

Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green Dye from aqueous solution by *Oplismenus frumentaceus* husk

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Abstract : In the present study, agricultural waste *Oplismenus frumentaceus* husk (OFH) was used as an adsorbent. Batch adsorption studies were performed for the removal of Brilliant Green Dye (BG) from aqueous solution by varying the parameters like solution pH, adsorbent dose and initial BG concentration. The experimental data were analyzed by the Langmuir and Freundlich adsorption isotherm models. The adsorption data were fitted well to Langmuir isotherm model than to Freundlich isotherm. Adsorption rate constants were determined by using pseudo-first order and pseudo-second order rate equations. The results clearly showed that the adsorption of BG onto OFH follows pseudo-second order model. Since *Oplismenus frumentaceus* husk has never been used as adsorbent for the removal of dyes, the result revealed that the *Oplismenus frumentaceus* husk is a cost effective adsorbent for the removal of BG from aqueous solution.

Keywords : *Oplismenus frumntaceus* husk, brilliant green dye, adsorption isotherm, kinetics.

Introduction

The effluent from textile, leather, paper, ink, cosmetic industries and the industries that produce dyes are severely contaminated with dyes and pigments¹. Fifteen percent of the total world production of dyes is lost during the dying process and is released in textile effluents². The release of the dyes influences the ecosystem, and cause eutrophication and of perturbation of the aquatic life. It also interferes with transmission of sunlight into stream and therefore reduces photosynthetic activity³.

Brilliant Green Dye (BG) is a basic organic dye belonging to the triphenylmethane family (Fig. 1). It is odor-

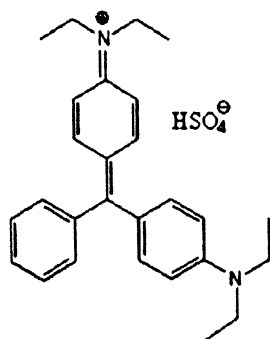


Fig. 1. Chemical structure of Brilliant Green Dye.

less yellow-green to green powder used for various purposes, e.g. for the production of cover in paper industry, biological stain, dermatological agent, veterinary medicine, and an additive to poultry feed to inhibit propagation of mold, intestinal parasite and fungus⁴. However, in human being BG causes irritation to the gastrointestinal tract; symptoms include nausea, vomiting and diarrhea. It also causes irritation to the respiratory tract, leading to cough and shortness of breath. Skin contact causes irritation with redness and pain⁵. Thus it becomes necessary to remove BG from waste water before it is released into aquatic environment.

There are many chemical and physical methods such as flocculation, electro-floatation, precipitation, coagulation, ion exchange, membrane filtration, electro chemical destruction, irradiation, ozonation, and katox treatment method that have been used to treat the waste water for the removal of dyes⁶ but these processes are costly and can't be used effectively to treat a large quantity of dyes. However, adsorption is most suitable method for solving this type of problem. Now a days activated carbon^{7,8} is widely used as adsorbent because of its large surface area, micro porous structure, high adsorption ca-

capacity etc., but some of its disadvantages are the high price of treatment and difficult to regenerate which increase the cost of the waste water treatment⁹. Several agro-industrial wastes have been used for the adsorption of dyes. These include hard wood¹⁰, banana pith¹¹, indian rose wood¹², waste coir pith¹³, bagasse pith¹⁴, neem leaf powder¹⁵, banana and orange pith¹⁶, barley husk¹⁷, cassava peels¹⁸, rice husk^{9,19}, mahogany saw dust¹⁹, Rahmana *et al.* have used reddish peel²⁰, jamun stem²⁰ and coal²⁰ as adsorbent for removal of BG. With the objective of exploring the adsorption potential of low cost bioadsorbents for the removal of hazardous BG from aqueous solution earlier we have used egg shell powder²¹. Recently Ghaedi *et al.* has used activated carbon prepared from Acorn²² as a adsorbent for the removal of BG.

Easily available, economical and highly effective adsorbent are still needed. *Oplismenus frumentaceus* (common name : Jhangora) is a commonly grown cereal in the hilly area of north India mainly in Uttarakhand, the seeds of this plant are in used for eating purpose as an alternative of rice. Its husk is a by-product that is used as fodder in a small amount and its maximum part is a waste for the people there, so they burnt this to dispose the material, instead of this if this could be used as an adsorbent there will be not any cost and large scale use of this adsorbent will save the environment from the pollution due to burning of *Oplismenus frumentaceus* husk.

This paper reports the adsorption potential of low cost bioadsorbent *Oplismenus frumentaceus* husk (OFH) for first time and successfully explored its application for the removal of hazardous BG from aqueous media.

