REMOVAL OF BRILLIANT GREEN DYE FROM WASTEWATER USING ACTIVATED CHICKPEA HUSK AS AN ADSORBENT

Sonia Rani*, Sudesh Chaudhary*

* Centre of Excellence for Energy and Environmental Studies, Deenbandhu Chhotu Ram University of Science and Technology, Murthal, Haryana, India

corresponding author: Sudesh Chaudhary, e-mail: sudesh_choudhary@yahoo.com, sudesh.energy@dcrustm.org

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ABSTRACT

A novel adsorbent was developed from chickpea husk and its powder form was used for elimination of brilliant green dye from wastewater. Activated carbon from chickpea husk has been prepared and distinguished with a Scanning electron microscope, Brunauer-Emmett-Teller surface area analyser and a Fourier transform infrared spectroscope. Different variables, like contact time of adsorbent and adsorbate, adsorbent amount, initial concentration of dye and pH were studied to perceive their effect on adsorption of dye. The elimination percentage of brilliant green dye by using chickpea husk was found to be 90.3 % in 150 min at a concentration of 20 mg/l and pH = 7 when a dose of 0.1 g was used. Adsorption kinetics was verified by pseudo 1st order and pseudo 2nd order. It was observed that rate of adsorption of brilliant green dye follows pseudo 2nd order model. Experimental equilibrium study was discussed using Langmuir and Freundlich isotherms models and it was observed that the Freundlich adsorption isotherm model was well fitted for the adsorption of brilliant green dye.

Keywords: *adsorption, brilliant green, activated chickpea husk, scanning electron microscope*

INTRODUCTION

Dyes are broadly used in plastic, cloth, paper, food colouring and cosmetics industry in India. Fresh water is used in dye industries and the polluted water containing dyes is released. Dyes are stable and not easily biodegradable; therefore, dyes contribute to water pollution. The toxic nature of dyes affects aquatic life as well as environmental pollution. They also cause certain health hazards like cancer, skin irritation, mutations. Dyes in wastewater also prevent passing of sunlight into water, thus minimizing photosynthesis process and cause environmental pollution. Therefore, its removal from water becomes necessary. There are numerous methods for dye removal from wastewater, such as coagulation, flocculation, biological treatments, photocatalysis, oxidation, precipitation, filtration, membrane separation and adsorption. However, most of these methods are expensive or less effective. Therefore, adsorption method gives satisfactory results, and it is simple to handle

and produces less amount of waste sludge compared to the other methods. Many types of adsorbents have been prepared to remove dye pollution by adsorption. Activated carbon has a high adsorption potential, large surface area, and permeable structure, so it shows great significance for dye removal [1 - 3].

Activated carbon produced from agro-waste is a very effectual adsorbent for dye adsorption from wastewater [4]. It is eco-friendly, low-cost, and easily available. Research has been focusing on materials that are cheap, biodegradable and reusable - fly ash [5], peanut [6], sawdust [7], pumice stone [8], rice husk [9], banana and orange peel [10], jackfruit [11], orange peel [12], coir pith waste [13], sugar beet pulp [14], neem leaf powder [15], pumpkin seed [16] and guava leaf powder [17] also have been prepared to eliminate dyes from wastewater. The objective of present study is to utilize chickpea husk waste as an adsorbent material for brilliant green (BG) dye removal. In this study, activated carbon was developed from chickpea husk *(Cicer arietinum)* and experimental work was carried out for BG dye removal by adsorption process. Activated chickpea husk adsorbent was characterised by BET (Brunauer-Emmett-Teller), SEM (Scanning electron microscopy) and FTIR (Fourier transform infrared spectroscopy). The effect of various variables, like time, pH of solution, adsorbent material dose and dye concentration were studied. The nature of adsorption was calculated by thermodynamic parameters. Kinetic models were also investigated using different models. This study will be beneficial for the elimination of dye from wastewater using adsorbent prepared from chickpea husk.

