsorption, a tertiary treatment process has gained a considerable interest as the process is simple in operation and economically viable [3,4]. Activated carbon is most effective adsorbent, but many researchers are considering in using non-conventional, agricultural waste materials as adsorbents due to high manufacturing cost of activated carbon [5]. Some of such materials used in the original form or in the modified form include: sawdust [6-8], parthenium hysterophorus [9], coconut coir dust [5], loofa egyptiaca [10], sugarcane bagasse pith [11,12], silk cotton hull, banana pith, maize cob [13], orange waste [14], sugar beet pulp [15], pomelo (*Citrus grandis*) peel [16], *Citrus sinensis* (mosambi) bagasse [17], lemna minor (Duckweed) [18], *etc*.

In the present study, Bengal gram seed husk (BGSH), an agricultural solid waste available abundantly in a tropical country like India was used in its original form as an adsorbent for the removal of Reactive Blue 25 (RB 25) dye from aqueous solution. Adsorption capacity of the adsorbent was determined using Langmuir and Freundlich isotherms. Lagergren's pseudo-first-order and second-order kinetic models were used for the analysis of kinetics and amount adsorbed at equilibrium.

EXPERIMENTAL

Analytical reagent (AR) grade chemicals such as KNO_3, HCl and NaOH (Merck, India) were used in batch adsorption investigations. Reactive Blue 25 dye was obtained from local textile industry situated at Ichalkaranji, India. A known concentration of solution was prepared and was further diluted to desired concentrations and used for the experiments.

Adsorbent: The adsorbent, Bengal gram seed husk was collected from the nearby field and washed thoroughly with tap water to remove the dust particles and sun dried. The sun dried Bengal gram seed husk was ground to powder passing through 150 μm and retained on 75 μm. The surface area of Bengal gram seed husk was determined by BET surface area analyser (ASAP 2020 V3.04 H, Micromeritics, USA) and was 0.90 m^2/g. The ultimate analysis (% dry-ash-free basis) of Bengal gram seed husk was analyzed using CHNS/O analyzer (Perkin-Elmer 2400) and it was found that Bengal gram seed husk has carbon = 41.02 %, nitrogen = 2.45 %, hydrogen = 6.10 % and oxygen (by difference) = 50.43 %. The surface morphology of Bengal gram seed husk was analyzed using

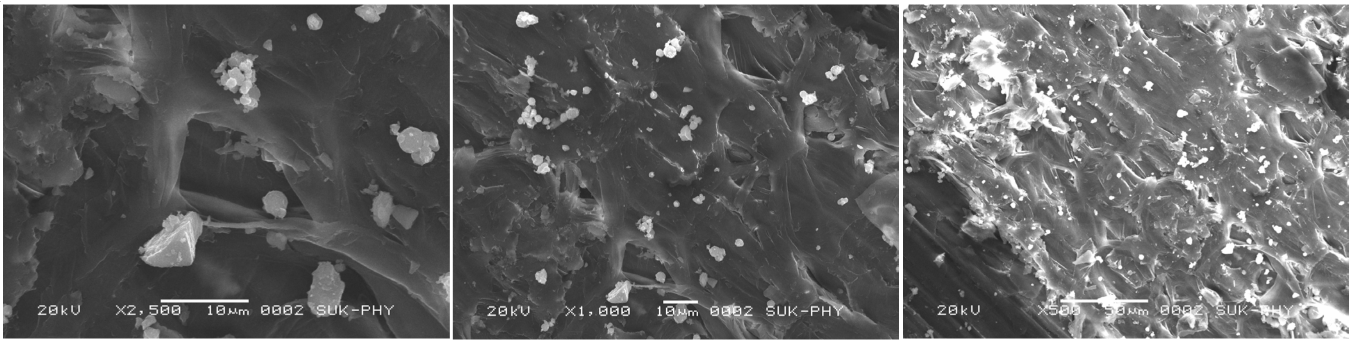

Fig. 1. SEM micrographs of Bengal gram seed husk

SEM as shown in Fig. 1. It can be seen from the figure that Bengal gram seed husk has fibrous structure with considerable number of pores to adsorb dye. Similar observations were also made by Reddy and Ashwini [19].