Results and discussion

Characterization of OFH :

OFH is composed of cellulose, hemicellulose, lignin etc. which contain polar functional groups such as alcohols, aldehydes, ketones, carboxylic, phenol and other groups. Fig. 2 shows the FTIR spectra of OFH. Spectral band observed at 2962–2853 cm^{-1} and 1485–1375 cm^{-1} represent C–H stretching and C–H bending group. The peak at 1725 cm^{-1} corresponds to C=O group. Carbonyl stretching vibration at 1725–1700 cm^{-1} , carboxylate ion stretching in 1610–1550 cm^{-1} region shows presence of carboxylic acid. IR spectra also represent aldehyde group as it shows carbonyl stretching vibration 1740–1695 cm^{-1} . Peak at 1620–1510 cm^{-1} is due to N–H bending vibration. Peaks at 900–1100 cm^{-1} and 700–900 cm^{-1} represents $\text{CH}_2\text{--O--Si}$ and Si--C group respectively.

Equilibrium time study :

The study of equilibrium time on different concentrations of BG solutions showed that as we increase the contact time the percentage removal of BG also increases. All solutions of different BG concentrations showed a saturation point at 50 min (Fig. 3). Equilibrium time is more for high dye concentration solutions. Fig. 3 also shows that rate of adsorption of BG was very fast during initial stage of adsorption process. The concentration gradient will be responsible for these changes in a rate of adsorption. In the beginning, because of high concentration gradient, the driving force helps in this rapid adsorption. However, as the concentration gradient decreases with time, the rate was reduced till the equilibrium is attended. This may the reason that after the equilibrium

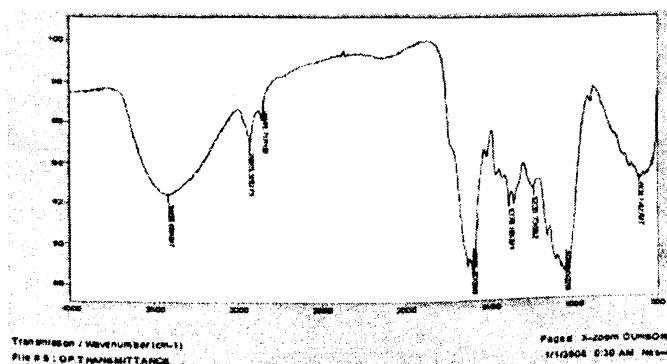


Fig. 2. FTIR spectra of OFH.

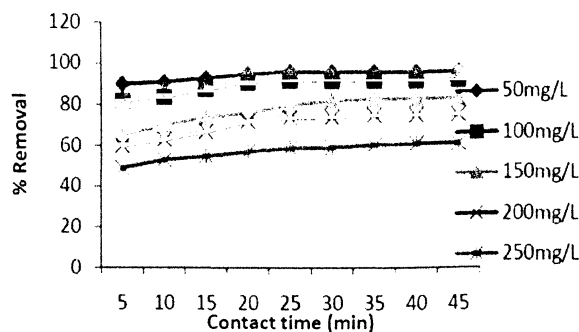


Fig. 3. Study of optimum contact time at various BG concentration.

time and a particular time interval adsorption percentage remains almost constant.

We found that maximum dye removal, 96% achieved within 50 min and above this no more adsorption takes place. So for further studies 50 min was taken as equilibrium time.

Effect of initial dye concentration :

In order to study the initial dye concentration in removal, experiments were conducted with fixed amount of OFH and varying amount of BG from 50 mg/L to 250 mg/L at the interval of 50 mg/L (Fig. 4) which shows that % removal of BG by OFH decreases as the initial BG concentration increased i.e. 96% at the dye concentration 50 mg/L and only 61% at the concentration 250 mg/L. However an increase in initial concentration of dye solution enhances the net adsorption uptake of dye. This is so because the initial dye concentrations provide the driving force to overcome the resistance to the mass transfer of the dye between the aqueous and the solid phase. The increase in initial concentration also enhances the interaction between adsorbent and dye.

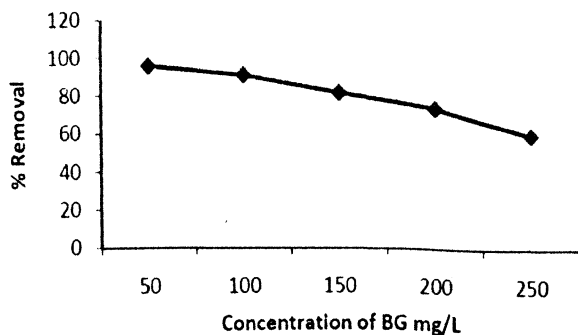


Fig. 4. Study of BG concentration on % removal.