MATERIALS AND METHODS

Chemicals and solutions

The adsorbate dye (brilliant green), having dye content of 95 % (C.I: 42040, MW: 482.65, λ_{max}: 625 nm), supplied by Loba Chemie Pvt. Ltd. Palghar, Maharashtra, India was used, and its molecules are present in cationic form in aqueous solution (Figure 1). 0.1 M HCl and 0.1 M NaOH solutions were used to maintain the pH of the prepared solution. Stock solution of 1000 mg/l concentration of brilliant green dye is prepared by dissolving the accurately weighted quantity of 1 g of powder form of BG dye in 1 L of double distilled water. All the solutions of required concentrations used in experiments were prepared by using consecutive dilutions of the dye stock solution. The dye amount is measured by using an UV spectrophotometer.

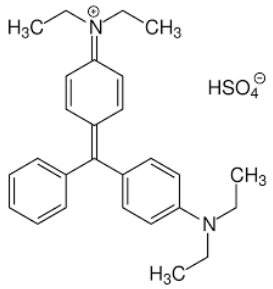


Figure 1. Structure of brilliant green dye [18]

Preparation of adsorbent from chickpea husk

Chickpea husk is disposed as a waste in a small-scale husking mill. The disposed waste is used as animal feed and as firewood in resorts and hotels. The chickpea husk *(Cicer arietinum)* was collected in dry form from a local husking mill nearby. Then it was washed with double-distilled water to remove dirt and dried in an oven at 70 - 80 °C. The material was crushed, powdered, and sieved to 0.150 - 0.300 mm mesh size. The material of 0.150 mm grain size was then mixed with sulphuric acid (H_2SO_4) in 1:1 ratio, then heated for 2 h at 500 °C in a muffle furnace. After cooling, the powder was washed with double-distilled water to neutralise the pH. After that, the powder was dried at 100 °C for 4 h. The powder prepared in this way is called activated chickpea husk.

Measurement of dye removal

The adsorbed BG dye quantity q_t (mg/g) on activated chickpea husk per unit weight at

given time *t*, and dye elimination efficiency percentage (*R*) are calculated as follows:

$$q_t = \frac{(c_0 - c_e)\cdot V}{m} \quad (1)$$

$$R = \frac{(c_0 - c_e)\cdot 100}{c_e} \quad (2)$$

where c_o denotes the BG dye concentration at initial point, c_e denotes the BG dye concentration at given time *t*, *V* denotes amount of prepared BG dye solution, while *m* denotes the mass of activated chickpea husk in grams.

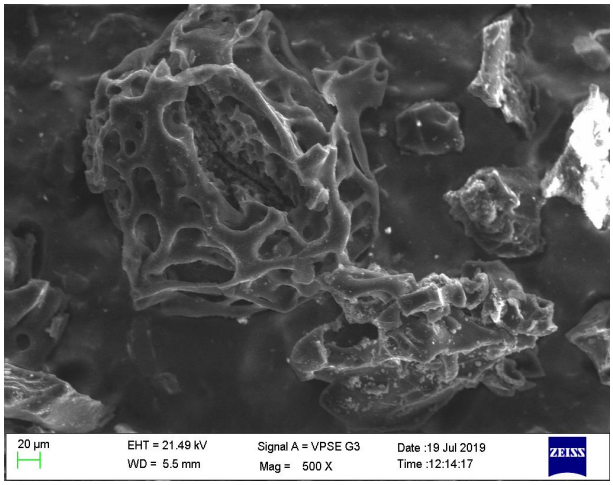
Experimental

Experiments were performed at room temperature using glass beaker of different sizes. To study the adsorption isotherm process, 0.1 g of activated chickpea husk was dissolved in 100 ml solution of various concentrations (20 - 100 mg/l) of BG dye at pH = 7.0 for 150 min. Continuous shaking was done at room temperature (25 ± 2 °C). After reaching equilibrium, the dye was adsorbed at the adsorbent's surface and the quantity of adsorbed dye was calculated by the variation in these two given concentrations. After performing three replica experiments for different variables, only average values of all variables were taken into account for all the experiments. 0.1 gram of adsorbent dose was taken in 100 ml solution having 20 mg/l of dye concentration at pH = 7.

