Batch adsorption of Brilliant Green dye on raw Beech sawdust: Equilibrium isotherms and kinetic studies

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Abstract

This paper deals with the adsorption study of a synthetic dye namely Brilliant Green (BG) used frequently in the textile industries, using a natural and a low-cost adsorbent, which is locally available. The adsorbent used in this work is the Beech sawdust, collected from an industrial unit of wood in Fez city (Morocco) and which is characterized before by various techniques. The study of the adsorption potential of this dye on Beech sawdust and the monitoring of the influence of several parameters on this adsorption were evaluated.
The analysis of the results obtained during this study showed that the adsorption rate of Brilliant Green dye reached a percentage of about 82% with a maximum concentration of 80 ppm. The optimum mass of Beech sawdust used is 1.25 g in a volume of 100 ml. The mixture was agitated for 90 min as a contact time at ambient temperature. The adsorption isotherms modeling obtained is consistent with the Langmuir model and the kinetic data follows the pseudo-second order model.
This study revealed that the Beech sawdust is very effective in removing Brilliant Green as a cationic dye, which making these sawdust an effective alternative for the removal of cationic dyes from polluted water.

Keywords: Brilliant Green; Adsorption; Beech; isotherm; kinetic.

1. Introduction

The colored waste effluents are considered among the main causes of water pollution, because the presence of synthetic dyes in waters is mostly toxic for the aquatic environment [1]. Nowadays there are more than 10,000 dyes with different types [2], which are classified as anionic, cationic and non-ionic depending on their chemical structures. Cationic dyes are known as the most toxic substances in comparison with the other ones [3]. The removal of these compounds from the industrial water effluents is became a necessity for the protection of aquatic organisms and their habitat, because dyes in the waste water undergo some changes (chemical and biological) that affect their structures and thus their chemical properties [4]. The currently used methods for the treatment and the removal of dyes from waste water are chemical coagulation/flocculation [5],

biodegradation, membrane filtration [6], chemical oxidation [7], ozonation [8], ion exchange, electrochemical methods and adsorption [9]. These techniques are effective but they based on the use of chemical products and they require a high cost and an intensive energy. Therefore, the development of efficient, eco-friendly and low cost techniques is strongly required to reduce the dye content in waste effluents. The adsorption is the most favorable method that respects these requirements and which is simple in its application [10, 11]. Following the same perspective, this work aims to study the adsorption potential of Brilliant Green (cationic dye) by the raw Beech sawdust collected from a wood sawmill in Fez city (Morocco) and which is defined as a natural and a biodegradable adsorbent.

2. Materials and methods

2.1. Materials

Beech sawdust was obtained from an industrial unit of wood (sawmill) in Fez city, Morocco. The sawdust collected was washed with distilled water, dried at 100 °C and then crushed and sieved into a range of 100-500 µm and then used in it raw state without any chemical activation. pHpzc of Beech sawdust is equal to 7.1.

Brilliant Green (BG; $C_{27}SH_{34}N_2O_4$; Mw = 482.64 g.mol^{-1} and purity greater than 85%) was chosen as model dye for adsorption study. The hydrochloric acid "HCl" and the sodium hydroxide "NaOH" are two reagents that have been used during the experiments in order to adjust the initial pH of BG solutions.

2.2. Adsorption Experiments

Brilliant Green adsorption experiments were carried out using the batch method. A mass of 2g of Beech sawdust was dispersed in 100 ml of BG solution at pH=7, using an initial concentration in the range from 0.2 to 200 ppm. The mixture was agitated (250 rpm) at ambient temperature. After each adsorption experiment, the Beech sawdust was separated from BG solutions by centrifugation followed by filtration. Then the remaining concentration of BG was determined by measuring the absorbance at 625 nm by UV spectrophotometry UV2300II type.

The adsorption rate (% Ads) of Brilliant Green on Beech sawdust was calculated using the equation (1):

$$\% Ads = \frac{c_0 - c_e}{c_0} \times 100 \qquad (1)$$

Where:

C_0 and C_e are respectively the initial and the equilibrium dye concentrations (mg/l).

The influence of operating conditions on the adsorption of BG on Beech sawdust was studied in a batch system by varying the adsorbent mass from 0.2 to 2 g, the initial dye concentration from 0.2 to 200 ppm and the pH of the BG solution in the range of 1-10.