General procedure: Conical flaks of 250 mL capacity were used for batch adsorption experiments. NaOH or HCl of AR grade was used to achieve the desired solution pH. Bengal gram seed husk of known quantity was added to each conical flask and were kept for shaking. Shaking of conical flask contents were carried out using rotary shaker (LABLINE). At regular intervals of time, the contents in the flasks were drawn and centrifuged using laboratory centrifuge (REMI). The Reactive Blue 25 dye concentration in the supernatant was analyzed following the standard method [20] using UV-visible spectrophotometer (Elico-BL 198). Wavelength, 600 nm was selected for the analysis of dye concentration. This is the wavelength at which maximum absorbency, λ_{max}, for Reactive Blue 25 dye was obtained during dye scanning operation.

RESULTS AND DISCUSSION

Point of zero charge: Point of zero charge of Bengal gram seed husk was determined as per the procedure reported by Ofomaja and Ho [21] and is depicted in Fig. 2. Bengal gram seed husk has point of zero charge at 5.5.

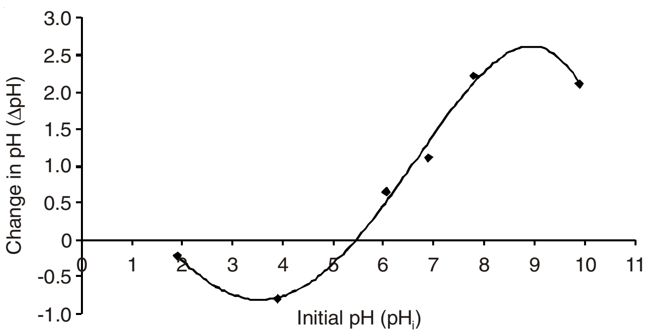

Fig. 2. Change in solution pH (ΔpH) *versus* initial pH (pH_i)

Effect of solution pH: A detailed investigation on the effect of solution pH on the adsorption of Reactive Blue 25 dye onto Bengal gram seed husk was conducted by varying the solution pH from 2 to 10 using either NaOH/HCl. Bengal gram seed husk dosage, initial Reactive Blue 25 dye concentration, were maintained as 1 g/L and 10 mg/L, respectively. The contents were agitated for a period of 60 min. Fig. 3 shows the effect of solution pH on the % adsorption of Reactive Blue 25 dye onto Bengal gram seed husk. Bengal gram seed husk adsorbed 84.6 % (amount adsorbed at equilibrium, q_e = 8.46 mg/g) of dye when the solution pH was 2. The dye adsorption onto Bengal gram seed husk decreased with an increase in solution pH. At pH 10, Bengal gram seed husk adsorbed 43.8 % (q_e = 4.38 mg/g) of dye. Fig. 3 also shows corresponding q_e values. Significant dye adsorption was achieved at pH < pHpzc as Reactive Blue 25 dye is anionic in nature.

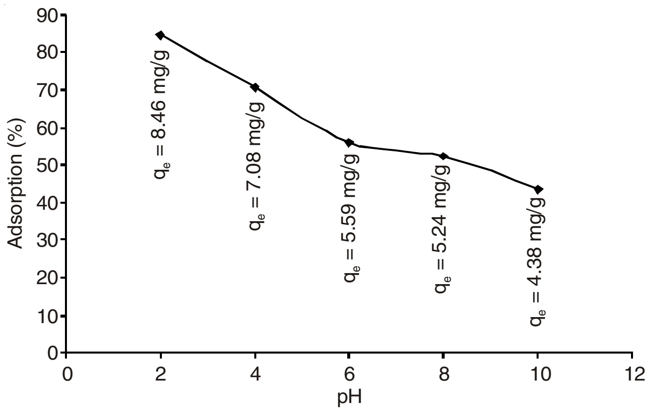

Fig. 3. Effect of initial solution pH on Reactive Blue 25 adsorption by Bengal gram seed husk

Effect of initial Reactive Blue 25 dye concentration: Effect of initial Reactive Blue 25 dye concentration on the adsorption of dye onto Bengal gram seed husk was studied by varying the initial dye concentration from 10 to 90 mg/L and the Bengal gram seed husk dosage was kept as 1 g/L, solution pH was maintained as 2 and the flask contents were agitated for a period of 60 min. Fig. 4 depicts the effect of initial Reactive Blue 25 dye concentration on dye adsorption onto Bengal gram seed husk. It can be concluded that with an increase in initial dye concentration, % adsorption onto Bengal gram seed husk was decreased. At 10 mg/L, the dye adsorption was 84.6 % and at 90 mg/L, it was decreased drastically to around 35.7 %, whereas, the dye adsorbed at equilibrium onto Bengal gram seed husk increased with an increase in initial dye concentration. Fig. 4 also depicts the values of q_e for different initial Reactive Blue 25 dye concentrations. At an initial dye concentration, 10 mg/L, q_e value was 8.46 mg/g and it increased to 32.09 mg/g when initial dye concentration increased to 90 mg/L. With an increase in initial dye concentration, the adsorbent sites also increased. Also the initial dye concentration offered a major driving force to overcome the all mass transfer

