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Valuation of a Material and some Biosorbents for the Removal of Textile Dyes

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ABSTRACT

The main objective of this study is to optimize a new natural biosorbent for the depollution of contaminated water. This pollution can have adverse effects on both human health and the environment. The subject of our study is to use a natural material, abundant and less expensive, like the Pineapple Bark (PB), for the treatment of colored water by adsorption method. In this case, the adsorptive power of the BP was tested on a cationic dye which is Methylene Blue (MB). Hence, the physicochemical and morphological compositions of PB were characterized by Infrared Spectroscopy (IR) and Scanning Electron Microscopy (SEM). A series of experiments were carried out in order to study the influence of certain parameters on the adsorption capacity in particular: the mass of the adsorbent, the initial concentration of the dye, the contact time, the pH and temperature. The optimum adsorption capacity of MB on PB is in the order of 0.78 mg.g^{-1} with a removal percentage of 96% for a MB concentration of 20 mg.l^{-1} an amount of 2 g.l^{-1} of the adsorbent, pH=6 and a temperature of 20°C. The results show that the kinetics of adsorption of the dye MB by PB is described by the second-order model, also the adsorption isotherms are described satisfactorily by the Langmuir model.

Keywords: Adsorption, Methylene blue, Pineapple bark, Isotherms, Kinetics

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INTRODUCTION

Colored effluents discharged into aquatic environments are toxic and present enormous damages to both the environment and to the human health [1]. Indeed, chemical dyes are widely used in many fields namely: technological products [2], in the plastics industry [3,4], in the leather tanning industry [5], in electrochemical photocells [6], in the manufacture of pulp [7] and the textile sector [8] etc. Given the high polluting load in the waters, regulations on water pollution control are becoming increasingly strict and the treatment seems to be very difficult because of its high cost [9].

Several methods of treatment are available, reliable, simple and inexpensive for the removal of dyes particularly: oxidation [10], coagulation-flocculation [9] membrane separation [11], degradation Photochemical [12], reverse osmosis [13] and adsorption [14]. The latter has been widely studied by researchers because of its ease of establishment for the treatment of colored effluents. The most commonly used adsorbent is active charcoal [15-17], but the high cost and difficulty in regeneration leads to the search for several efficient and less expensive adsorbents such as: walnut shells [18], clay [19], chitin-chitosan [20], corn support [14] and bituminous shale [21].

From this perspective, PB appears to be an interesting and effective material in the treatment of organic effluents because of its affordable cost and abundance. In this work, we present the results relating to the adsorption of MB on BP. For this reason, we studied the influence of several parameters in terms of: the adsorbent mass, the contact time, the initial concentration of the dye, the pH and the temperature. This study also allows us to better understand the phenomenon of adsorption. In this case, several models of the adsorption kinetics have been tested, in particular the pseudo-first order model and the pseudo-second order model. Adsorption isotherms were achieved by applying Langmuir and Freundlich isotherms.

MATERIALS AND METHODS

Materials

The organic dye used in this study is Methylene Blue (MB) which has the chemical formula $C_{16}H_{18}ClN_3S$ with a molar mass of 319.85 g.mol^{-1}. The structure of Methylene Blue is illustrated in Figure 1.

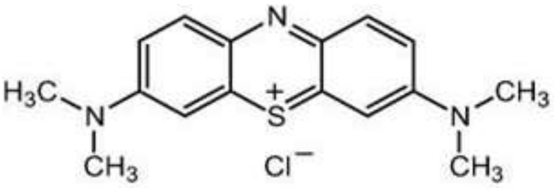

Figure 1: Structure of methylene blue

The bark of the crude pineapple used as adsorbent was washed with tap water, dried in the open air and then ground and sieved to obtain a fraction (< 125 nm). The powder was then washed several times with ultrapure water until impurities were removed and then dried in an oven at a temperature of 60°C during 48 h to obtain a material named PB.

Methods

Characterization of the adsorbent

The chemical and morphological analyzes of the PB were accomplished at the center of innovation, research and interface of the university Sidi Mohammed Ben Abdellah, Fez. The chemical analysis was carried out by Infrared Spectroscopy using a Bruker spectrometer (Vertex 70) in the range 400-4000 cm^{-1} and the morphological analysis was achieved by Scanning Electron Microscopy (SEM).

