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ORIGINAL RESEARCH PAPER

ADSORPTIVE REMOVAL OF BRILLIANT GREEN DYE FROM AQUEOUS SOLUTIONS USING CEDAR AND MAHOGANY SAWDUSTS

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Abstract: The objective of this study is the valorization of industrial wood wastes and their application in the adsorption of a cationic dye "Brilliant Green (BG)" in solution. These experienced natural wastes are Cedar and Mahogany sawdusts, which are part of the range of abundant and inexpensive lignocellulosic products that can replace the conventionally used materials such as charcoal, silica gel and alumina.
The results of the adsorption tests of Brilliant Green, show that under appropriate conditions, the adsorption rate is about 89 % on Cedar and 80 % on Mahogany sawdusts, for a concentration of 100 $mg \cdot L^{-1}$ of dye, by adding 8 $g \cdot L^{-1}$ of cedar and 20 $g \cdot L^{-1}$ of Mahogany as optimal doses of adsorbents, during a contact time of 40 min and at room temperature.
The modeling of adsorption isotherms obtained is consistent with the Langmuir model. The kinetics data indicate that the process of Brilliant Green adsorption on both sawdusts follows the pseudo second order model.
According to this study, these sawdusts are very effective in sorbing the BG and which could be used for the removal of other cationic dyes.

Keywords: *adsorption, cationic dye, depollution, kinetics, isotherm, wood wastes*

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INTRODUCTION

The wood processing industry represents 4 % of the national industry in number of companies, sawmills alone count more than 49 companies, which is about 66 % of the wood processing industries of the Moroccan country. The average production of residues during the sawing process is about 35 % and 55 % of the logs biomass used for softwood and hardwood respectively [1].
In order to valorize these wastes and to contribute to the protection of the environment and the whole forest area, several research teams have directed towards low cost and ecological treatment processes, using natural materials of which sawdust is a part. Therefore, the valorization of these sawdusts, without generating pollutants is a big challenge and is recommended for a sustainable industrial development in order to preserve the environment.
Nowadays, coloring materials and dyes have become increasingly for industrial sectors such as textile, pulp and paper, food, carpet, etc. [2, 3]. Dyes and pigments are widely classified as anionic, cationic and non-ionic, depending on the ionic charge of its molecules. The cationic dyes are considered as more toxic class in comparison with the anionic and non-ionic ones [4]. The liquid discharges of these industries, especially the textile industry, are heavily laden with dyes, which pose not only an aesthetic problem but also dangerous toxicological impacts for the environment [2, 5].
Brilliant Green is one of the cationic dyes used in the dying textile, silk, leather, jute, cotton, in paper printing and in veterinary medicine [6]. It's considered highly toxic and can cause injury to the eyes of humans and animals [2]. It may form also hazardous compounds such as nitrogen oxides and sulfur oxides when heated to decomposition [7].
There are several physical, chemical and biological methods for the treatment and the discoloration of polluted effluents such as coagulation and flocculation [8], biodegradation [9], membrane filtration [10], chemical oxidation, ozonation, ion exchange, electrochemical methods [11] and adsorption [12]. The adsorption is the most favorable method for the elimination of dyes; it has become an analytical method of choice, very effective and simple in its application [13].
Current research is focused on the use of low cost, locally available adsorbents. Sawdust as a biodegradable material has been widely used as an adsorbent for treating colored effluents because of their highly porous structure, and their great adsorption capacity.
The objective of our study is to use sawdust from Cedar and Mahogany in the treatment of colored water, especially for the discoloration of the effluents containing Brilliant Green as a synthetic cationic dye.

MATERIALS AND METHODS

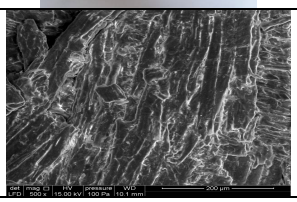
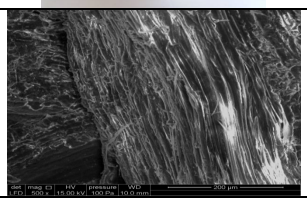
Materials

Adsorbent

The sawdusts used are collected from a local industrial unit of Fez-Morocco, washed with distilled water, dried at 100 °C and then crushed and sieved at different diameters

(1000, 800, 500 and 100 µm). Some characteristics of these sawdusts are represented in Table 1 [14].

Table 1. *Various properties of adsorbents*

Parameters	**Characteristics**	
	Cedar	Mahogany
Family	Softwood	Hardwood
Color	Dark beige	Mahogany red
Morphology		
SEM pictures		
Moisture (%)	21.8	13.3
Loss on ignition (%)	100	98.9

Adsorbate

Brilliant Green (BG) is a cationic dye, whose chemical formula is $C_{27}SH_{34}N_2O_4$ (Figure 1), it has a molecular weight of 482.64 g·mol^{-1} with purity greater than 85 %. It is one of the most important cationic dyes, but it causes a number of adverse effects on humans (irritation of the gastrointestinal tract, severe eye irritation and burns, nausea and vomiting, skin and respiratory irritation) and their environment [2]. This adsorbate is used in the form of aqueous solutions at different concentrations.

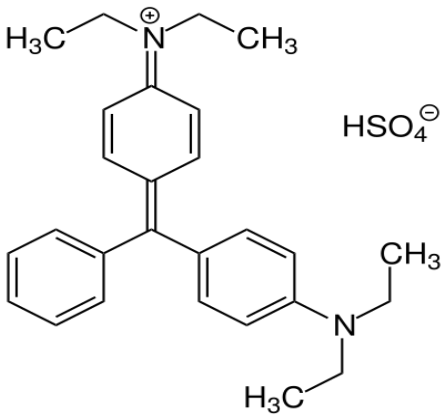


Figure 1. *Molecular structure of Brilliant Green dye*

Chemical products

Two reagents, from Sigma Aldrich, have been used in this study in order to adjust the initial *p*H of colored solutions: the hydrochloric acid HCl (0.1 mol·L^{-1}, purity 37 %) and the sodium hydroxide NaOH (0.1 mol·L^{-1}, purity > 97 %).