Effect of pH of the adsorption medium :

The percentage removal of BG with change in pH of solution reveals that OFH had maximum BG adsorption (96%) over the pH range of 7–10 it may be due to the fact that at high pH values, the surface of adsorbent become negative which enhance the adsorption of positively charged BG the cationic dye through electrostatic attraction force. Whereas the removal decrease upto 67% at pH 2 (Fig. 5). The low pH is unfavorable for BG adsorption on OFH. Acidic medium of the test solution decrease the negatively charged adsorption site which did not favors the adsorption of positively charged dye cations due to electronic repulsion and also the acidic pH due to presence of H^+ ion competing with dye cations for the adsorption.

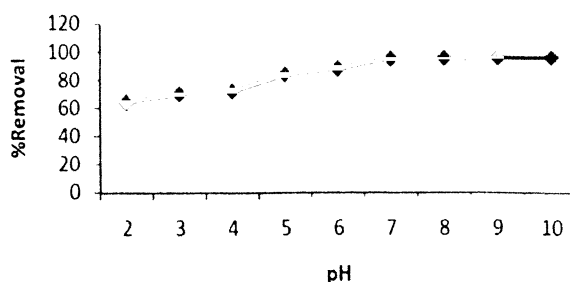


Fig. 5. Study of pH on BG % removal.

Effect of adsorbent dose :

For the evaluation of adsorption process as a function of adsorbent dose, the adsorbent dose was increased from 0.1 g to 0.5 g at the interval of 0.1 g at the dye concentration 50 mg/L for the agitation time 50 min. From the studies of the effect of OFH dose on the percent removal of BG, it was observed that the percent removal of BG dye increase from 67.4% to 95.8% with increase in OFH dose from 0.1 to 0.2 g (Fig. 6). It is due to the increase of the availability of sorption surface and more adsorption sites. Further increase of adsorbent dose of OFH did not cause any significance change because equilibrium was achieved between solid and solution phase.

Adsorption isotherm :

The adsorption isotherm data were analyzed by Langmuir and Freundlich isotherm models.

Langmuir isotherm :

The Langmuir isotherms are based on an assumption

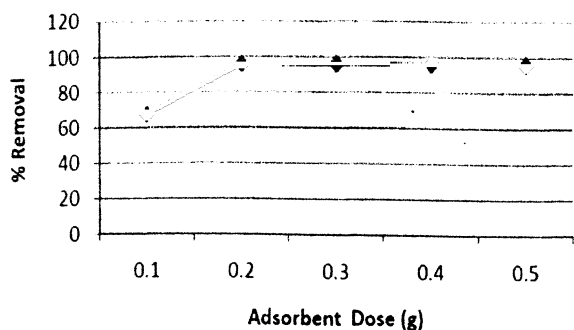


Fig. 6. Study of adsorbent dose on BG % removal.

of monolayer adsorption on to a surface containing a finite number of adsorption sites of uniform energies of adsorption. It is represented as follows²³

$$q_e = q_m K_L C_e / 1 + K_L C_e \quad (1)$$

Linear form of eq. (1) can be written as :

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (2)$$

where, q_e (mg/g) and C_e (mg/L) are the amount of adsorbed adsorbate per unit weight of adsorbent and adsorbed adsorbate concentration in solution in equilibrium, respectively. The constant K_L (L/mg) is the Langmuir equilibrium constant and the K_L/q_m gives the theoretical monolayer saturation capacity, q_m . Therefore a plot of C_e/q_e versus C_e gives a straight line of slope $1/q_m$ and intercepts $1/q_m K_L$.

The essential factor of Langmuir isotherm can be expressed in term of a dimensionless constant called separation factor (R_L , also called equilibrium parameter) which is defined by the following equation :

$$R_L = 1/1 + K_L C_0 \quad (3)$$

where C_0 (mg/L) is the initial adsorbate concentration and q_m (mg/g) is the Langmuir constant related to the energy of adsorption. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$). Linear ($R_L = 1$). Favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

For the construction of Langmuir isotherm C_e/q_e was plotted against C_e (Fig. 7). The correlation coefficient of this is straight line and value of $R^2 = 0.998$.