Adsorption procedure

All the adsorption experiments were performed in a batch system; the principle is to introduce an initial mass of the adsorbent PB into 100 ml of a solution containing the adsorbate MB at an initial concentration previously brought to the desired temperature to using a thermostatically controlled bath. The solution is stirred constantly for 60 min. The samples were taken every 5 min using a 0.45 µm diameter (Minisart, Sartorium Stedim Biotech) syringe filter and then the supernatant was assayed immediately by a UV-Visible spectrophotometer (Jasco V530) At a wavelength which corresponds to the maximum absorbance of the MB which is λ_{max}=664 nm. The mass of the adsorbent studied is between 0.5 and 3 $g.l^{-1}$, the methylene blue concentration ranges from 20-50 $mg.l^{-1}$, the pH is adjusted to from 2-12 and the temperature is maintained at values between 20 and 50°C. The amount of the fixed dye per gram of adsorbent is given by the following Equation:

$$Q\left(mg.g^{-1}\right)=\frac{\left(C_0 - C\right).V}{m} \qquad (1)$$

Were, Q: Absorption capacity ($mg.g^{-1}$); V: Volume of the solution (ml); C_0: Initial concentration at t=0 in ($mg.l^{-1}$); C: Concentration at time ($mg.l^{-1}$); m: Mass of the adsorbent (g).

RESULTS AND DISCUSSIONS

Characterization of the adsorbent by MEB

The images of the morphology of the PB obtained by SEM are represented in Figure 2.

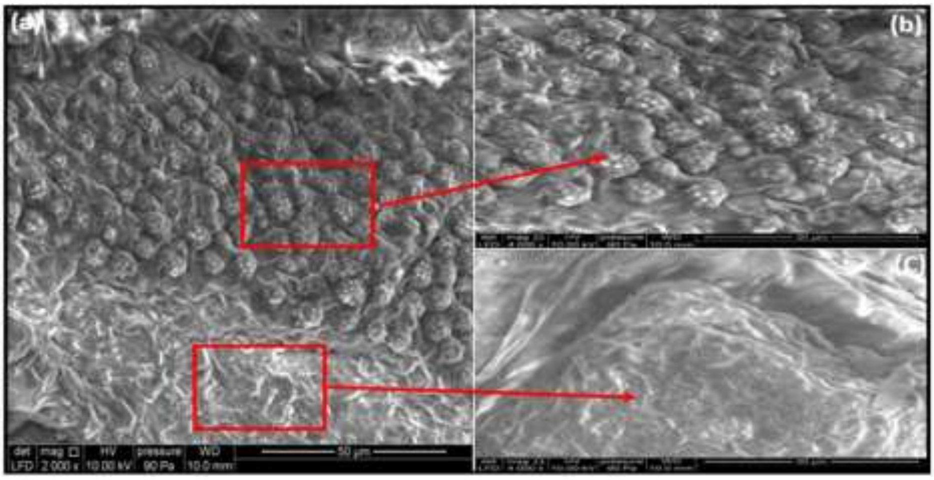

Figure 2: SEM microscopy for Pineapple Bark: Magnification: (a) 2000x, (b) 4000x, (c) 4000x

The image (a) obtained at different magnification of the PB sample shows that the latter reveal both a granular structure (b) close to the appearance of the grape and a filamentous and fibrous structure (c) which favors the fixing of dyes. These results are similar to the results obtained by Miyah et al., which show that our adsorbent material PB also has the same adsorption power of MB [15].

Infrared analysis

The Infrared spectrum relating to the PB is given by Figure 3.