Methods

Adsorption Experiments

Adsorption experiments were carried out using batch method in glass flasks containing 100 mL of Brilliant Green dye. After adding a known quantity of each adsorbent (Cedar and Mahogany) to the dye solutions separately, the flaks were agitated at 250 rpm for 90 min to ensure that adsorption equilibrium was attained.

After each adsorption experiment, the adsorbent was removed by centrifugation. Then the filtrate obtained was analyzed by UV spectrophotometry UV2300II type provided by BP Integrated Technologies, Inc. company (Philippines), working at 625 nm (maximum wavelength of Brilliant Green dye) in order to determine the remaining concentration of dye.

We have studied the effect of the main parameters influencing the adsorption capacity such as sawdust diameter, adsorbent mass, initial dye concentration, temperature, agitation speed, contact time and *p*H.

The amounts of the adsorbed dye were calculated from the concentrations of the solutions before and after adsorption by the Equation 1:

$$q_e = \frac{c_0 - c_e}{m} \times v \qquad (1)$$

where: q_e is the amount of BG adsorbed at equilibrium ($mg \cdot g^{-1}$), C_0 and Ce represent the initial and the equilibrium dye concentrations ($mg \cdot L^{-1}$), m is the mass of adsorbent (g) and v is the volume of Brilliant Green solution (mL).

The adsorption percentage of Brilliant Green is calculated by the Equation 2:

$$\%Ads = \frac{c_0 - c_e}{c_0} \times 100 \qquad (2)$$

where:

C_0 and C_e are respectively the initial and the equilibrium dye concentrations ($mg \cdot L^{-1}$).

Study of adsorption kinetics

Two models of kinetics have been chosen to interpret the experimental data, namely the pseudo-first-order model (PFO) and the pseudo-second-order model (PSO).

Pseudo-first-order model (PFO)

The pseudo-first-order model is expressed by the Equation 3 [15]:

$$Ln(q_e - q_t) = Ln(q_e) - K_1 t \qquad (3)$$

where: q_e and q_t represent the amounts of BG adsorbed at equilibrium and at time t respectively ($mg \cdot g^{-1}$), K_1 is the rate constant of the first order adsorption reaction of BG on sawdust (min^{-1}) and t is the contact time (min).

The adsorption rate constant and the equilibrium adsorption capacity were calculated from the plot of Ln (q_e-q_t) versus time (t) [7].

Pseudo-second-order model (PSO)

The pseudo-second-order model is expressed by the Equation 4 [16]:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

where: q_t and q_e represent the amounts of BG adsorbed at time t and at equilibrium respectively (mg·g^{-1}), K_2 is the rate constant of the second order adsorption reaction of BG on sawdust (g·mg^{-1}·min^{-1}) and t is the contact time (min).
The plot of (t / q_t) versus time (t) allows the determination of the parameters K_2 and q_e.
The pseudo-second order model is applicable in a wider time interval (usually the whole process of adsorption) [7].

Study of adsorption isotherms
To model the adsorption isotherms, we have chosen two models with two parameters that are most commonly used: the Langmuir and Freundlich models.

Langmuir model
The Langmuir model is given by the Equation 5 [17]:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max}} c_e + \frac{1}{q_{\max} K_1} \quad (5)$$

where: C_e represents the equilibrium dye concentration (mg·L^{-1}), q_e is the amount of BG adsorbed at equilibrium (mg·g^{-1}), q_{max} is the maximum theoretical adsorption capacity (mg·g^{-1}) and K_1 represents the constant of thermodynamic equilibrium of adsorption (L·mg^{-1}).
The plot of ($\frac{C_e}{q_e}$) versus (Ce) allows to determine q_{max} from the slope $\frac{1}{q_{max}}$ and K_1 from the ordinate at the origin $\frac{1}{q_{max}K_1}$.

Freundlich model
The Freundlich model is given by the Equation 6 [18]:

$$Log(q_e) = Log(K_f) + \frac{1}{n_f} Log(c_e) \quad (6)$$

where: q_e is the amount of BG adsorbed at equilibrium (mg·g^{-1}), K_f represents Freundlich constant and this is an indication of the adsorption capacity of the dye, C_e is the equilibrium dye concentration (mg·L^{-1}) and n_f is the intensity of adsorption it indicates the type of adsorption:
If $n_f < 1$, the adsorption is chemical, if $n_f = 1$, the adsorption is linear and if $n_f > 1$, adsorption is physical [19].
The parameters K_f and n_f are determined from the plot of Log (q_e) versus Log (C_e).

RESULTS AND DISCUSSIONS

Effect of agitation speed on Brilliant Green adsorption

The study of the effect of agitation speed on the discoloration of solutions containing Brilliant Green is an indispensable step, as an important variable which contributes to distribution of the adsorbate in the adsorbent and to the determination of the maximum adsorption rate of the dye [20]. The agitation speeds used in this study are between 150 and 750 rpm with steps of 100 rpm.
The results illustrated in Figure 2 show that the fixation of the Brilliant Green on the two sawdusts is maximum and constant at a speed of 250 rpm, which is probably due to an equilibrium phenomenon at the adsorbent-adsorbate interface [21, 22]. These results are in agreement with M.M. Abd EL-Latif *et al* [23].