## 3. Results and discussions

3.1. Influence of pH

The analysis of the results obtained from the effect of pH (Figure1) show that BG adsorption on Beech sawdust is strongly depends on pH values. BG adsorption increases at pH conditions higher than the pHpzc of the adsorbent (pHpzc=7.1). The adsorption rate increases from 48 % to82%, when the pH increases from 1 to 10. This result is explain by the fact that at pH> pHpzc, the charge of Beech sawdust surface becomes negative, enhancing electrostatic attractions with positively charged BG cations. Nevertheless, at low pH values, Beech sawdust surface increases its number of sites positively charged; which decreases the interaction of the BG dye with the adsorbent (repulsion forces); leading to a decrease on the adsorption rate of BG dye. The same remarks were reported by Adnan Ozcan and al. during the study of the "Reactive Blue 19" adsorption onto bentonite [12].
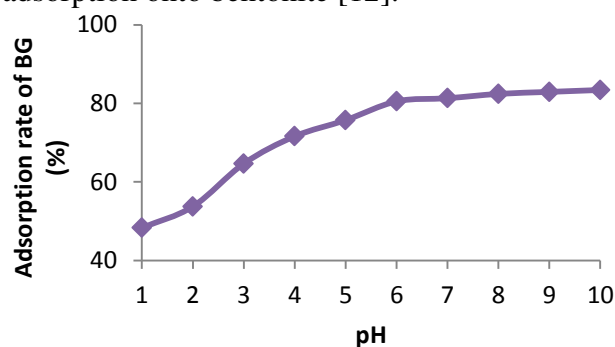
Figure 1. Effect of pH on BG adsorption (Initial concentration = 50 ppm, T = 25 °C, mass of adsorbent = 2 g, contact time = 90 min, agitation speed = 250 rpm, 100µm <Φ<500µm).

### 3.2. Effect of Beech sawdust quantity

The analysis of the plot obtained (Figure 2), show that the BG adsorption rate increases significantly with the increase in the amounts of Beech sawdust. We observe also that the adsorption capacity reaches its maximum value with a quantity of 1.25 g. This result can be explained by the increase in the number of active adsorption site, resulting from the increase in the quantity of the Beech sawdust. A similar observation was obtained by Makhlouf and al. in the adsorption of phenolic compounds on mesoporous material [13].
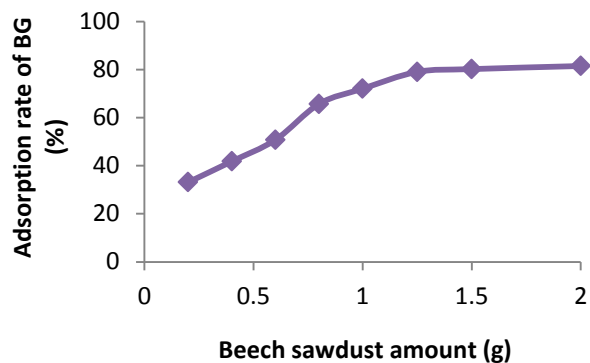
Figure 2. Effect of adsorbent amount on BG adsorption (Initial concentration = 50 ppm, T = 25 °C, pH = 7, contact time = 90 min, Agitation speed = 250 rpm, 100µm <Φ <500µm).

3.3. Effect of initial concentration of BG

The results obtained (Figure3) indicate that the percentage of BG dye adsorption is very low when the initial concentration is less than 10 ppm; however, it increases with the initial concentration. This increase is due to the attraction forces of the concentration gradient which accelerate the diffusion of the dye into the surface of the adsorbent used [14-15].The maximum adsorption rate of BG is reached for a concentration of 80 ppm, but above this concentration, the removal rate fall because the available adsorption sites of sawdust become fewer and hence the removal of BG decrease. The same results were reported in our earlier paper [16].
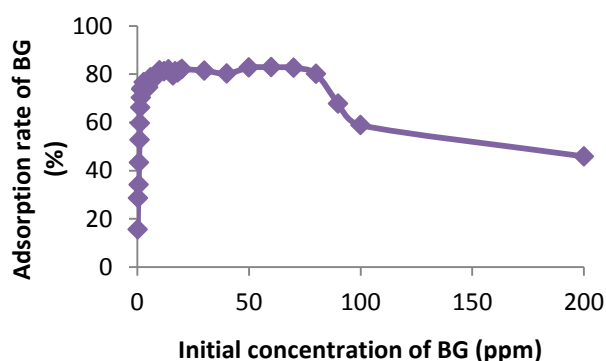
Figure 3. Effect of initial concentration on BG adsorption rate. (t= 90 min, agitation speed = 250 rpm, T = 25 °C, pH = 7, m = 1.25 g, 100 µm <Φ<500 µm) ;