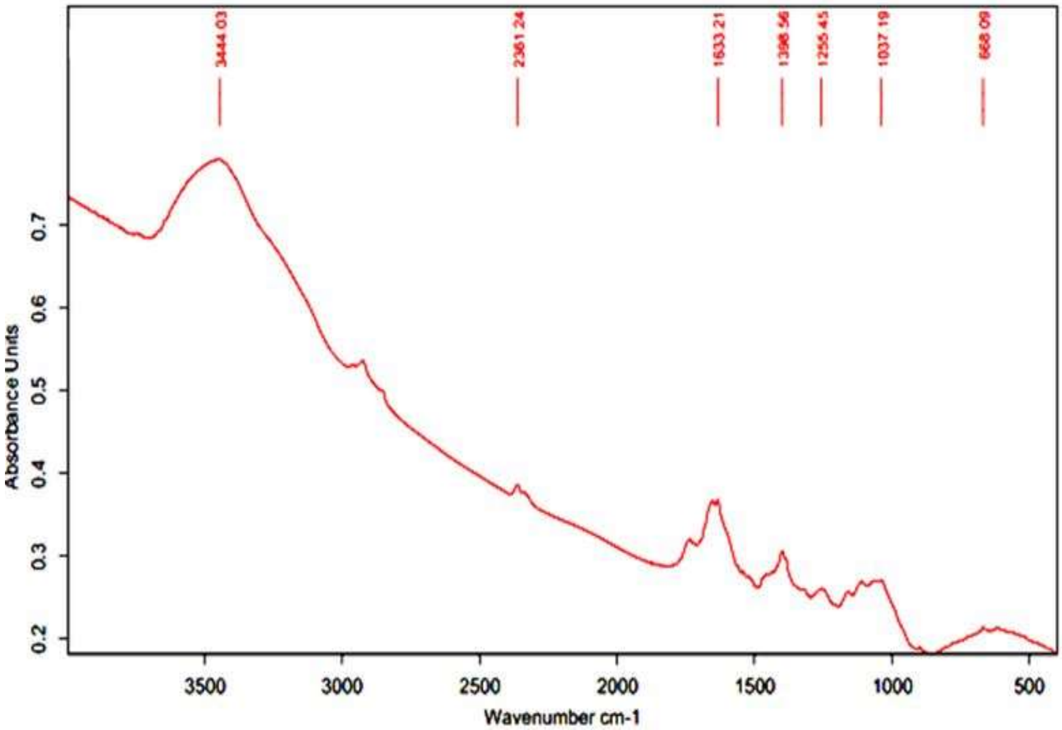

Figure 3: PB infrared spectrum

The spectrum has a wide band at about 3444.03 cm^{-1} which corresponds to the presence of a bound O-H group, the band at 2925.38 cm^{-1} assigned to the C-H elongation vibrations, the band at 2361.24 cm^{-1} coincides with to the triple bond nitriles C≡N, the band at 1633.21 cm^{-1} originates from the vibration of the groups C=O, the band 1398.56 cm^{-1} corresponds to the O-H alcohol aromatic bond, the band 1255.45 cm^{-1} identifies with to the C-O bond, and on the other hand the 1037.19 cm^{-1} and 668.09 cm^{-1} are attributed respectively to the primary alcohol C-OH function and the ≡C-H.

Effect of some parameters on adsorption

Effect of contact time on the adsorption of MB

The adsorption experiments to evaluate the contact time effect on the adsorbed quantity of MB by the adsorbent selected from PB were carried out at room temperature in 100 ml solutions enriched in MB which the initial concentration range varies from 20-50 mg.l^{-1}. The mass of the added PB is of the adsorbent of 2 g.l^{-1} and at a temperature of 20°C. The whole is carried with stirring for duration of 60 min.