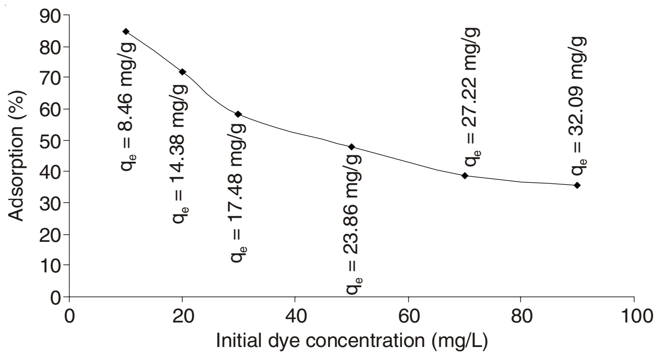

Fig. 4. Effect of initial dye concentrations on Reactive Blue 25 adsorption by Bengal gram seed husk

resistance and that resulted in an increased Reactive Blue 25 dye adsorption onto Bengal gram seed husk.

Effect of Reactive Blue 25 dye-Bengal gram seed husk contact time: Fig. 5 illustrates the effect of Reactive Blue 25 dye-Bengal gram seed husk contact time. The batch adsorption experiments to study the effect of contact time were conducted at an initial dye concentration, 10 mg/L, solution pH, 2 and Bengal gram seed husk dosage, 1 g/L. After every 10 min of intervals the contents in the flask were withdrawn and analyzed for Reactive Blue 25 dye concentrations. It was observed that the 73.4 % (q_e = 7.34 mg/g) of dye was adsorbed when the contents were agitated for a period of 10 min. At 20 min of contact time, % adsorption of Reactive Blue 25 dye was 79.4 % (q_e = 7.94 mg/g) and gradually rose to 84.6 % (q_e = 8.46 mg/g) when contents were agitated for 50 min and attained plateau with further agitation.

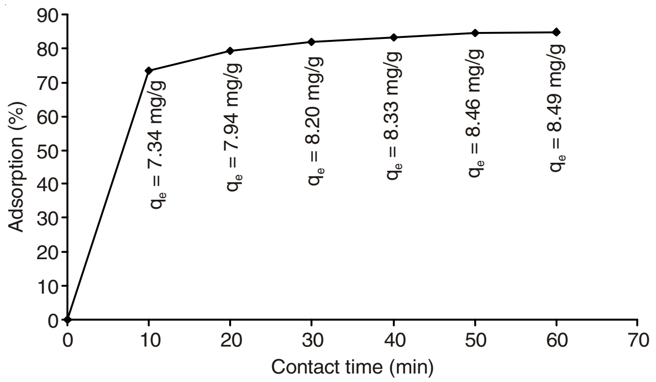

Fig. 5. Effect of agitation time on Reactive Blue 25 adsorption by Bengal gram seed husk

Effect of Bengal gram seed husk dosage: Effect of Bengal gram seed husk dosage on % adsorption of Reactive Blue 25 dye is shown in Fig. 6. The adsorption experiments to investigate the effect of Bengal gram seed husk dosage on adsorption of dye were conducted by varying the Bengal gram seed husk quantity as 1, 1.5, 2 and 5 g/L. The solution pH was maintained at 2, initial dye concentration was kept constant as 10 mg/L and the adsorbate-adsorbent were agitated for a period of 50 min. At 1 g/L of adsorbent dosage, dye adsorption was 84.9 % (q_e = 8.49 mg/g) and it increased to 89.9 % (q_e = 5.99 mg/g) when the dosage was increased to 1.5 g/L. With further increase in adsorbent dosage, the increase in dye adsorption was negligible. This may be due to overlapping of adsorbent active sites due to overcrowding of adsorbent particles [22].