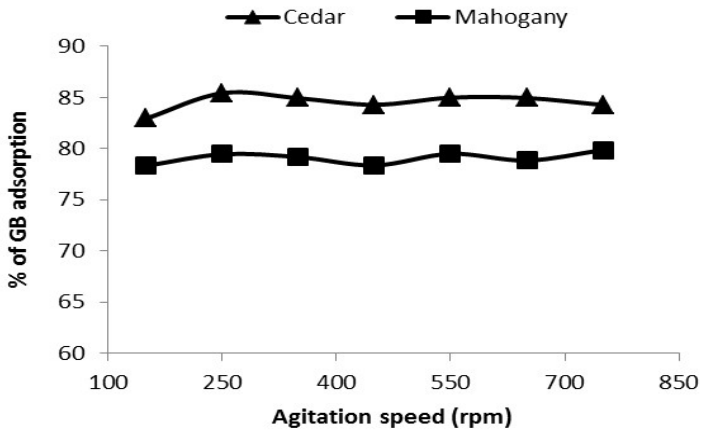


Figure 2. *Effect of agitation speed on the adsorption of BG on Cedar and Mahogany sawdusts (Ci = 50 mg·L^{-1}, T = 25 °C, pH = 6, contact time = 90 min, mass of adsorbent= 2 g, V = 0.1 L, 100 µm <Φ <500 µm)*

Effect of particle mesh size on Brilliant Green adsorption

The study of the influence of sawdust mesh sizes on the adsorption of Brilliant Green dye is a very important step, because it influences the transfer speed of matter. An increase of the adsorbent grains diameter causes a decrease in the transfer rate of the material [24, 25].
The adsorption experiments were carried out using sawdusts with different diameters Φ > 1000 µm, 800 µm < Φ < 1000 µm, 100 µm < Φ < 500 µm and Φ < 100 µm.
The results obtained show that the adsorbed quantity of Brilliant Green increases when the particle size of the two sawdust (Cedar and Mahogany) decreases.
The below histograms (Figure 3) indicate that the percentage of Brilliant Green removal decreases from 87 % to 76 % and from 79 % to 63 % with Cedar (softwood) and Mahogany (hardwood) successively when the diameter of these saw dusts changes from 100 µm to 1000 µm. A similar observation was reported by Muhammad Saif Ur Rehman and al. in the adsorption of Brilliant Green onto red clay [26].

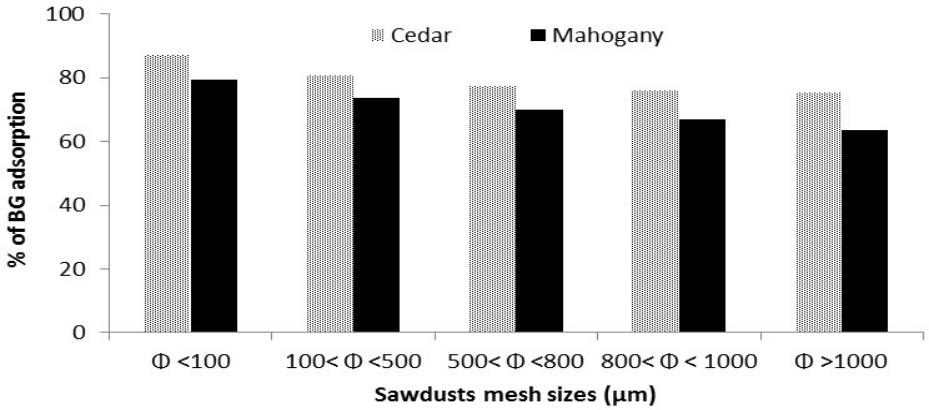


Figure 3. *Effect of particle mesh sizes of Cedar and Mahogany on BG adsorption (Ci = 50 mg. L^{-1}, T=25 °C, agitation speed = 250 rpm, contact time = 90 min, mass of adsorbent = 2 g, V = 0.1 L, pH = 6)*

Effect of temperature on Brilliant Green adsorption

Temperature is an important factor that can affect the adsorption process of dyes [27]. The temperatures used in this experimental phase vary from 20 to 80 °C with steps of 10 °C.

The results obtained (Table 2) show that the absorption capacity of BG on the two types of wood remains similar for a temperature range from 20 to 50 °C, which suggests under these conditions that the type of the adsorption process is physical, but when the temperature exceeds 50 °C the woods release its tannins in the solutions, which affects the adsorption phenomenon, so the overheating discriminate against the progress of the adsorption phenomenon and may result in an increase of desorption kinetics of wood extractives (tannins). Therefore, the best results are obtained at room temperature [28]. The same observation was reported by B. K. Nandi *et al.* [3].

Table 2. *Effect of temperature on Brilliant Green adsorption on Cedar and Mahogany sawdusts (Ci = 50 mg·L^{-1}, pH = 6, mass of adsorbent = 2 g, contact time = 90 min, agitation speed = 250 rpm, 100 µm < Φ < 500 µm)*

T [°C]		**20**	**30**	**40**	**50**
% of BG adsorption	Cedar	85.001	86.92	86.73	86.23
	Mahogany	79.57	80.89	80.23	79.80

Effect of *p*H on Brilliant Green adsorption

The *p*H of the aqueous solution is an important parameter that can influence the adsorption capacity [29], because it affects the colored matter in solution by the ionization of dye molecules as well as the shift in the surface charge of the adsorbent particles [30]. These phenomena lead to the ion exchange between absorbent surface and dye ions. The adsorption rate of the dye increases at *p*H conditions higher than the *p*Hpzc of the adsorbent. In this study, we worked with different *p*H ranging from 1 to 10.

