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Kinetic and thermodynamicstudy of the adsorption of twodyes:brilliant green and eriochrome black T using a natural adsorbent "sugarcane bagasse".

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Abstract

The aim of this study is to find an effective and inexpensive natural material used as an adsorbent for the textile dyes removal. Indeed, we have been interested in testing the effectiveness of sugarcane bagasse (SB) as a biosorbent to remove brilliant green (BG) and eriochrome black T (EBT). In our experiments, different parameters such as initial dye concentration, contact time, adsorbent dose and solution temperature have been analyzed in a batch system. Similarly, the studies of thermodynamic, kinetic and adsorption isotherm have been evaluated. The sugarcane bagasse (SB) without any modification has been characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The maximum adsorption capacity of BG and EBT on the SB adsorbent has been 37.58 and 12.30 $mg.g^{-1}$respectively, for a concentration of $40mg.g^{-1}$ at a temperature of 20°C and $1g.L^{-1}$ of adsorbent. The results of the adsorption kinetics have proved that the pseudo-second order model correctly describes the adsorption phenomenon of the two dyes studied. The Langmuir and Freundlich isotherms have been applied to experimental equilibrium data. The various thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and standard entropy (ΔS°) have indicated that the adsorption is spontaneous and endothermic in brilliant green and exothermic in eriochrome black T

Keywords: adsorption, sugarcane bagasse, adsorption isotherms, thermodynamics.

1.Introduction

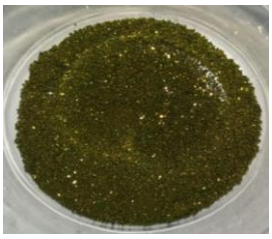
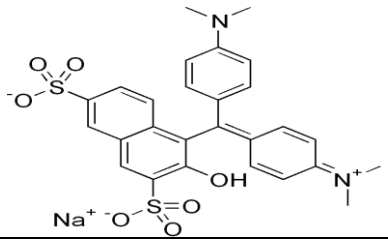
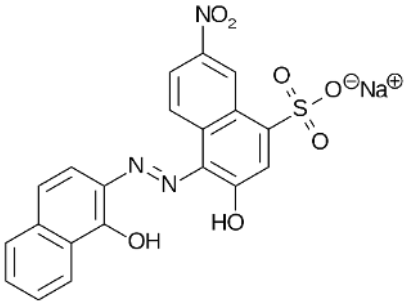
Recently, there are more than 10 000 dyes with various chemical structures and more than 7×10^6tonnes/year of synthetic organic dyes that are produced worldwide [1]. They are compounds used in many industrial fields namely: food, paper, leather, pharmaceuticals, plastics, cosmetics and textiles [2]. For more than 100 years, dyes have been used to colour cellulose due to the ease of application and the presence of a wide range of products at a modest cost [3]. Dyes are known to be toxic and persistent compounds in the environment [4]; the latter are mainly classified in to anionic, cationic and non ionic dyes, indeed, cationic dyes are more toxic than anionic dyes [5]. Pollution from industrial discharges is currently receiving particular attention worldwide. Nowadays, there are more and more cases of ecosystem alterations and public health problems that can lead to the elimination of living species (plants, animals, humans). Numerous studies have shown that certain dyes are responsible for several diseases [6-7-8] and can cause skin irritation, allergic dermatitis, kidney, central nervous system, liver and brain dyes functions [9-10] and can also cause cancer and mutations. The release of colored effluents in to water courses prevents the penetration of light. Thus, reducing the photo synthetic activity of aquatic life [11-12]. Hence, the need to treat these colorful effluents before their discharge into water [13]. The discoloration of industrial textile waste is often very difficult due to their stability to solar radiation and oxidizing agents and their resistance to aerobic digestion [14-15-16]. Therefore, the treatment of coloured waste water is an important consideration. Researchers are looking for sustainable and inexpensive methods to remove these dyes to protect the environment. Right now, various treatment processes such as biological processes (aerobic or anaerobic) [17-18], coagulation/flocculation, membrane filtration, oxidation and electrolysis, reverse osmosis and adsorption have been used to remove dyes from waste water [19-20]. The latter is one of the most effective processes adopted for the removal of organic pollutants from effluents [21] due to its simplicity, ease of use and availability as well as the possibility of regeneration. The most abundant and widely used adsorbent for dye removal is activated carbon, which has a high adsorption capacity [22]. However, the use of this adsorbent remains limited due to its high price and the difficulty of being regenerated [23-24]. This is why the search for other efficient and low-cost adsorbents has been targeted by several researchers. Recently, agricultural waste has been considered as a potential free and abundant dye adsorbent, such as rice husk [25], rice straw [26], corn carrier[27], palm ash[28], sawdust[29], nutshells[30] and sugarcane bagasse [31], etc. The main target of our study is to study the adsorption capacity of two organic dye stuffs: brilliant green (BG) and eriochrome black T (EBT) on sugarcane bagasse, which is a fibrous residue that constitutes an important waste in the sugar industry [32]. We will study the effect of different experimental parameters on the bleaching power of the material used, including contact time, initial concentration, adsorbent mass and temperature. To better understand adsorption, a kinetic study has been studied using pseudo-first-order and pseudo-second-order models. The adsorption capacity of sugarcane bagasse has been determined by applying Langmuir and Freundlich isotherms. The effect of temperature on the adsorption of two dye stuffs has been also studied and thermodynamic parameters have been determined.