3.4. Adsorption kinetic studies

The adsorption kinetic describes the BG dye removal rate. During this study, two kinetic models were applied to evaluate the kinetic parameters of the adsorption of BG on Beech sawdust, namely the pseudo-first-order and the pseudo-second-order. The uniformity between the experimental data and model-predicted values was expressed by correlation coefficients R^2.

-The pseudo-first-order kinetic model is largely used in the adsorption process. It is expressed by the Lagergren equation (2) [17]:

$$Ln(q_e - q_t) = Ln(q_e) - K_1 t \qquad (2)$$

Where: q_e and q_t are the amounts of BG adsorbed at equilibrium and at time t successively (mg/g), K_1 is the rate constant of the first order adsorption reaction (min^{-1}) and t is the contact time (min).

-The pseudo-second-order reaction is based on the amount of BG dye adsorbed on the surface of Beech sawdust and the amount adsorbed at equilibrium. It was expressed as follows (3) [18]:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \qquad (3)$$

Where: q_t and q_e are the amounts of BG adsorbed at time t and at equilibrium successively (mg/g), K_2 is the rate constant of the second order adsorption reaction (g/mg/min) and t is the contact time (min). The pseudo-first-order (Figure 4-a) and the pseudo-second-order (Figure 4-b) kinetic models are shown below. The values of K_1, K_2, the calculated q_e and the correlation coefficient R^2 obtained from the plots for BG adsorption on Beech sawdust are presented in table 1.
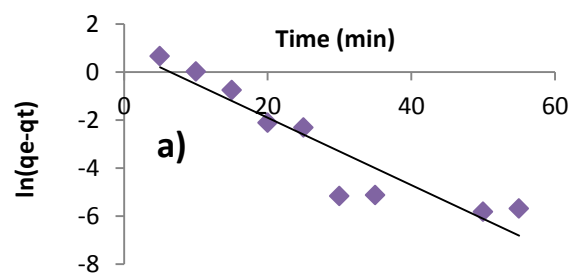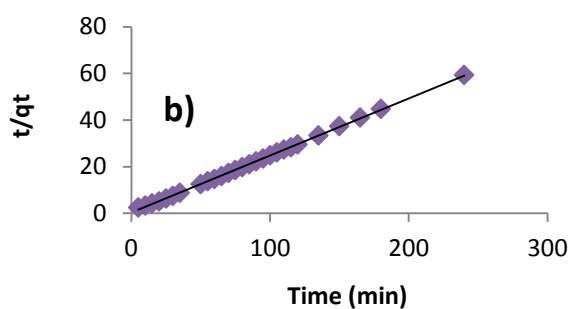
Figure 4. Pseudo-first-order (a) and pseudo-second-order (b) kinetic models for BG adsorption onto Beech sawdust; (Initial concentration= 50 pm, m = 1.25 g, agitation speed = 250 rpm, T = 25 °C, pH = 7, 100 μm <Φ<500 μm).

The analysis of the results obtained (Table 1 and Figure 4) show that these later are matching to pseudo-second-order kinetic. The correlation coefficients R^2 obtained of pseudo-first-order kinetic is about 0.86, which is lower than the R^2 of pseudo-second-order kinetic (0.99). Additionally, q_e values determined using the pseudo-second-order kinetic model (q_e=4.08 mg/g) are more in agreement with the experimentally values (q_e, $_{exp}$=4.03 mg/g) than those obtained with the pseudo-first-order model (q_e=2.43 mg/g). Such results suggest that the adsorption of BG on Beech sawdust was controlled by chemical process and chemisorption [19-20].