The results obtained (Figure 4) show that the adsorption capacity of BG is low when the medium is very acidic (1 < *p*H < 4), but it starts to increase with increase in *p*H and this from *p*H = 5 up to a *p*H = 10. When the *p*H exceeds 10, the aqueous solutions takes a black color, which is due to the dissolution of the tannins of sawdusts and the degradation of these latters under the effect of the saturated alkaline solution, thereby disturbing the measurement of the residual concentration of the Brilliant Green dye by the UV spectrophotometry.
This can be explained by the fact that at low *p*H values (1-4), the surface of the adsorbents (Cedar and Mahogany sawdusts) would be surrounded by the H^+ ions which decreases the interaction of the Brilliant Green ions (cationic dye) with the adsorbent sites (having a *p*Hpzc of about 6.5-7), but at high values of *p*H (5-10), the concentration of H^+ decreases which generates a good interaction between the dye ions and the sites of the sawdusts surface. Similar results were reported by Alok Mittal *et al*. [2].

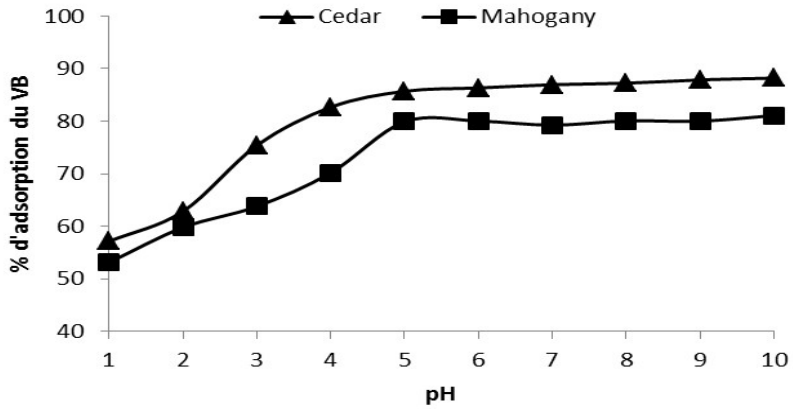


Figure 4. *Effect of pH on BG adsorption*
(Ci = 50 mg·L^{-1}, T = 25 ° C, mass of adsorbent = 2 g, contact time = 90 min, agitation speed = 250 rpm, 100 µm < Φ <500 µm)

Effect of sawdust amount on Brilliant Green adsorption

The influence of the adsorbents amount on the removal of Brilliant Green by Cedar and Mahogany sawdusts was studied; the experiments were conducted using 0.1 L of Brilliant Green with a concentration of 50 mg·L^{-1}, on which different amounts of the sawdust were added (0.2 - 2 g).
According to the results obtained (Figure 5), it appears that the adsorption capacity increases significantly with the amounts of sawdusts added to the reaction medium, until it reaches its maximum value with 0.8 g of Cedar, and 2 g of Mahogany.
This increasing elimination of Brilliant Green in solution can be explained by the growth of the specific surface involved, resulting from the increase in the mass of the adsorbents and the number of active adsorption site [31]. The same remark was reported by B. K. Nandi *et al*. [3].

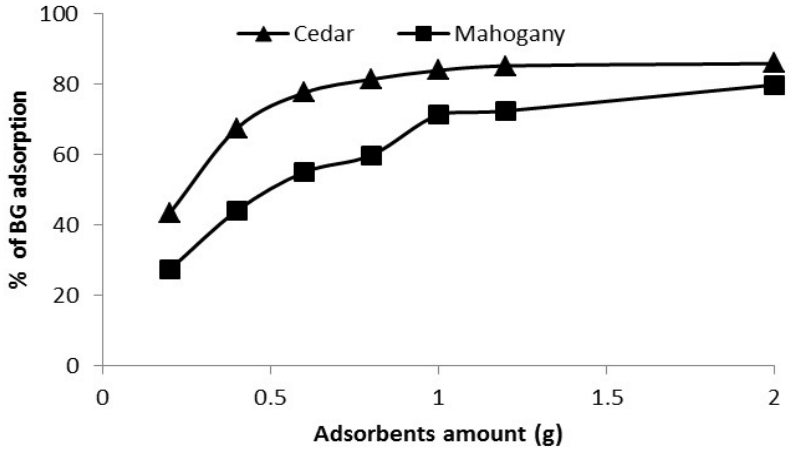


Figure 5. *Effect of adsorbent amount on BG adsorption (Ci = 50 mg·L^{-1}, T = 25 °C, pH = 6, contact time = 90 min, Agitation speed = 250 rpm, 100 µm <Φ <500 µm)*

Effect of initial concentration of Brilliant Green adsorption

The solute concentration is a very important factor which has been studied by stirring 2 g of Cedar and Mahogany sawdusts, for 90 minutes in Brilliant Green solutions whose concentration varies from 0.2 to 200 mg·L^{-1}. The results obtained (Figure 6) show that the adsorption capacity of Brilliant Green dye is very low, with a concentration less than 10 mg·L^{-1}, but it increases with the increase of the initial concentration for the two adsorbents studied. At higher initial dye concentration (above 100 mg·L^{-1} for Cedar, and 50 mg·L^{-1} for Mahogany), a decrease in BG adsorption rate is observed due to the saturation of the active sites of the adsorbents in the presence of a high content of dye, because the available adsorption sites of sawdusts become fewer and hence the removal of BG depends upon the initial concentration [32].