2.Materials and methods

1. Reactivedyes

We studied a cationic dye (brilliant green) and an anionic dye (eriochrome black T) and were used without purification. The characteristics of the two dyes are presented in Table 1.

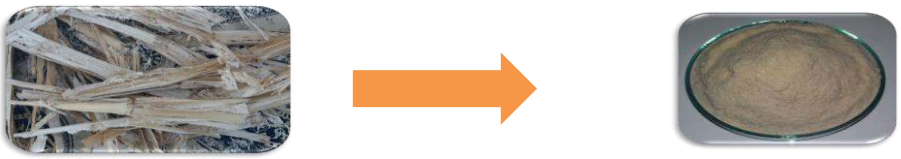
Tableau 1:Characteristics of the dyesused as adsorbates.

Dyes	Molecularweight (g/mol)	Chemical structure	Wavelength (nm)	Chemical formula
Brilliant Green 	576.616		625	$C_{27}H_{25}N_2NaO_7S_2$
Eriochrome black T	461,381		520	$C_{20}H_{12}N_3O_7SNa$

2. Preparation of the adsorbent

The sugarcane bagasse was collected from the juice sellers after extraction of the drink syrup from the cane.

The material studied has been cut into pieces and it has been washed several times with distilled water to remove any kind of dust or adhering impurities, then dried in the open air and then in an oven at 60°C for 24 hours. The resulting support has been crushed and sieved to a grain size of less than 500µm.



Characterization of material

2.1Fourier TransformInfraredSpectroscopy (FTIR)

The sugarcane bagasse powderwasanalyzed by BRUKER Fourier transforminfraredspectroscopy (Vertex70). IR spectrawerescanned over a range of 400-4000 cm^{-1}.

2.2Scanning electronmicroscopyanalysis (SEM)

The surface morphology of sugarcane bagasse wasobserved on a scanning electron microscope (Quanta 200 FEI).

3. Preparation of adsorbed solution

The stock solution was prepared by dissolving 100g of dye (brilliant green and eriochrome black T) in one liter of distilled water. The experimental solutions of the desired concentration were obtained by diluting the stock solution with distilled water.

4. *Adsorption procedure*

The The effect of several parameters such as the dose of sugarcane bagasse powder (0.2-1g.L^{-1}), initial dye concentration (20-40mg.L^{-1}), contact time (0-60min) and solution temperature (20-60°C) were studied. The adsorption tests have been carried out in a batch reactor with constant agitation in beakers containing 200ml of the coloured solution. Samples have been taken every 5 min, then the BS has been separated from the stained solution by filtration through a syringe filter with 0.45 µm pores, then the concentration of the brilliant green and black eriochrome T dyes has been determined by measuring the absorbance of the solution at a maximum wavelength of λ_{max}= 625 nm and at λ_{max}=520 nm respectively, using a UV-visible spectrophotometer (Selecta Vr-2000 spectrophotometer). All experiments have been carried out in duplicate. The adsorption quantities have been evaluated from the modification of the concentration of the solution using the following equation:

$$\mathbf{Q(mg/g)} = \frac{(\mathbf{C_0} - \mathbf{C}).\mathbf{V}}{\mathbf{m}} \qquad (1)$$

Where: Q is the absorption capacity (mg.g^{-1}), V is the volume of the solution (ml) and m is the mass of the adsorbent (g),C_0 is the initial dye concentration (mg.L^{-1}), and C is the final dye concentration in an aqueous solution after phase separation (mg.L^{-1}). The results have been also analyzed by various adsorption isotherms incorporating Freundlich and Langmuir isotherms and simulated with different kinetic models, including pseudo first-order and pseudo second order models.