Freundlich isotherm :

The Freundlich isotherm can be applied to non ideal adsorption on heterogeneous surface as well as multi-

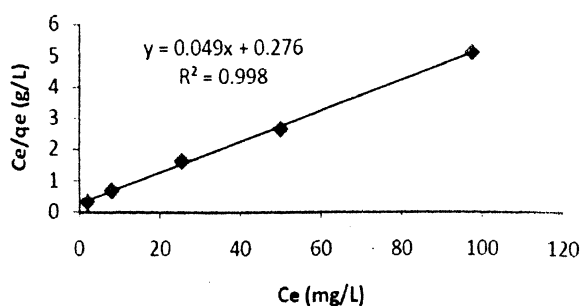


Fig. 7. Langmuir isotherm.

layer sorption and is expressed by the following equation²⁴

$$q_e = K_F C_e^{1/n} \quad (4)$$

A liner form of this expression is

$$\log q_e = \log K_F + 1/n \log C_e \quad (5)$$

where K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) is the Freundlich constant and n is the Freundlich exponent. Therefore a plot of $\log q_e$ versus $\log C_e$ enables the constant and exponent n to be determined.

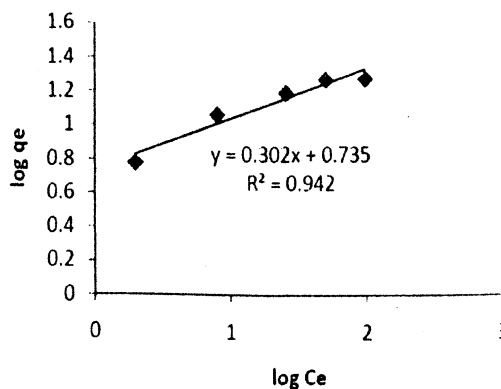


Fig. 8. Freundlich isotherm.

For the value of correlation coefficient of Freundlich isotherm we plot $\log q_e$ versus $\log C_e$ (Fig. 8) and the value of $R^2 = 0.942$.

The adsorption isotherm data of both Langmuir and Freundlich isotherm models with the correlation coefficient are summarized in Table 1. It can be seen that data followed Langmuir isotherm model better than Freundlich isotherm model. Higher value of Langmuir correlation coefficient suggested that the BG adsorption is largely monolayer and the surface is relatively homogeneous in term of active sites.

Table 1. Analysis of Langmuir and Freundlich adsorption isotherm parameter

Langmuir isotherm				Freundlich isotherm		
q_m (mg/g)	K_L	R_L	R^2	K_F	N	R^2
2.04	1.77	0.011–0.0023	0.998	5.432	3.31	0.942

The adsorption capacity of BG on different adsorbents is summarize in Table 2. It can be observed that the adsorbent capacity of both OFH and activated carbon derived from acorn is higher than other adsorbents used. Value of adsorption capacity of OFH and activated carbon prepared from acorn is comparable. However the use of OFH as adsorbents is cost effective and hence can easily be adopted.

Table 2. Adsorption capacity of BG on different adsorbents

Adsorbent	q_m (mg/g)	Refs.
Reddish peels	0.069	20
Jamun stem	0.566	20
Coal	0.929	20
Activated carbon prepared from acorn	2.11	22
OFH	2.04	Present study

Kinetics study :

In order to investigate the mechanism of adsorption and to determine the rate controlling step the following kinetic rate equations have been used to test the experimental data.

Pseudo-first order equation :

The pseudo-first order equation of Lagergren is generally expressed as follows²⁴ :

$$dq_t/dt = k_1 (q_e - q_t) \quad (8)$$

After integrating and applying boundary condition, $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$; then integration form of eq. (8) becomes

$$q_t = q_e (1 - e^{-k_1 t}) \quad (9)$$

However, eq. (9) is transformed into its linear form for use in kinetic analysis of data as

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

where, q_e (mg/g) and q_t (mg/g) are the amount of adsorbed adsorbate at equilibrium and at time t , respectively, and k_1 (min^{-1}) is the rate constant of pseudo-first order adsorption.

Pseudo-second order equation :

If the rate of adsorption has second-order mechanism, the pseudo-second order chemisorptions kinetic rate equation is expressed as follows²⁴ :

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (11)$$

Integrating this equation for the boundary condition, gives

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad (12)$$

which is integrated rate law for pseudo-second order reaction eq. (12) can be rearrange to its linear form as

$$t/q_t = 1/k_2 q_e^2 + 1/q_e t \quad (13)$$

where, k_2 (g/mg min) is the equilibrium rate constant of pseudo-second order adsorption. If the pseudo-second order is applicable, the plot of t/q_e against t should given a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot, and there is no need to know any parameter beforehand.