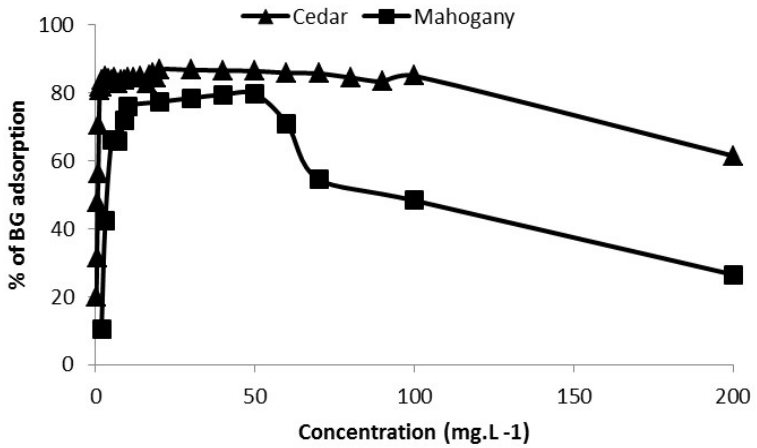


Figure 6*. Effect of initial concentration on BG adsorption (contact time = 90 min, agitation speed = 250 rpm, temperature = 25 °C, pH = 6, amount of sawdust = 2 g, 100 µm < Φ < 500 µm)*

Effect of contact time on Brilliant Green adsorption

To evaluate the effect of contact time on the adsorption of Brilliant Green on Cedar and Mahogany sawdusts, several experiments were carried out with an initial concentration of 50 mg·L^{-1} by varying the contact time from 5 to 240 minutes.
The results shown in Figure 7 reveal that the adsorbed amounts of Brilliant Green increase rapidly in the first 40 minutes to reach an optimum of 88 % with Cedar and 80 % with Mahogany sawdusts and it remains approximately constant after 40 minutes, indicating a state of equilibrium.
This shows that the adsorption equilibrium of Brilliant Green dye by the adsorbents used is very fast and established in the first 40 min. Then the adsorption rate gradually slows down. Similar results were obtained by Venkat S. Mane *et al.* [6].

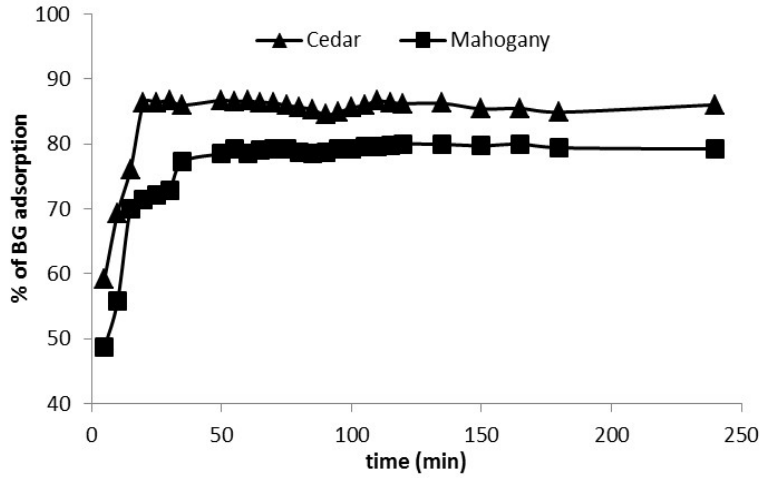


Figure 7. *Effect of contact time on BG adsorption (Ci = 50 mg·L^{-1}, agitation speed = 250 rpm, temperature = 25 ° C, pH = 6, sawdust mass = 2 g, 100 µm < Φ <500 µm)*

Adsorption kinetic modelling

In the present study, the applicability of the pseudo-first-order and pseudo-second-order models was tested for the adsorption of Brilliant Green (BG) onto Cedar and Mahogany sawdusts. Both these models have been fitted with experimental data, the results obtained (Figure 8, Table 3) show that in the case of first order model, the equilibrium quantity adsorbed (determined experimentally) is different to the calculated one. In contrast, the equilibrium adsorbed quantity (determined experimentally) is closer to that calculated using the second-order model. Hence, the pseudo second order model applies well in the case of sawdusts / cationic dye systems, given the values obtained of R^2 which are very close to the unity.