RESULTS AND DISCUSSION

Characterization of prepared adsorbent

Analysis of activated chickpea husk surface was performed by SEM before and after adsorption of the given dye. Figures 2a and 2b represent SEM images of activated chickpea husk before and after adsorption at magnification of 500x and 1000x, respectively. Figure 2a indicates the porous structure of activated chickpea husk. The porous structure supports the adsorption process, so that activated chickpea husk works as an effective adsorbent in removing brilliant green dye. Figure 2b shows the dye particles that were diffused into the pores of adsorbent.



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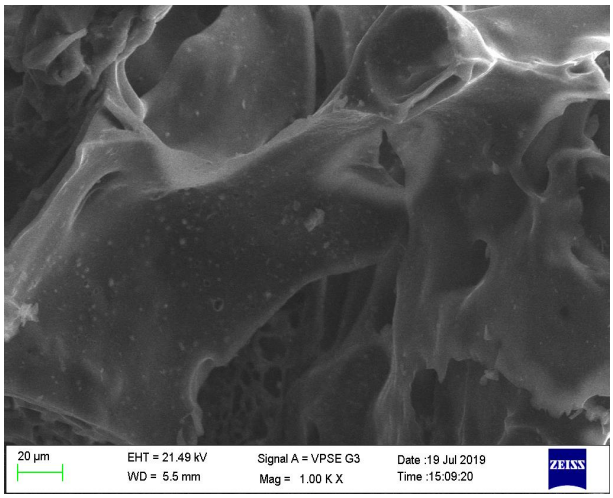


b)

Figure 2. SEM images of activated chickpea husk before adsorption (a) and after adsorption (b)

The surface area of the activated chickpea husk, determined by BET method, is 9.79 m^2/g, pore volume is 0.01 cc/g and pore diameter is 4.467 nm.

An FTIR spectrum gives information regarding the functional groups available in the given adsorbent. FTIR spectrum of activated chickpea husk before and after adsorption of BG dye in the wavelengths range

of 400 - 4000 µm is shown in Figure 3. The band between 3700 - 3800 cm^{-1} indicates the availability of OH group. After adsorption, this spectrum indicates that there may be hydrogen bonding between BG dye and adsorbent. The band at 3500 cm^{-1} shows the availability of N-H groups. The band between 1500 - 1600 cm^{-1} shows the availability of C=O in spectrum of activated chickpea husk. There is a band present between 1020 - 1200 cm^{-1} which indicates stretching of C=OH groups.

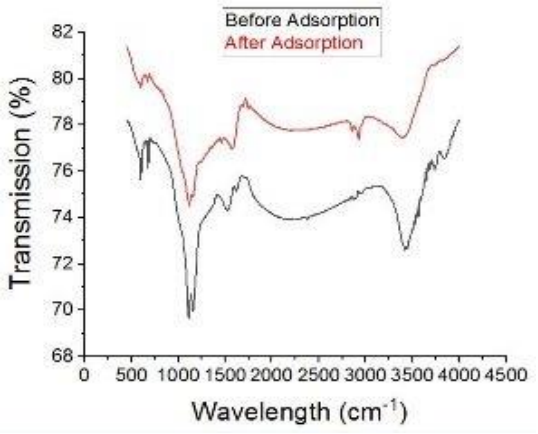


Figure 3. FTIR spectra of activated chickpea husk before and after adsorption of BG dye

Batch adsorption studies

Effect of pH of the solution

The pH of the dye solution is a vital factor in the dye removal study, and it also affects the brilliant green dye structure and its colour quality. Adsorption of BG dye was carried out in pH range of 4 - 12 with 20 mg/l initial concentration and adsorbent dose of 0.1g. Figure 4a shows the removal percentage of dye at various pH. It can be seen from the figure that removal of dye increases with increasing pH and maximum dye adsorption occurs at pH = 10. The increase in adsorption with increase in pH value of given dye solution appears because of equalization of the charges at the adsorbent surface. In an acidic medium, adsorbent particles acquire a positive charge which leads to lesser dye removal percentage due to competition with hydrogen ion. At higher pH, adsorbent surface acquires negative charge which increases the electrostatic force of attraction between dye particles and adsorbent surface [19].