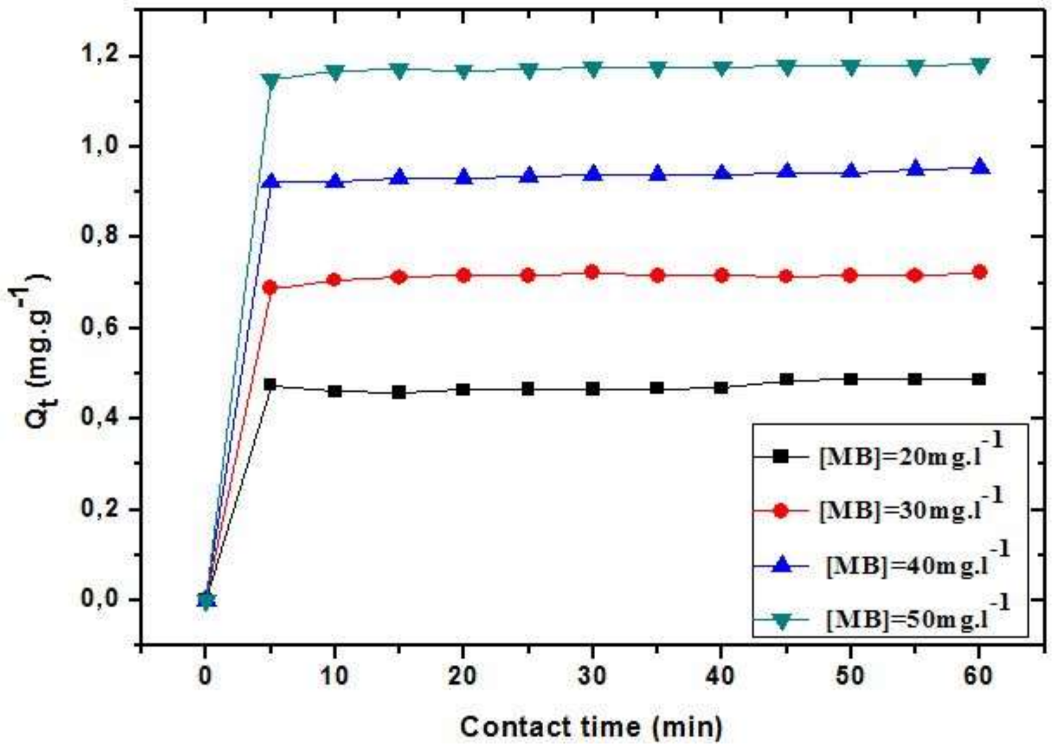

Figure 4: Effect of contact time and MB dye concentration

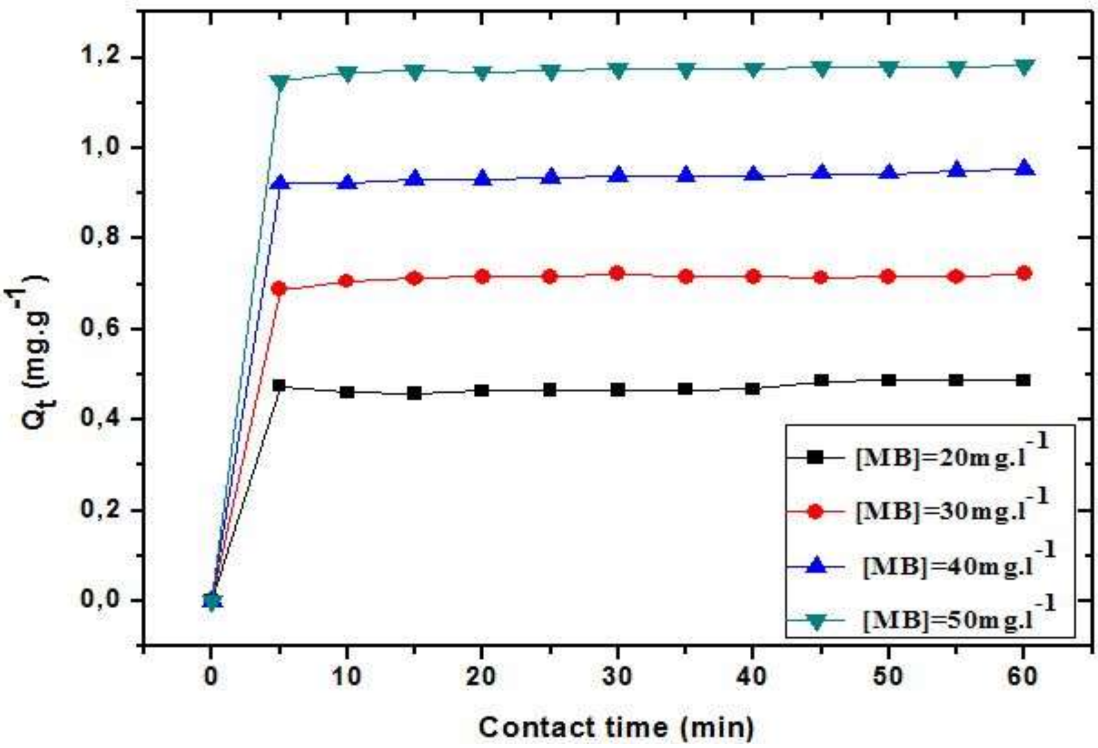

Figure 5: Effect of the contact time on the ER (%) of the MB

And the elimination rate as a function of the contact time. It is noted that both the adsorbed amount and the elimination rate are rapidly increased in the first 5 min and stabilization remains constant after 10 min, which indicates a state of equilibrium (Figures 4 and 5). This explains the fact that a very rapid diffusion of the molecules of the MB to the surface of the PB until saturation. The optimum adsorption amounts are in the order of 0.48, 0.71, 0.95 and 1.15 mg.g^{-1} respectively for concentrations 20, 30, 40 and 50 mg.l^{-1} of the MB.