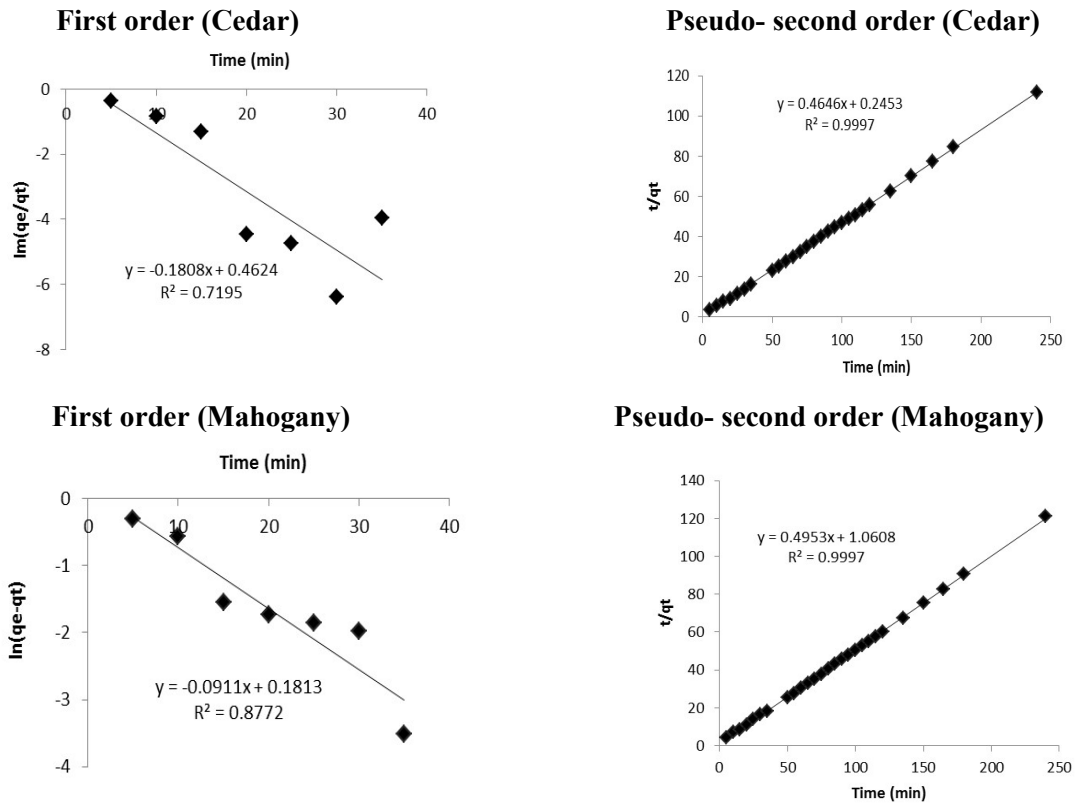


Figure 8. *Graphical representation of the BG adsorption kinetics modeling onto Cedar and Mahogany sawdusts; first order and pseudo-second order models*

The table below presents the calculation of parameters of the BG adsorption kinetics onto Cedar and Mahogany.

Table 3. *Parameters of the BG adsorption kinetics onto Cedar and Mahogany sawdusts (Pseudo-first and pseudo-second order)*

	Pseudo-first order		**Pseudo-second order**	
	K_1 [min^{-1}]	q_e [$mg \cdot g^{-1}$]	K_2 [$g \cdot mg^{-1} \cdot min^{-1}$]	q_e [$mg \cdot g^{-1}$]
Cedar	0.1808	1.5878	0.8800	2.1523
Mahogany	0.0911	1.1987	0.2312	2.0189

Adsorption isotherms modeling

Adsorption isotherms are often used to determine the maximum adsorption capacity of Brilliant Green as a cationic dye on natural biosorbents (Cedar and Mahogany sawdusts), and also for the identification of adsorption type [33].
The processed results according to the Langmuir and Freundlich models (Figure 9) allowed us to calculate the maximum adsorption capacity as well as the adsorption parameters (Table 4).

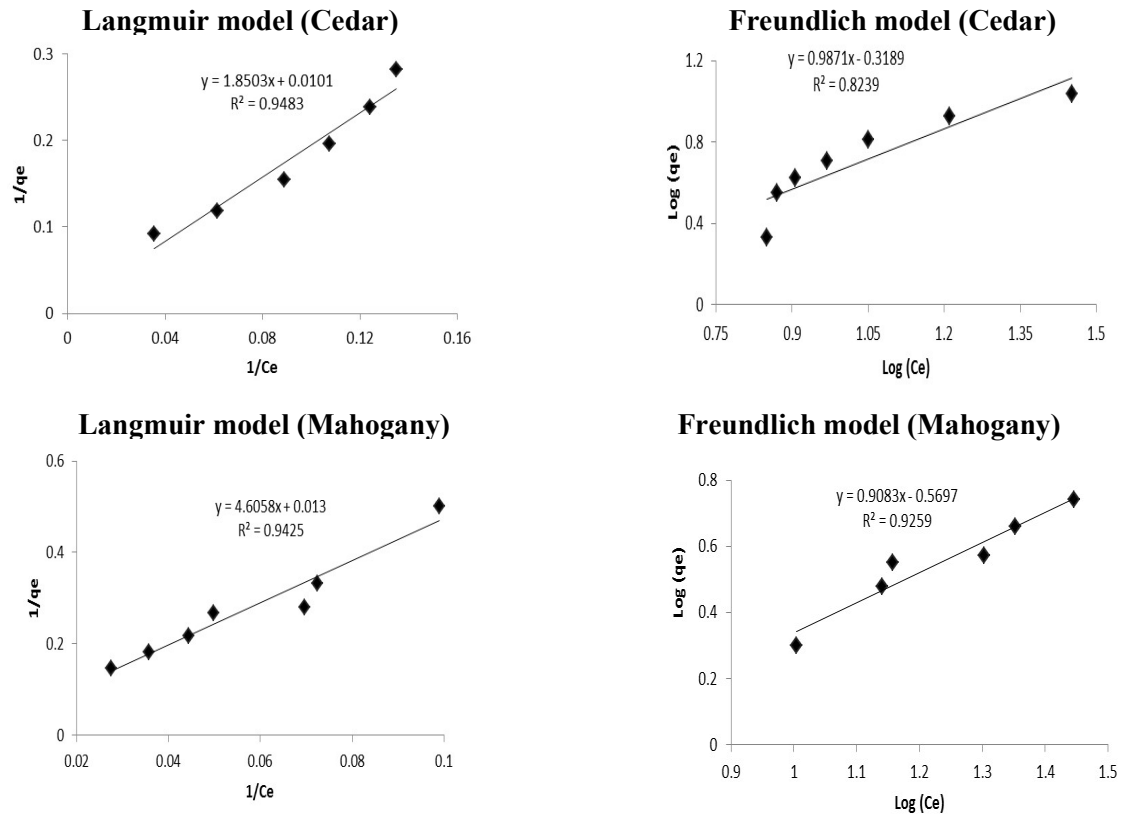


Figure 9. *Linear isotherms modeling of Langmuir and Freundlich adsorption of BG on Cedar and Mahogany sawdusts*

The values of the regression coefficients indicate that the adsorption process of Brilliant Green on Cedar and Mahogany sawdust is favorably described by the Langmuir isotherm with excellent linear regression coefficients (R^2) which are very close to unity and with adsorption capacities of 99 $mg \cdot g^{-1}$ and 77 $mg \cdot g^{-1}$ for Cedar and Mahogany successively.