3.Results and discussion

1. Caracterization of material

1.1Fourier TransformInfraredSpectroscopy (FTIR)

Figure 1 shows a broad 3407.16 cm^{-1} band attributed to the hydroxyl, O-H groups presented in cellulose and hemicellulose[33]. At 2917.99 cm^{-1}, the stretch peak corresponds to asymmetrical and symmetrical vibrations of the -CH_2 group [34]. The presence of peaks at 1732.93 and 1605.18 cm^{-1}indicating a carbonyl group, C = O and an alkene group, C = C a stretching vibration. 1250 cm^{-1} corresponds to the C-O stretch due to the aryl group in the lignin. The peak at the region of 1321.80 cm^{-1}represents the OH, C-C or C-O groups. The peak at 1161 cm^{-1}indicates the asymmetric vibrations of the C-O-C and C-OH groups, sincethis group comprises the region of 1100-1300 cm^{-1}[35].

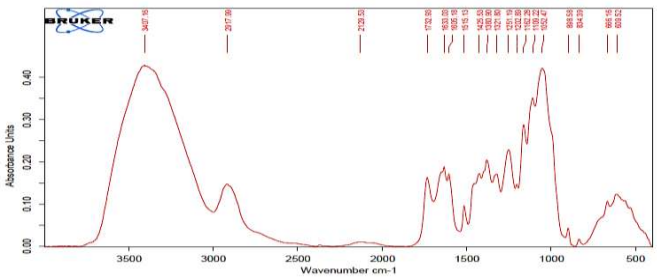


Figure 1:Fourier transformation by infraredspectroscopy of sugarcane bagasse (SB).

1.2Scanning electronmicroscopyanalysis (SEM)

The figure 2presents the images obtainedwith the scanning electron microscope, the sugarcane bagasse is in the form of parallelsheets (fig 2a), and one can observe microcavities on the surface of SB of diameterbetween 27 µm and 52 µm (fig 2b) whichfacilitates adsorption. Figure 3 shows the evolution of the adsorption capacity of the two dyes BG and EBT as a function of the reaction contact time, at different initial concentrations (20.30 and 40mg.L^{-1}) while

keeping the mass of adsorbents constant at 0.2g and the temperature at 20°C for a period of 60 min, it has been found that with the increase in the initial concentration, the amount of adsorbed BG and BET increases rapidly within the first 5 minutes from 15.22 to 31.17 $mg.g^{-1}$ and from 9 to 10.03 $mg.g^{-1}$ respectively, with the increase in the initial concentration from 20 to 40 $mg.L^{-1}$, which can be explained by the existence of a significant number of active sites on the adsorbent surface [36]. After 40 minutes the adsorbed quantity remains constant indicating a steady state. This is due to the saturation of the binding sites; the dye molecules slowly occupy the remaining sites due to repellent forces between the dye molecules and those already adsorbed on the adsorbent [37].

(a)

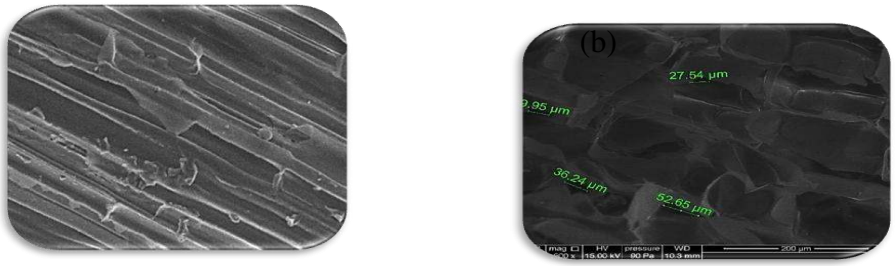


Figure 2: Surface images of sugar cane bagasse, obtained by scanning electronmicroscopy.