Effect of adsorbent amount

The amount of adsorbed at equilibrium and the elimination rate for the different PB mass values are shown in Figures 6 and 7.

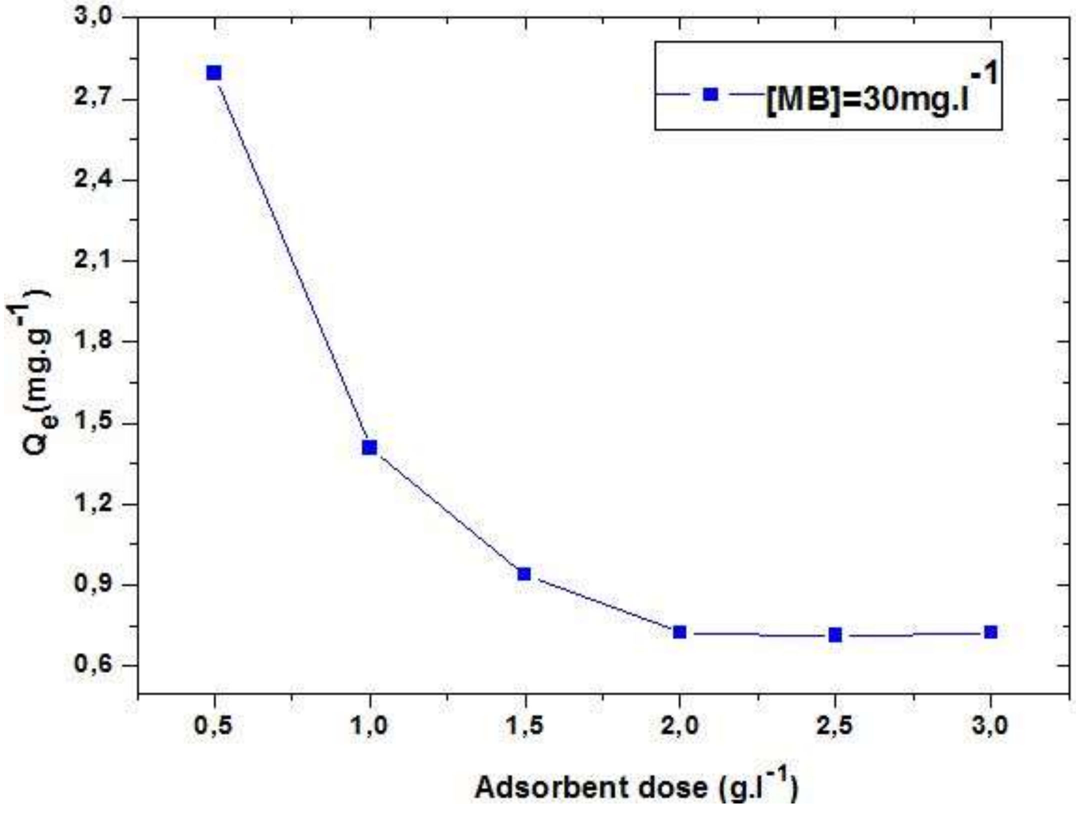

Figure 6: Effect of adsorbent dose (PB) on the $Q_{ads\ (éq)}$.
m=0.5-3 g.l^{-1}, MB=30 mg.l^{-1}, T=20°C, pH=6, $V_{steering}$=400 tpm and agitation time 60 min