The following table presents the calculation of Langmuir and Freundlich adsorption isotherms parameters for Brilliant Green removal on Cedar and Mahogany.

Table 4. *Langmuir and Freundlich parameters for BG adsorption on Cedar and Mahogany*

		Brilliant Green	
Isotherms	**Parameters**	**Cedar**	**Mahogany**
Langmuir	Q_{max} [$mg \cdot g^{-1}$]	99	76.92
	K_l [$L \cdot mg^{-1}$]	0.0054	0,0028
Freundlich	K_f [$mg \cdot g^{-1}$]	0.479	0,269
	nf	1.013	1.10

This study can be compared with other adsorption studies as given in table 5.

Table 5. *Comparison of maximum adsorption of BG onto various adsorbents*

Adsorbent	Maximum adsorption capacity [mg·g^{-1}]	Reference
Rice husk ash	25.13	[7]
Kaolin	65.42	[3]
NaOH treated sawdust	58.47	[6]
Carbonized acorn seed waste	2.11	[13]
Cedar sawdust	99	This study
Mahogany sawdust	77	

CONCLUSION

In this study, the capacity of Cedar and Mahogany sawdusts to adsorb Brilliant Green (BG) dye from aqueous solutions was evaluated. Adsorption experiments were carried out at different initial concentrations of dye (0.2 - 600 mg·L^{-1}), contact time (5 - 240 min) with steps of 5 min, *p*H ranging from 1 to 10 and sawdust doses from 0.2 to 2 g. Other factors affecting the absorption process such as agitation speed, particles size and temperature of the reactional medium were also examined.
The results show that the adsorption rate of Brilliant Green on sawdusts increases within a defined range of each parameter and then stabilizes at precise values, this stabilization is due to the saturation of the active sites of the adsorbents used.
The adsorption capacity of Brilliant Green can reach a maximum of 89 % with Cedar and 80 % with Mahogany under the following optimal conditions: ambient temperature, initial *p*H of the solution (*p*H = 7), agitation speed of 250 rpm, adsorbents amount of 0.8 g for cedar and 2 g for Mahogany, contact time of 40 min, grain diameter less than 100 µm and an initial concentration of Brilliant Green from 10 mg·L^{-1} up to 100 mg·L^{-1} in the case of adsorption onto Cedar and from 10 mg·L^{-1} up to 50 mg·L^{-1} in the case of Mahogany.
Adsorption data were modeled using the Langmuir and Freundlich adsorption isotherms. The equilibrium of biosorption process using sawdust as adsorbent adapted very well to the Langmuir model with adsorption capacities of 99 and 77 mg·g^{-1} for Cedar and Mahogany successively.
Adsorption kinetics was verified by pseudo-first-order and pseudo-second-order models. The results obtained indicated that the adsorption process of Brilliant Green onto Cedar and Mahogany followed the pseudo-second-order model.
According to this study, Cedar and Mahogany sawdusts are very effective in sorbing the Brilliant Green and which could be used for the removal of other cationic dyes.

REFERENCES

1. Rihani, M.: Examination of the residues of timber processing and the waste of slaughterhouses of red meat in Morocco, **2006**, project report http://uest.ntua.gr/archive/Morocomp/1ST%20PROGRESS%20REPORT_MOROCOMP_all_pdf_ENG/DELIVERABLE_1/ANNEXES/ANNEX_4.pdf;