2. Study of the effects of different adsorption parameters

2.1 Effect of contact time and initial concentration

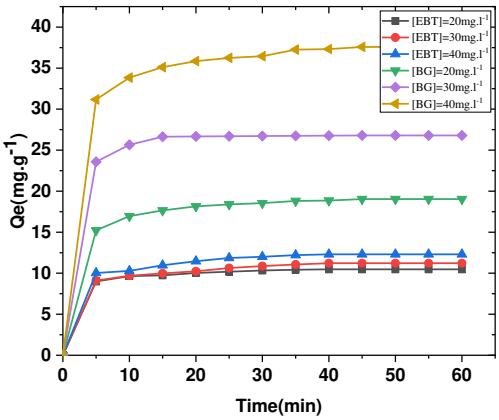


Figure 3:Effect of contact time and initial concentration of BG and EBT dyes (initial concentration (20-40 $mg.L^{-1}$), m= 0.2 g, V= 200 ml, T= 20±2°C and agitation time 60 min).

2.2 Effect of the dose

The study of the influence of the mass of sugarcane bagasse on the amount of brilliant green and eriochrome black T adsorbed at equilibrium Q_e has been studied. Using 200 ml of the coloured solution of BG and EBT at 40$mg.L^{-1}$ and 20 mg. L^{-1} respectively, to which various amounts of 0.2 to 1g have been added, the resulting mixture has been then stirred at a constant rate for 60 min. The adsorption capacities of brilliant green on the BS are 37.58, 13.08, 9.07 and 7.97 $mg.g^{-1}$ and eriochrome black T are 10.47, 6.85, 4.55 and 3.65$mg.g^{-1}$, obtained by the material masses 0.2, 0.5, 0.75 and 1g, respectively. The results obtained are shown in Figure 4, which shows a significant decrease in the amount adsorbed with the increase in the adsorbent dose. This can be explained by the decrease in the number of dye molecules and the difficulty of adsorbent-adsorbate interaction, which explains the saturation of the adsorbent's active

sites. In fact, the increase in the mass of the adsorbent increases the number of sites available for the binding of dye molecules, and consequently the promotion of discoloration phenomena [38].

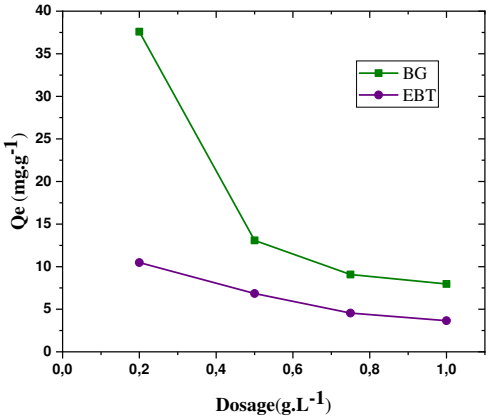


Figure 4:Effect of time of adsorbent dose (adsorbent dose (0.2-1g),C_0:[BG]=40mg.L^{-1},[EBT]=20 mg.L^{-1}, V = 200 ml, T = 20±2°C and agitation time 60 min).

*2.3**Effect of temperature***

Temperature is an important parameter that can be considered as a significant factor in the adsorption process. In this work, we have studied the effect of temperature on the adsorbed amount of brilliant green and eriochrome black T on sugarcane bagasse between 20 and 60°C (Fig. 5). The experiments have been carried out on 200 ml coloured solutions at the concentration of [EBT]= 20 mg.g^{-1} and[BG]=40 mg.g^{-1}, with a mass of one gram of BS.

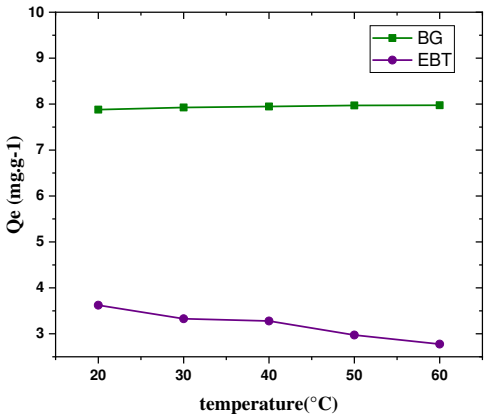


Figure 5:Effect of temperature time (temperature (20-60°C), m=1g,C_0 : [BG]=40 mg.L^{-1}, [EBT]=20 mg.L^{-1}, V =200 ml and agitation time 60 min).