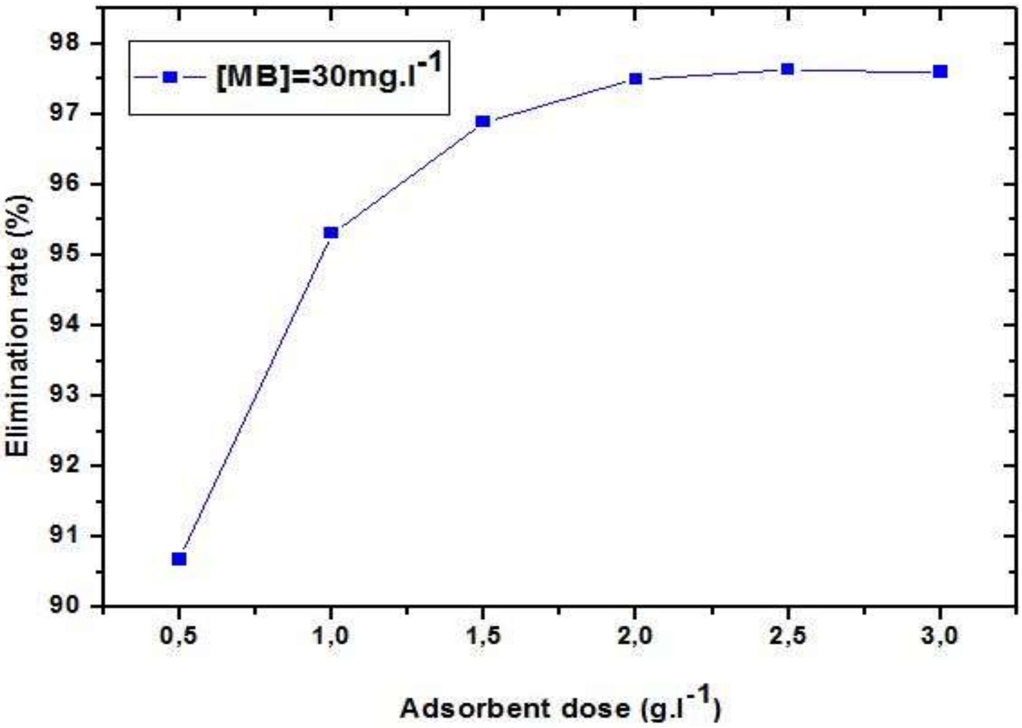

Figure 7: Effect of adsorbent dose (PB) on the ER (%)
m=0.5-3 g.l^{-1}, MB=30 mg.l^{-1}, T=20°C, pH=6, V$_{steering}$=400 tpm and agitation time 60 min

The analysis of the curve of Figure 6 exhibits a large decrease in the adsorbed quantity Q_e (mg.g^{-1}) with the increase in the mass of the adsorbent. This phenomenon is due to the decrease of the molecules of the MB which have a low concentration and very dispersed in the solution and equally important to the difficulty of interaction between adsorbent and adsorbate, which explains the saturation of the active sites of our adsorbent material. While Figure 7 shows a curve proportional to that of the adsorbed quantity; it can be deduced that the removal rate increases with the increase in the mass of the adsorbent. The optimum mass of the adsorbent used is in the order 2 g.l^{-1} for an adsorbed amount of 0.78 mg.g^{-1}.

Effect of pH

The study of the effect of pH on the equilibrium adsorbed quantity Q_e (mg.g^{-1}) is represented in Figure 8 allowing to both understanding the behavior of the adsorbent and the adsorbate at different pH and significantly to study the adsorption mechanism using pH values that vary between 2 and 10. The pH adjustment was carried out using a solution of Hydrochloric acid (HCl) (0.1 N) or sodium hydroxide NaOH (0.1 N).