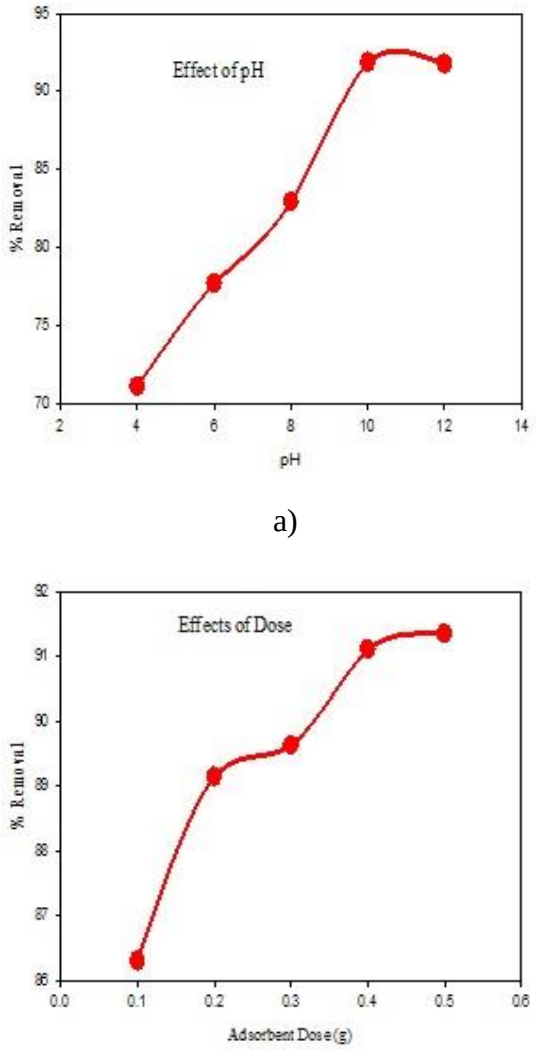


Figure 4. Effect of pH of the dye solution (a) and adsorbent dose (b) on BG dye removal

Effect of the dose amount

The elimination of brilliant green dye with activated chickpea husk at 20 mg/l concentration is affected by different doses of adsorbent, which is shown in Figure 4b. To check the discrepancy in adsorption percentage due to adsorbent dose, a range of doses (0.1 - 0.5 g/100 ml) of activated chickpea husk was used and experiments were done using 20 mg/l of brilliant green dye concentration at pH = 7 for 150 min. Adsorption percentage increases with increasing adsorbent dose. The reason for this

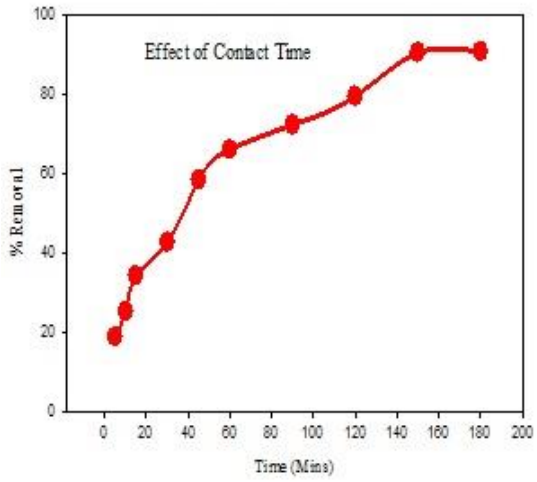
is the increase in available sites on the surface of the prepared adsorbent.