In this respect, analysis of the curve (Fig. 5) shows that the amount of brilliant green adsorbed increases slightly from 7.87 to 7.97 mg. g^{-1} by increasing the temperature of the solution from 20°C to 60°C. This suggests that the interaction of material (BS) and adsorbate (BG) is endothermic in nature. On the other hand, the adsorption capacity of eriochrome black T decreases by increasing the temperature of the range studied, revealing that the adsorption of EBT on the BS is exothermic in nature, and the low temperature promotes adsorption.

*3. **Adsorption kinetics***

Kinetic adsorption studies are carried out to study the rate of adsorption (fast or slow), determine the time required to reach the equilibrium state between two phases and determine the equilibrium constants of adsorption of the dyes.
The kinetics of dye adsorption on adsorbent supports is a prerequisite for selecting the best operating conditions for large-scale processing. Two classical kinetic models: a pseudo-first-order kinetic model and a pseudo-second order kinetic model were used to test the experimental adsorption data.

*3.1**Pseudo-first-order model (Lagergrenequation)***

The model of first-order kinetics is presented by Lagergren's relationship,[39] cited by Ru-Ling et al., [40], based on the adsorbed quantity and the first velocity equation. This model is represented by the following relationship [41-42]:

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

Where: K_1 : adsorption rate constant for the first order (min^{-1}), q_t : quantity adsorbed at time t ($mg.g^{-1}$), q_e : quantity adsorbed at equilibrium ($mg.g^{-1}$), t : time (min). By plotting ln (q_e-q_t) as a function of time t, the adsorption rate constant k_1 can be determined.

*3.2**Pseudo- second order model***

In the case of the pseudo-second order kinetic model, the pseudo-second order reaction rate is related to the amount adsorbed to the solid surface and the amount adsorbed to the equilibrium. This model can be represented as follows [43-44]:

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

Where: K_2: pseudo second order velocity constant (mg/g.min), q_e : Equilibrium adsorbate quantity per gram of adsorbent ($mg.g^{-1}$). The quantity adsorbed at equilibrium q_e and the pseudo-second order constant K_2 can be determined experimentally from the slope and y-axis of the line origin t/q_t as a function of t.

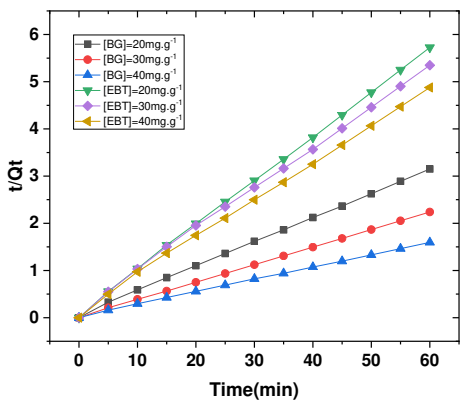


Figure 6:Pseudo-second order model of adsorption kinetics.

After verifying the Lagergren relationship, it can be noticed that the quantity adsorbed at the experimentally determined equilibrium is different from that calculated. So the adsorption kinetics of BG and EBT on BS do not correspond to the pseudo-first order kinetics. On the other hand, the linear representation of t/Q_t as a function of time (Fig. 6), the equilibrium adsorption quantities and correlation coefficients for the second-order kinetic model (Table 2) show that the correlation coefficients R^2 =0.999 are very close to the unit of this model. Similarly, the values obtained are comparable with the experimental values for the two dyes studied. This confirms that this model describes the experimental results of adsorption of brilliant green and eriochrome black T on sugarcane bagasse

Tableau 2:Parameterscharacterizing the adsorption kinetics of brilliant green and black eriochrome T on the BS adsorbent.