2. Alok, M., Dipika, K., Mittal, J.: Applicability of waste materials—bottom ash and deoiled soya—as adsorbents for the removal and recovery of a hazardous dye, brilliant green, *Journal of Colloid and Interface Science*, **2008**, **326**, 8–17;
3. Nandi, B.K., Goswami, A., Purkait, M.K.: Adsorption characteristics of brilliant green dye on kaolin, *Journal of Hazardous Materials*, **2009**, **161**, 387–395;
4. Hao, O.J., Kim, H., Chiang, P.C.: Decolorization of wastewater, *Critical Reviews in Environmental and Technology*, **2000**, **30**, 449-505;
5. Anees, A., Mohammad, R., Othman, S., Mohamed Hakimi, I.: Scavenging behavior of Meranti sawdust in the removal of dye from aqueous solution, *Journal of Hazardous Materials*, **2009**, **170** (1), 357-365;
6. Venkat, S.M., Vijay B.P.V.: Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust, *Desalination*, **2011**, **273**, 321–329;
7. Venkat, S.M., Mall, I.D., Shrivastava, V.C.: Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash, *Journal of Environmental Management*, **2007**, **84**, 390–400;
8. Pollock, M.: Neutralizing dye-house wastes with flue gases and decolorizing with fly ash, *American Dyestuff Reporter*, **1973**, **62**, 21-23:
9. Ledakowicz, S., Solecka, M., Zylla, R.: Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes, *Journal of Biotechnology*, **2001**, **89**, 175-184;
10. Purkait, M.K., DasGupta, S., De, S.: Micellar enhanced ultrafiltration of eosin dye using hexadecyl pyridinium chloride, *Journal of Hazardous Materials*, **2006**, **136**, 972-977;
11. Gupta, V.K.: Application of low-cost adsorbents for dye removal – a review, *Journal of Environmental Management,* **2009**, **90**, 2313-2342;
12. Ghaedi, M., Hossainian, H., Montazerozohori, M., Shokrollahi, A., Shojaipour, F., Soylak, M., Purkait, M.K.: A novel acorn based adsorbent for the removal of brilliant green, *Desalination*, **2011**, **281**, 226-233;
13. Sachin, S., Anup, P., Rohit, P., Jitendra, N., Parag, G., Shirish, S.: Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly (acrylic acid) hydrogel loaded with kaolin clay: A comparative study, *Ultrasonics Sonochemistry*, **2013**, **20** (3), 914-923;
14. El hajam, M., Idrissi Kandri, N., Harrach, A., El khomsi, A., Zerouale, A.: Physicochemical characterization of softwood waste "Cedar" and hardwood waste "Mahogany": comparative study, *Materials today: Proceedings*, **2019**, **13**, 803-811;
15. Lagergren, S.: Zur theorie der sogenannten adsorption gelöster stoffe, *Kungliga Svenska Vetenskapsakademiens Handlingar*, **1898**, **24** (4), 1-39;
16. HO, Y.S., Mckay, G.: Sorption of dye from aqueous solution by peat, *Chemical Engineering Journal*, **1998**, **70** (2), 115-124;
17. Rangabhashiyam, S., Anu, N., Selvaraju, N.: Sequestration of dye from textile industry wastewater using agricultural waste products as adsorbents, *Journal of Environmental Chemical Engineering*, **2013**, **1** (4), 629-641;
18. Matandabuzo, M., Ajibade, P.A.: Removal of metal ions from aqueous solutions using activated carbon prepared from zea mays stem, *Scientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2018**, **19** (2), 117-132;
19. Dawood, S., Sen, T.K.: Removal of anionic dye congo red from aqueus solution by raw pine and acid- treated pine cone powder as adsorbent: Equilibrium, thermodynamic, kinetics, mechanism and process design, *Water Research*, **2012**, **46** (6), 1933-1946;
20. Wang, X.S., Huanga, J., Hu, H.Q., Wang, J., Qin, Y.: Determination of kinetic and equilibrium parameters of the batch adsorption of Ni(II) from aqueous solutions by Na-mordenite, *Journal of Hazardous Materials*, **2007**, **142** (1-2), 468-476;
21. Figueira, M.M., Volesky, B., Ciminelli, V.S.T.: Assessment of Interference in Biosorption of a Heavy Metal', *Biotechnology and Bioengineering*, **1997**, **57** (4), 344- 350;

22. Sekar, M., Sakthi, V., Rengaraj, S.J.: Kinetics and Equilibrium Adsorption Study of Lead (II) onto Activated Carbon Prepared from Coconut Shell, *Journal of Colloid and Interface Science*, **2004**, **279** (1), 307-313;
23. Abd El-Latif, M.M., Amal M.I., El-Kady, M.F.: Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite, *Journal of American Science*, **2010**, **6** (6), 267-283;
24. Choy, K.K.H., Ko, D.C.K., Chun, C.W., Porter, J.F., Mckay, G.: Film and intraparticle mass transfer during the adsorption of metal ions onto bone char, *Journal of Colloid and interface science*, **2004**, **271** (2), 284-295;
25. Barka, N., Ouzaouit, K., Abdennouri, M., El Makhfouk, M.: Dried prickly pear cactus (*Opuntia ficus* indica) cladodes as a low-cost and eco-friendly biosorbent for dyes removal from aqueous solutions, *Journal of Taiwan Institute of Chemical Engineers*, **2013**, **44** (1), 52-60;
26. Ur Rehman, M.S., Munir, M., Ashfaq, M., Rashid, N., Nazar, M.F., Danish, M., Han, J.I.: Adsorption of Brilliant Green dye from aqueous solution onto red clay, *Chemical Engineering Journal*, **2013**, **228**, 54-62;
27. Kumar, P.S., Ramalingam, S., Dinesh, S., Murugesan, A., Vidhyadevi, T., Sivanesan, S.: Adsorption behavior of nickel (II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design, *Chemical Engineering Journal*, **2011**, **167** (1), 122-131;
28. Aarfane, A., Salhi, A., El Krati, M., Tahiri, S., Monkade, M., Lhadi, E.K., Bensitel, M.: Kinetic and thermodynamic study of the adsorption of Red195 and methylene blue dyes on fly ash and bottom ash in aqueous medium, *Journal of Materials Environmental and Science*, **2014**, **5** (6), 1927-1939;
29. Mirilă, D.C., Pîrvan, M.S., Roşu, A.M., Zichil, V., Nistor, I.D.: Activated adsorption on clay of micropollutants from paper printing industry, *Scientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2018**, **19** (1), 063-072;
30. Elliot, H.A., Huang, C.P.: The Adsorption of Cu(II) Complexes onto Aluminosilicates, *Water Research*, **1981**, **15** (7), 849-855;
31. Makhlouf, M., Hamacha, R., Villièras, F., Bengueddach, A.: Kinetics and thermodynamics adsorption of phenolic compounds on organic-inorganic hybrid mesoporous material, *International Journal of Innovation and Applied Studies*, **2013**, **3** (4), 1116-1124;
32. Bentahar, S., Dbik, A., El khomri, M., El messaoudi, N., Bakiz, B., Lacherai, A., Study of removal of congo red by local natural clay, *Scientific Study & Research Chemistry & Chemical Engineering, Biotechnology, Food Industry*, **2016**, **17** (3), 295-307;
33. Langmuir, I.: The constitution and fundamental properties of solids and liquids. Part I. Solids, *Journal of the American Chemical Society*, **1916**, **38** (11), 2221-2295.