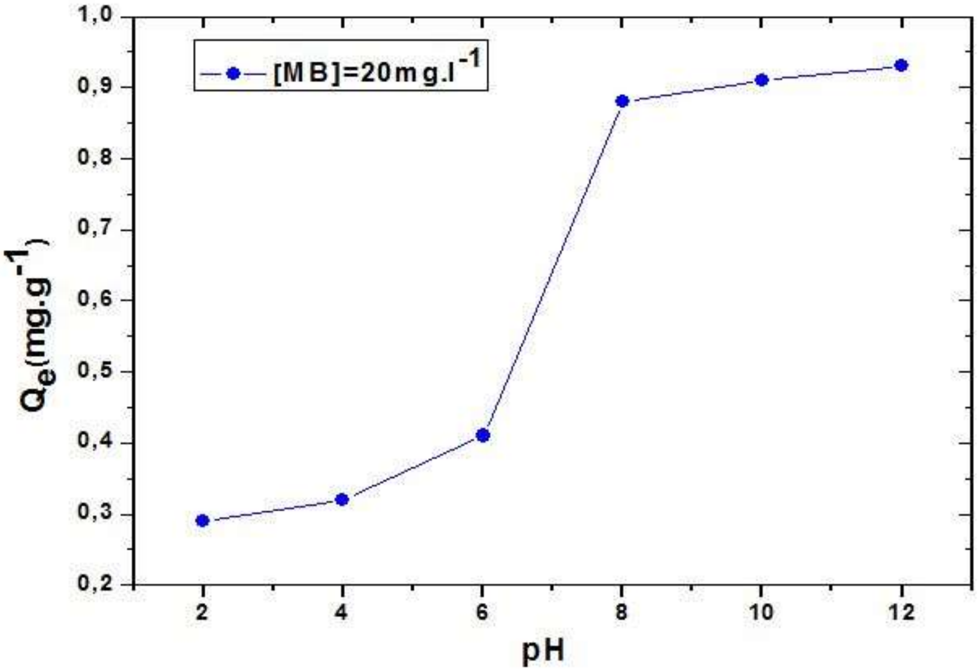

Figure 8 : Effect of pH on adsorbed quantity of MB onto PB

m=2 g.l^{-1}, MB=30 mg.l^{-1}, T=20°C, pH=2-12, V$_{\text{Steering}}$=400 tpm and agitation time 60 min

Figure 8 displays a slight increase in the amount adsorbed in the pH range (2-4) and then an increase in this amount in the pH which varies between 6 and 8 and a plateau is observed which stabilizes beyond the pH=8. This increase in the adsorbed amount of MB can be explained by the increase in pH as follows: The addition of the H^+ cations to lower the pH leads to an increase of the cations in the solution, which disadvantage the adsorption of the blue of methylene in acid medium. Moreover, when the pH increases there is an increase of the OH^- anions, which neutralize the MB and give better adsorption in the basic medium [4].

Effect of temperature

The outcomes of the effect of temperature on the adsorption amount (mg.g^{-1}) and the removal rate (%) are shown in Figures 9 and 10.

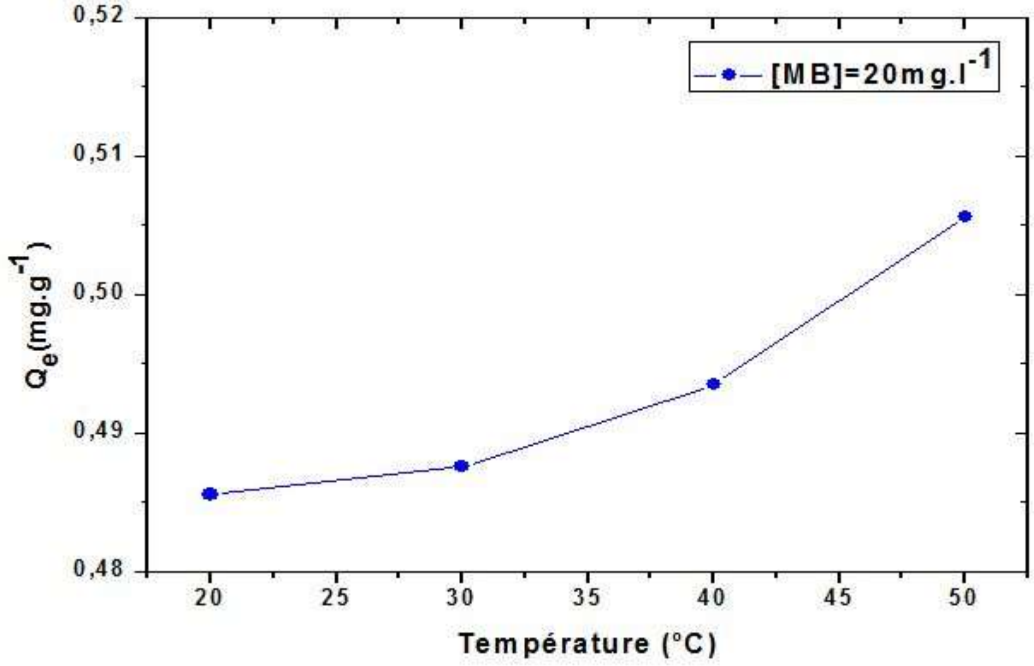

Figure 9: Effect of temperature on Q$_{\text{ads (éq)}}$
m=2 g.l^{-1}, MB=20 mg.l^{-1}, T=20-50°C, pH=6, V$_{\text{steering}}$=400 tpm and agitation time 60 min