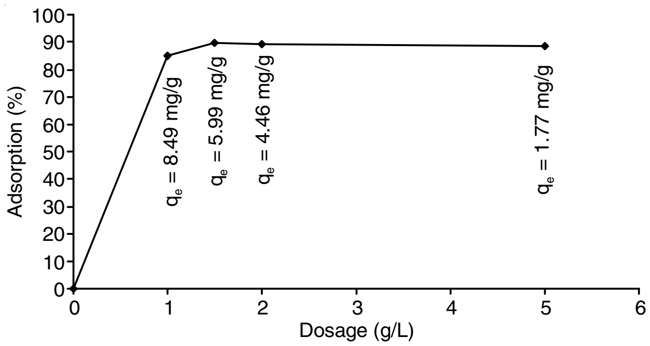

Fig. 6. Effect of adsorbent dosage on Reactive Blue 25 adsorption by Bengal gram seed husk

Isotherm studies: The adsorption capacity of Bengal gram seed husk for Reactive Blue 25 dye can be determined by using isotherm models. Two well known isotherms such as Langmuir and Freundlich were used in the present study and the adsorption capacity of Bengal gram seed husk for dye was determined theoretically.

Langmuir adsorption isotherm, a physical adsorption model, assumes surface adsorption and the linear form of it is given as eqn. 1 [23]:

$$\frac{c_e}{q_e} = \frac{c_e}{Q_o} + \frac{1}{bQ_o} \qquad (1)$$

A dimensionless constant, R_L is generally used to indicate favourable/unfavourable adsorption and is given as eqn. 2:

$$R_L = \frac{1}{1 + bc_o} \qquad (2)$$

The favourable adsorption is possible only when $0 < R_L < 1$.

Fig. 7 shows c_e/q_e *vs.* c_e for Reactive Blue 25 dye adsorption on to Bengal gram seed husk. The model constants with R^2 and RMSD values are tabulated in Table-1.

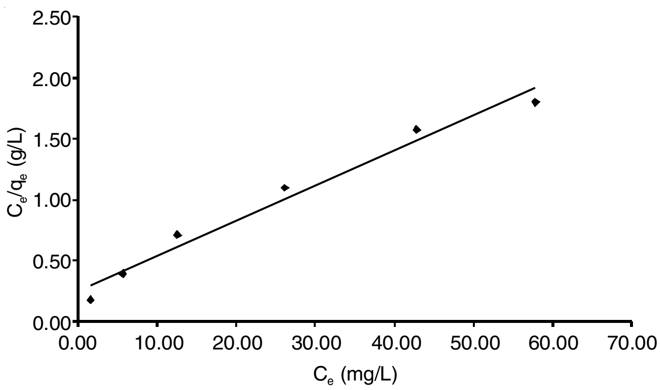

Fig. 7. Linear Langmuir adsorption isotherm

Another well-known empirical model is Freundlich isotherm model and its linear form is given as [24]:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e \qquad (3)$$

log q_e *vs.* log c_e plot is shown in Fig. 8. The isotherm constants with R^2 and RMSD values are also tabulated in Table-1. The R^2 value of Freundlich isotherm model is 0.995 and RMSD = 0.15. Based on this it can be concluded that Reactive Blue 25 dye adsorption onto Bengal gram seed husk follows Freundlich model.

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS

RB 25 dye concentration (mg/L)	R_L	Langmuir constants			RMSD
		Q_o (mg/g)	b (L/mg)	R^2	
10	0.67	34.84	0.11	0.975	3.40
20	0.50				
30	0.40				
50	0.28				
70	0.22				
90	0.18				

Freundlich constants			
k_f (mg/g)	n	R^2	RMSD
7.38	2.81	0.995	0.15

RB 25 = Reactive blue 25

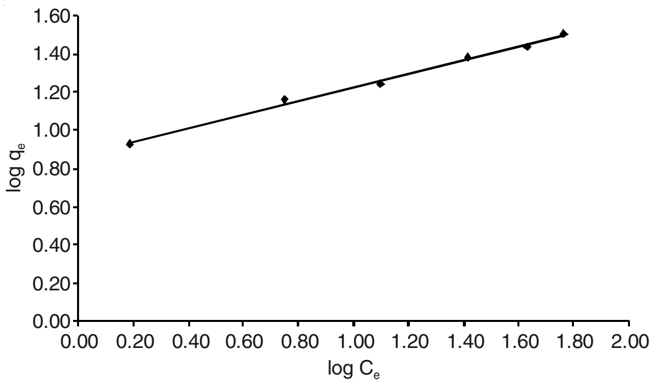

Fig. 8. Linear Freundlich adsorption isotherm

Kinetic studies: Lagergren's pseudo-first-order and pseudo-second-order kinetic equations were used to investigate the kinetics of Reactive Blue 25 dye adsorption onto Bengal gram seed husk. The linear form of Lagergren's pseudo-first-order kinetic equation is [25]:

$$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303} \tag{4}$$

The linear form of pseudo-second-order kinetic equation is [26]:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