Effect of the contact time

The study of contact time of adsorbate and adsorbent is very useful in determining the dye removal percentage at fixed time intervals by selected amount of adsorbent. Figure 5a shows the deviation in the percentage of brilliant green dye elimination over time for 20 mg/l initial concentration, pH = 7.0 and 0.1 g of activated chickpea husk. From Figure 5a it can be estimated that the adsorption takes approximately 150 minutes. After reaching equilibrium, a very small amount of BG dye was adsorbed. Figure 5a also shows that most of the adsorption takes place in the initial 45 min of time and increases slowly after this. At the beginning of contact time, the adsorption was very fast because of accessibility of available sites on surface of adsorbent. Equilibrium was achieved after 150 min, i.e., when the highest dye adsorption ability was reached.

Effect of BG dye concentration

The concentration of dye directly affects the dye adsorption because the reactions in the adsorption process are directly proportional to the solute concentration. Five initial concentrations - 20, 40, 60, 80 and 100 mg/l were used in experiments to check the influence of initial dye concentration on the elimination rate of brilliant green dye (Figure 5b). More than 90 % removal was achieved at low initial concentration of 20 mg/l, pH = 7 and dose of 0.1 g for 150 min, while 75.5 % dye removal was achieved for highest concentration of 100 mg/l at pH = 7 and dose of 0.1 g for 150 min. Taking the above values, it can be observed that adsorption is fast when dye concentration is low. The removal percentage decreases with increasing concentration of dye because of increased struggle for the dynamic sites.



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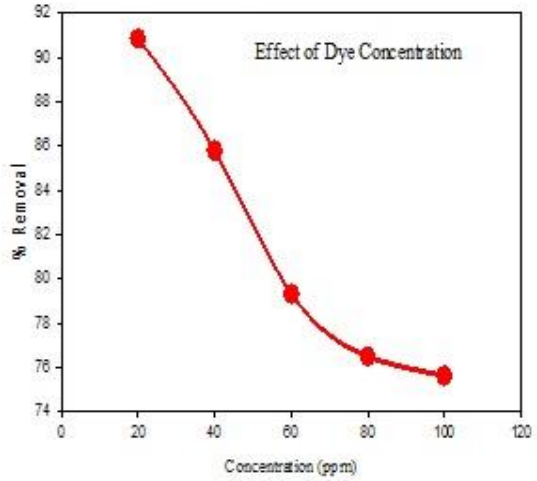

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Figure 5. Effect of contact time (a) and dye concentration (b) on BG dye removal

Kinetics of adsorption

Different kinetic models are available to study the process of dye adsorption. Adsorption of BG dye on activated chickpea husk was described separately by means of pseudo 1st order model and pseudo 2nd order model.

Pseudo 1st order kinetic model

Pseudo 1st order kinetic model proposes that the difference in adsorbent amount used with time and concentration of BG dye is directly proportional to the solute consumption rate

with time duration. The adsorption constant value is articulated as a pseudo 1st order rate expression, shown as follows [20]:

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \qquad (3)$$

where q_e and q_t denote the dye adsorbed quantities in mg/g at equilibrium and at time t (min), and k_1 is the pseudo 1st order rate constant (min $^{-1}$). When the above expression is integrated at start time (t = 0), q_t = 0, quantity of adsorbed dye is q_t and after adjusting equation (3), pseudo 1st order reaction becomes:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \qquad (4)$$

The slope and intercept in the graph of log(q_e - q_t) vs t helps calculate the pseudo 1st order rate constant k_1 and q_e. The graph of log(q_e - q_t) versus t should give a straight line which shows the applicability of the model. Figure 6a shows that experimental values are not in a linear form and the stirring speed used in this study may be the reason for this. Table 1 shows the determined k_1 and q_e values. From Table 1, it can be concluded that the brilliant green dye adsorption kinetics on activated chickpea husk cannot be described by the pseudo 1st order model.