The adsorption kinetics of BG on OFH was studied. We compared the q_e experimental value with the value of q_e calculated of pseudo-first order equation and found that they varied a lot, whereas, in case of pseudo-second order equation the calculated q_e value are much closer to the experimental q_e value (Table 3). From the Table 3 it is clear that the value of regression correlation coefficient R^2 are more close to 1 in case of pseudo-second order equation in comparison to pseudo-first order equation.

Table 3. Adsorption kinetic parameter of Brilliant Green Dye on OFH

Kinetic model (mg/L)	50	100	150	200	250
Pseudo-first order :					
k_1 (L/min)	0.048	0.064	0.052	0.052	0.038
q_e .expt. (mg/g)	6	11.56	15.56	18.75	19.86
q_e .calcd. (mg/g)	0.8147	3.459	8.74	8.74	6.16
r^2	0.900	0.897	0.960	0.960	0.987
Pseudo-second order :					
k^2 (g/mg min)	3795.64	1647.29	1851.11	–	4210
q_e .expt. (mg/g)	6	11.56	15.56	–	19.86
q_e .calcd. (mg/g)	6.13	12.04	16.66	–	20.0
r^2	0.999	0.998	0.998	–	0.999

Conclusion :

The adsorption process is a suitable technique for the

removal of BG. Agricultural waste product as *Oplismenus frumentaceus* husk is an efficient and cost effective adsorbent. Large scale use of this adsorbent will save the environment from the pollution due to burning of *Oplismenus frumentaceus* husk. Experiment also shows that its adsorption capacity for Brilliant Green Dye is higher than many other adsorbents. It is found that % removal increases as we decrease the initial concentration of BG, increase the contact time, pH and amount of adsorbent. Langmuir isotherm model gave better fitting with experimental data than Freundlich isotherm model. Kinetic experiments clearly indicate that Brilliant Green Dye adsorption follows pseudo-second order kinetic model and adsorption was controlled by chemisorptions process.

Experimental

Adsorbent OFH :

Oplismenus frumentaceus husk (OFH) is a farming waste, obtained from a mill of Pauri Garhwal, Uttarakhand, India. This husk was washed four to five times with distilled water then dried in the sunlight until all the moisture was evaporated. The OFH was ground to a fine powder, the husk was sieved and 0.25 mesh was used for the batch experiment.

Adsorbate :

Reagent grade Brilliant Green Dye having molecular formula $C_{27}H_{34}O_4N_2S$, C.I. No. = 42040, nature = basic dye, m.p. = 210 °C, λ_{max} = 624.6 nm. An accurate quantity of dye was dissolved in double distilled water to prepare stock solution (500 mg/L). Experimental solutions of desired concentration were obtained by appropriate dilutions of the stock solution.

Instruments :

Digital pH meter (Systronics 335), Orbital shaker (Shivam ISO 900/2000), UV-Vis spectrophotometer (Systronics 2202) and FTIR spectrophotometer (ABB FTLA 2000) were used in this work.

Infrared study of OFH :

Fourier transformation infrared spectrophotometer (FTIR) spectra of OFH were recorded in KBr pellet on FTIR spectrophotometer. The spectrum was recorded in the mid-IR range from 4000–500 cm^{-1} .

Batch adsorption experiment :

The adsorption experiments were carried out in a batch

process. All experiments were performed by using conical flask of 100 mL capacity, containing 0.2 g of OFH in 25 ml of dye solution. The pH adjustments were carried out either by dilute hydrochloric acid or by dilute sodium hydroxide solution. Digital pH meter was used for the pH measurement. The reaction mixture was mixed with the adsorbent and kept in orbital shaker of 100 rpm for desired time and after that samples were filtered out using Whatman filter paper No. 42 and then adsorption process were analyzed by double beam spectrophotometer.

The effect of initial BG concentration on the removal of BG was investigated by employing different concentration i.e. 50, 100, 150, 200, 250 mg/L of 25 mL BG solution with fixed adsorbent dose (0.2 g). The percentage removal of dye of these solutions recorded at different time intervals at a constant pH 7. All the solutions were showed a saturation point at 50 min. For further studies 50 min was taken as optimum time. To study the effect of pH on BG adsorption on adsorbent, batch adsorption studies were carried at different pH. The experiments were carried on 25 mL of solution containing 50 mg/L of BG, treated with 0.2 g of adsorbent in the pH range between 2 to 12 with 50 min contact. The adsorption of adsorbent dose (OFH) on BG was also studied by varying the mass of adsorbent on 50 mg/L solution of the dye varying the adsorbent dose 0.1, 0.2, 0.3, 0.4 and 0.5 g keeping the contact for 50 min. All these experiment were carried out at the temperature 303 K.

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