Table 1. Pseudo-first-order and pseudo-second-order kinetic models parameters for BG adsorption onto Beech sawdust

|	1st order			2nd order		
$q_{e, exp}$ (mg/g)	R^2	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg.min)	q_e (mg/g)
Beech sawdust 4.03	0.86	0.1402	2.43	0.99	0.2002	4.08

3.5. Adsorption isotherms

The isotherms of adsorption reveal how the dye molecules are distributed between the liquid phase (solution) and the solid phase (adsorbent) when the adsorption phenomenon reaches its equilibrium state [21].Two isotherm models were used to analyze the adsorption equilibrium data, namely, Langmuir and Freundlich models.

The Langmuir and Freundlich isotherms were described by the following equations (4) and (5) respectively [22-23]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} c_e + \frac{1}{q_{max} K_l} \quad (4)$$

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n_f} \text{Log } C_e \quad (5)$$

Where, q_e represents the equilibrium adsorption capacity of Beech sawdust (mg/g), c_e is the equilibrium BG concentration (mg/l), q_{max} is the maximum capacity of Beech sawdust (mg/g), and K_l is the Langmuir constant (l/mg). K_f and n_f are the Freundlich constants. The Langmuir (Figure 5-a) and Freundlich (Figure 5-b) isotherms of the BG dye adsorption onto Beech sawdust are presented in Figure 5. The parameters of the two isothermal models are listed in Table 2.
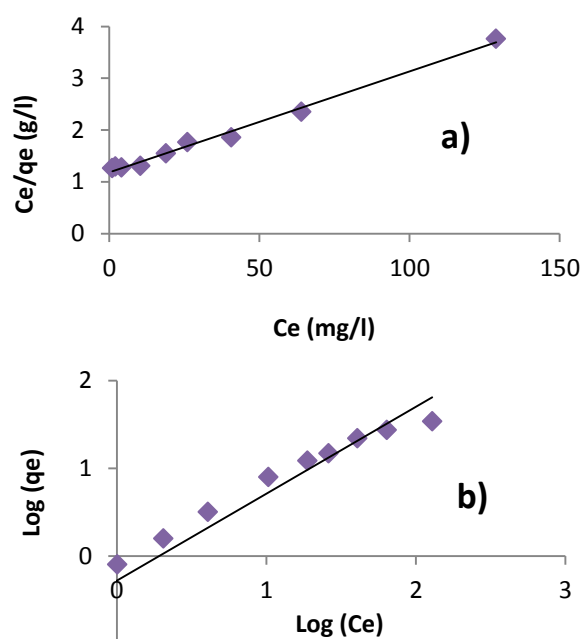
Figure 5. Langmuir (a) and Freundlich (b) isotherms for BG dye adsorption onto Beech sawdust.

The analysis of the results obtained (Figure 5 and Table 2) indicates that the correlation coefficient (R^2=0.997) of Langmuir isotherm is higher than that of Freundlich isotherm (R^2=0.91). The adsorption data are well fitted with Langmuir isotherm. The maximum adsorption capacity (51.28 mg/g) of raw Beech sawdust toward BG dye is estimated by Langmuir isotherm.

Table 2. Adsorption isotherms parameters for BG adsorption onto Beech sawdust

	Langmuir			Freundlich		
	R^2	K_l (l/mg)	q_{max} (g/mg)	R^2	K_f (g/mg)	n_f (mg/g)
Beech sawdust	0.99	0.016	51.28	0.91	0.524	1.01

4. Conclusion

In this study, the raw Beech sawdust was used as adsorbent in the removal of Brilliant Breen dye from aqueous solutions. The results obtained show that this kind of lignocellulosic materials can be used as an efficient and an inexpensive adsorbent to remove cationic dyes from the wastewater. The optimum conditions allowing to achieve a high adsorption rate of BG dye using raw Beech sawdust are: an adsorbent dose of 1.25 g in a volume of 100 ml, a pH of 7, an initial concentration of 80 ppm and a contact time of 90 min at ambient temperature. The adsorption capacity of Beech sawdust is highly controlled by the pH values; maximum adsorption efficiency toward BG is obtained at alkaline conditions (pH>7).

The Kinetic studies indicate that the adsorption process is very well represented by the pseudo-second-order kinetic model. The Langmuir model fits better for the adsorption isotherms as compared to Freundlich model. The raw Beech sawdust seems to be promising alternative for fast removal of cationic dye.

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