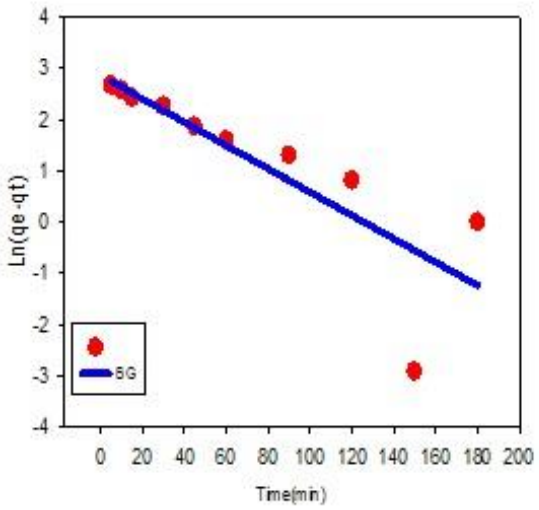
Pseudo 2nd order kinetic model

Adsorption of dyes generally follows the pseudo 2nd order model. Adsorption kinetics can be expressed by pseudo 2nd model [19], as follows:

$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \qquad (5)$$

where k_2 denotes the pseudo 2nd order rate constant (g/mg·min). After integration of equation (5) and rearranging, the following form is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_t} \qquad (6)$$



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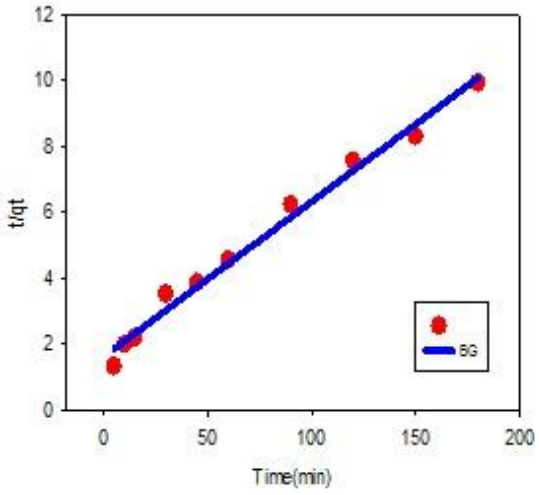

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Figure 6. Pseudo 1st order model (a) and pseudo 2nd order kinetic model (b) for BG dye removal by means of activated chickpea husk

Table 1. Kinetic parameters calculated from the models

Pseudo 1st order			Pseudo 2nd order		
k_1	q_e (mg/g)	R^2	q_e (mg/g)	k_2	R^2
0.022	17.47	0.695	21.22	0.0014	0.987

A straight line is shown between the slope ($1/q_e$) and intercept ($1/k_2q_e$) on the graph of t/q_t versus t (Figure 6b). The slope and intercept in the graph were used for calculating values of equilibrium adsorption capacity q_e and k_2, respectively. The determined values of k_2,

amount of dye adsorbed (q_e) and coefficient of determination (R^2) are given in Table 1. It can be seen that the value of R^2 is 0.987 for 20 mg/l of brilliant green dye which is nearly 1. Therefore, we can say that the adsorption kinetics for brilliant green dye on activated chickpea husk follows the pseudo 2nd order model. These results show that the pseudo 2nd order model better explains the brilliant green dye adsorption on activated chickpea husk than the pseudo 1st order model. Therefore, the adsorption of brilliant green dye on the surface of activated chickpea husk is a chemical adsorption [20].

Adsorption isotherms

Adsorption isotherm defines the characteristics of interaction between the molecules of adsorbate and adsorbent. Isotherms provide information about the adsorbent used. There are several adsorption isotherms available for analysing the experimental equilibrium adsorption data. Langmuir and Freundlich adsorption isotherms are the most commonly used.