C0 ($mg.g^{-1}$)	Qexp ($mg.g^{-1}$)	Kinetics of 2nd order		
		K_2 ($g.mg^{-1}.min^{-1}$)	Q_{cal}($mg.g^{-1}$)	R^2
[BG]=20 $mg.L^{-1}$	19.040	0.046	19.379	0.999
[BG]=30 $mg.L^{-1}$	26.791	0.121	26.954	0.999
[BG]=40 $mg.L^{-1}$	37.585	0.026	38.167	0.999
[EBT]=20 $mg.L^{-1}$	10.477	0.111	10.638	0.999
[EBT]=30 $mg.L^{-1}$	11.266	0.058	11.494	0.998
[EBT]=40 $mg.L^{-1}$	12.300	0.055	12.610	0.999

4. *Adsorption isotherm*

Isothermal adsorption models are generally used to determine maximum pollutant binding capacities on adsorbents and adsorption parameters [45]. In this work, adsorption isotherms have been studied using different concentrations of brilliant green and black eriochrome T ranging from 5 to 60 mg. L^{-1} and an adsorbent concentration of 1.0 $g.L^{-1}$ for sugarcane bagasse. The adsorption tests have been carried out in a beaker containing 200 ml of solution. The adsorbent and adsorbate were placed in contact for 60 minutes under agitation to ensure that the adsorption/desorption equilibrium is established. The fixing data of the two dyes on BS are processed according to the linear equations of Langmuir and Freundlich.

4.1 ***Isotherm of Langmuir***

The linear form of Langmuir is expressed by the following equation [46-47]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \qquad (4)$$

Where : C_e: equilibrium concentration ($mg.L^{-1}$), and Q_e: equilibrium adsorbed amount ($mg.g^{-1}$), Q_{max}: maximum adsorbed amount ($mg.g^{-1}$), and K_L: Langmuir equilibrium constant, temperature dependent ($L.mg^{-1}$).

The line is obtained by plotting C_e/Q_e against C_e.

4.2 ***Freundlich Isotherm***

The linear Freundlich form is expressed by the following equation [48]:

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \qquad (5)$$

Where : K_f, n_f : Freundlich coefficients, Q_e: the amount of dye adsorbed per mass amount ($mg.g^{-1}$), C_e: the concentration of the adsorbate in the equilibrium solution ($mg.L^{-1}$). The graphical representation of $\ln(Q_e)$ as a function of $\ln(C_e)$ is a straight line of reference coefficient 1/n and ordinate at origin $\ln(K_f)$. The results of adsorption isotherms obtained by stirring 1g of sugar cane bagasse in different concentrations ranging from 5 to 60 $mg.L^{-1}$understirring for a period of 60 minutes, are shown in Figures 7 and 8. Based on the calculated maximum adsorption quantity values and Langmuir equilibrium constants and correlation coefficients (Table 3), it can be deduced that the process studied is well described by the Langmuir isotherm for BG since the correlation coefficient R^2 = 0.99 isvery close to 1. unlike BET where the correlation coefficient R^2 = 0.96. The values shown in Table 3 have been calculated from the intersection with the y-axis and the slope of the line. The values of the correlation coefficients for the two

dyes R^2=0.999 are good since they are close to 1, indicating a good linearity for the material understudy. Thus, the value of n between 1 and 10 also confirms that the adsorption is favorable.

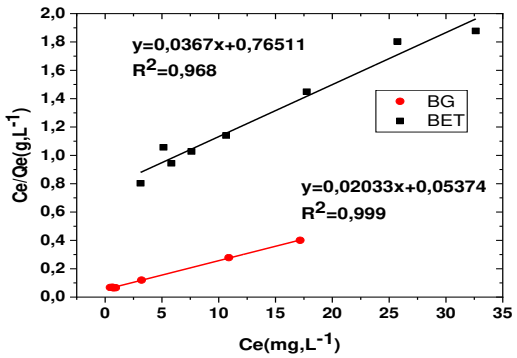


Figure 7:Isotherm of Langmuir

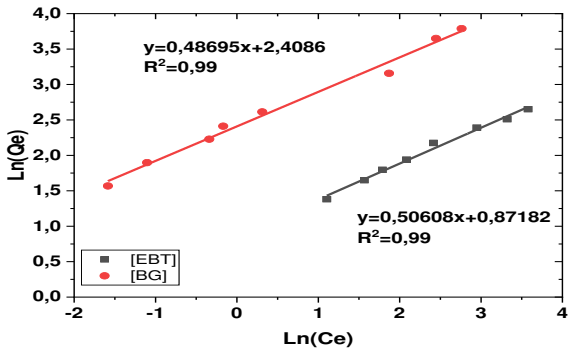


Figure 8: Isotherm of Freundlich

Tableau 3:Parameters of the Langmuir and Freundlich model

	Langmuir			Freundlich		
	Q_{max} (mg.g^{-1})	K_L (L.mg^{-1})	R^2	K_f (mg.g^{-1})	n_f	R^2
[BG]	49.18	0.378	0.999	11.118	2.055	0.99
[EBT]	27.24	0.047	0.968	2.391	1.975	0.99