Fig. 9 depicts log (q_e-q) *vs.* *t* (Lagergren's pseudo-first-order kinetic equation). t/q *vs.* t (pseudo-second-order kinetic equation) is shown in Fig. 10. The kinetic equation parameters are summarized in Table-2. It can be concluded based on the R^2 value and q_e, calculated; the Reactive Blue 25 dye adsorption onto Bengal gram seed husk follows pseudo-second-order kinetics. Table-3 tabulates the optimum parameters obtained for the adsorption of Reactive Blue 25 dye onto Bengal gram seed husk for the initial dye concentration of 10 mg/L.

Conclusion

Bengal gram seed husk, agricultural waste available abundantly was used as adsorbent for the adsorption of Reactive Blue 25 from aqueous solutions. Optimum parameters for the adsorption of dye onto Bengal gram seed husk were determined and found that maximum adsorption was occurred at pH, 2, adsorbent dosage, 1.5 g/L and adsorbate-adsorbent contact time, 50 min for an initial Reactive Blue 25 of 10 mg/L. The adsorption of Reactive Blue 25 onto Bengal gram seed husk followed Freundlich isotherm model. The kinetics of dye adsorption by Bengal gram seed husk is better explained by the pseudo-second-order kinetic model.

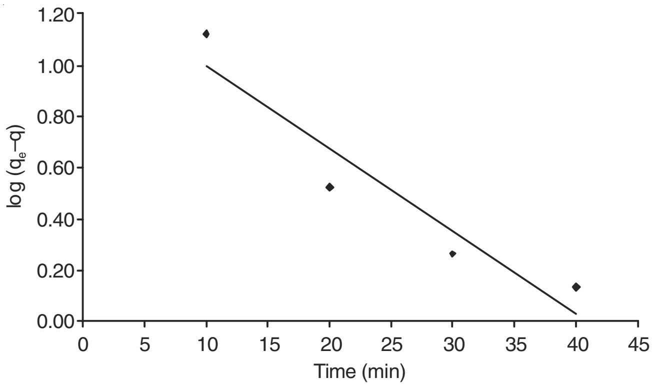

Fig. 9. Pseudo-first-order kinetics for adsorption of Reactive Blue 25 onto Bengal gram seed husk

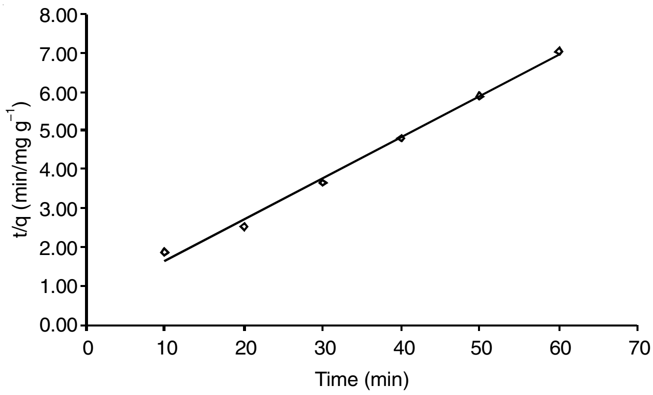

Fig. 10. Pseudo-second-order kinetics for adsorption of Reactive Blue 25 onto Bengal gram seed husk

TABLE-2
PSEUDO-FIRST-ORDER AND SECOND-ORDER KINETIC MODEL PARAMETERS

q_e experiment (mg/g)	Pseudo-first-order		
	K_1 (min^{-1})	q_e (mg/g)	R^2
8.49	0.0742	20.89	0.90
q_e experiment (mg/g)	Pseudo-second-order		
	K_2 (g/mg) min^{-1}	q_e (mg/g)	R^2
8.49	0.0243	9.38	0.99

TABLE-3
OPTIMUM PARAMETERS FOR ADSORPTION OF REACTIVE BLUE 25 ONTO BGSH AT AN INITIAL DYE CONCENTRATION (10 mg/L)

Parameters	Optimum conditions
pH	2
Adsorbent dosage (g/L)	1.5
Adsorbate-adsorbent contact time (min)	50

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