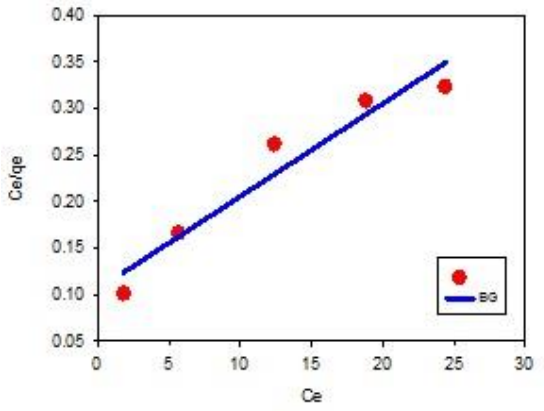
Langmuir isotherm model

The Langmuir isotherm supposes that there are specific homogenous sites which are equally scattered over the absorbent exterior on which adsorption occurs (Figure 7a).

The Langmuir isotherm model equation in linear form may be written as follows [21]:

$$\frac{c_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{c_e}{q_m} \qquad (7)$$

where q_m is maximum adsorption capacity and K_L is Langmuir isotherm constant. These values are given in Table 2.



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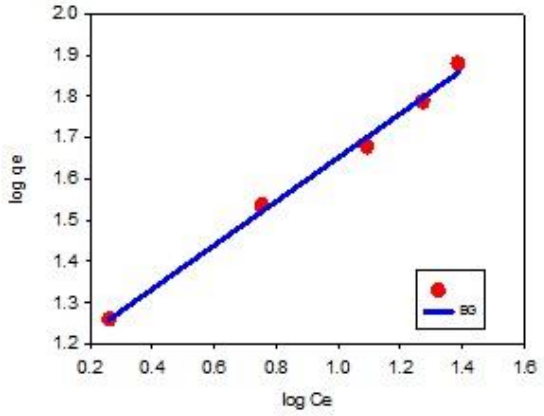

b)

Figure 7. Langmuir adsorption isotherm (a) and Freundlich adsorption isotherm (b) for BG dye removal by means of activated chickpea husk

Table 2. Calculated equilibrium modelling parameters

Langmuir			Freundlich		
q_m	K_L	R^2	n	K_f	R^2
100	0.09	0.933	1.8	3.06	0.994

Freundlich isotherm model

The Freundlich isotherm model is presented as follows [22]:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \qquad (8)$$

where q_e denotes the dye adsorbed quantity at equilibrium, and K_f and n are constants related to the adsorption potential and intensity of prepared adsorbent. The plot of Freundlich adsorption isotherm for brilliant green dye on chickpea husk is given in Figure 7b and Freundlich constants were also determined and given in Table 2. It can be noted that Freundlich isotherm model better explains the adsorption process than the Langmuir isotherm model for the present research. Since the adsorption is assumed to be chemisorption in nature, as discussed earlier, it is possible that a monolayer of dye molecules was formed on the surface of adsorbent. Thus, adsorption should be physically represented by Freundlich isotherm model.

CONCLUSION

The present study shows that activated chickpea husk can be used as a valuable adsorbent for brilliant green dye removal from wastewater. The brilliant green dye adsorption is controlled by dose of activated chickpea husk, concentration of brilliant green dye, contact time with dye and pH of dye solution. The percentage of adsorption increases with contact time, pH of dye solution, and dose of activated chickpea husk, but decreases with increasing concentration of brilliant green dye. The adsorption kinetics follows the pseudo 2nd order kinetic model (R^2 = 0.987) instead of pseudo 1st order model (R^2 = 0.695). Equilibrium adsorption data for brilliant green dye was better explained by Freundlich isotherm model (R^2 = 0.994). The experimental study shows that activated chickpea husk can be used as adsorbent for efficient dye elimination from wastewater. Further research study is under investigation focusing on the recovery of brilliant green dye and reuse of waste produced during this study.

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