*5. **Adsorption thermodynamics***

Adsorption is a phenomenon that can be endothermic or exothermic depending on the adsorbent used and the nature of the molecules adsorbed [49]. The thermodynamic parameters of adsorption: the standard free enthalpy ΔG°, the standard entropy ΔS° and the standard enthalpy ΔH° have been calculated using the following equations[50].

$$K_d = \frac{Q_e}{C_e} \quad (6)$$

$$\Delta G^\circ = -RT.\ln_{K_d} \quad (7)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R}.\frac{1}{T} \quad (8)$$

Where : R: is perfect gas constant (R = 8.314 J.mol^{-1}.K^{-1}), T: absolute temperature (K) K_d: distribution coefficient, Q_e: quantity adsorbed at equilibrium (mg.g^{-1}), and C_e: concentration at equilibrium (mg.L^{-1}). The values of the free enthalpy, standard entropy and standard enthalpy calculated are shown in Table 4. The negative values of the free enthalpy ΔG °(Table 4) indicate that the adsorption process of brilliant green is feasible and spontaneous within the temperature range studied, whereas for eriochrome black T it is found that from 40°C the adsorption becomes spontaneous, while the values of the standard entropy ΔS° (Table 4) show that the adsorption process is carried out with an increase in disorder at the solid/liquid interface and the negative values show the decrease in disorder at the solid/liquid interface for BG and EBT respectively. As well as the positive values of the standard enthalpy ΔH° reveals that the adsorption is endothermic in nature for BG and exothermic for EBT.

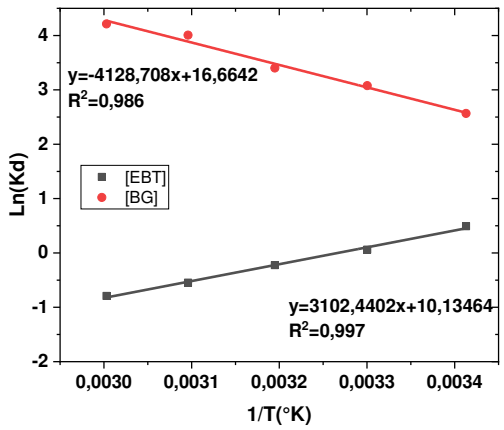


Figure 9:Trace of ln K_d as a function of 1/T (m=1g, C_0 :[BG]=40 mg. L^{-1}[EBT]=20 mg.L^{-1}).

Table 4 :Equilibrium constant and thermodynamicparameters for the adsorption of BG and EBT onto BS biosorbents

	ΔH° (kJ.mol^{-1})	ΔS° (J.mol^{-1}.K^{-1})	ΔG° (kJ.mol^{-1})				
			20°C	30°C	40°C	50°C	60°C
BG	34.32	138.56	-6,250	-7,753	-8,849	-10,762	-11,661
EBT	-25.79	-81.03	1.194	0.153	-0.584	-1.469	-2.190

4.Conclusion

This study focuses on the use of low-cost natural waste as an effective biological adsorbent for the removal of dyes: brilliant green and eriochrome black T. The main conclusions that can be deduced from this work are presented below: The adsorbed amount of BG and EBT increases rapidly in the first 5 min from 15.22 to 31.17 mg.g^{-1} and from 9 to 10.03 mg.g^{-1} respectively, with the increase in the initial concentration from 20 to 40 mg.L^{-1} and the steady state time is reached after 40 min. The adsorption kinetics study revealed that the pseudo-second order kinetic model better describes the adsorption data of the two dyes studied. As well as the adsorption isothermal data have been well described by the Freundlich and Langmuir models. The thermodynamic parameters showed that the adsorption process is an endothermic physico-chemical reaction for brilliant green and exothermic for eriochrome black T. Based on the results obtained in this study, we can infer that sugarcane bagasse has been an effective and promising bioadsorbent for the removal of textile dyes.

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