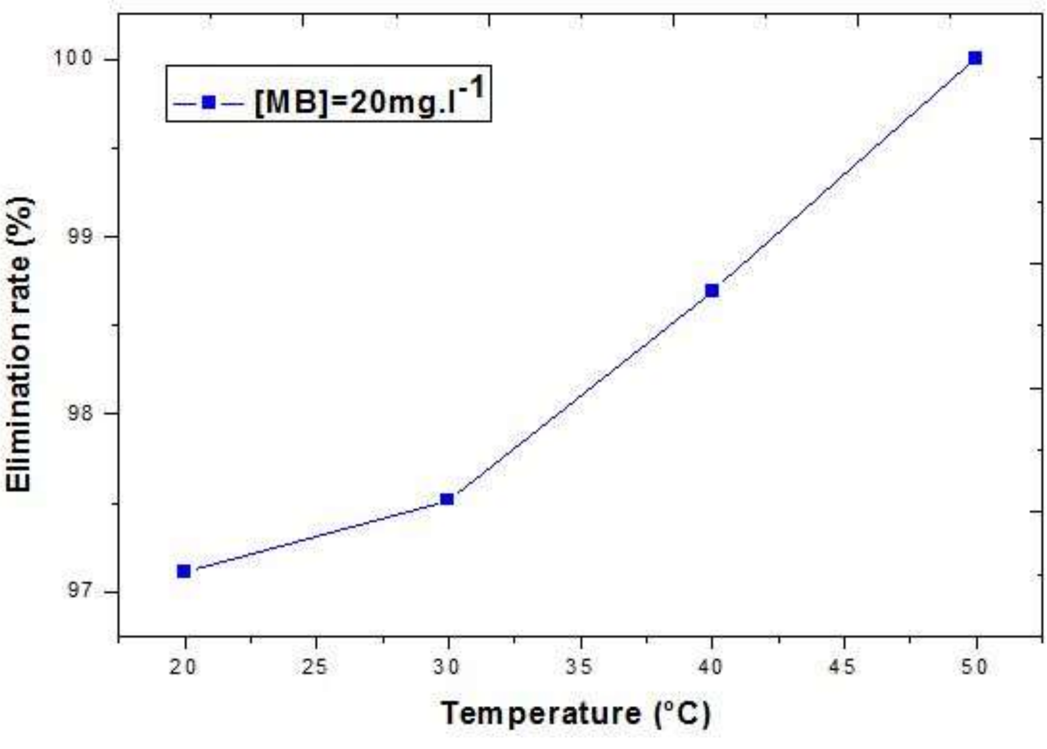

Figure 10: Effect of temperature on ER (%)
m=2 g.l^{-1}, MB=20 mg.l^{-1}, T=20-50°C, pH=6, V$_{\text{steering}}$=400 tpm and agitation time 60 min

Figures 9 and 10 show an increase in adsorbed amount and equilibrium elimination rate with increasing temperature, resulting in reduction of solution viscosity and increased migration availability of the molecules of MB on the active sites of our adsorbent PB and thereafter the reduction of the contact time. The maximum adsorption is 0.50 $mg.g^{-1}$ at a temperature of 50°C. It can also be inferred that the interaction of the adsorbent of the PB and of the adsorbate MB is of endothermic nature. In general, the rise in temperature favors adsorption.

Adsorption kinetics

Several models have been proposed to describe isothermal adsorption curves in aqueous media. Considering the adsorption phenomenon as equilibrium between the concentration of the dye and the amount of adsorption of the dye fixed to the adsorbent surface. The equations will logically bind the equilibrium concentration C_e ($mg.l^{-1}$) to the adsorbed amount at equilibrium q_e. Many researchers have studied this issue and have proposed equations that are more accurately model the behavior observed, taking into account the physical reality of the adsorption phenomenon.

Pseudo first-order model (Lagergren equation)

The first-order kinetics model is most suitable for the lowest solute concentrations. This model presented by the Lagergren relation [22] based on both the adsorbed amount and on the first equation of velocity which is established to describe the adsorption kinetics in a liquid/solid system. This pseudo-first order model is represented by the following relation [23,24]:

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

Where, q_t: quantity of adsorbate adsorbed at time t ($mg.g^{-1}$); q_e: amount adsorbed at equilibrium ($mg.g^{-1}$); K_1: adsorption rate constant of the pseudo-first order model (min^{-1}); t: time (min). If the relation of Lagergren is satisfied, carrying ln (q_e-q_t) as a function of time, we must obtain a line of slope -K_1.

Pseudo-second order model

The pseudo-second order equation is often used successfully to describe the kinetics of the pollutant-binding reaction on the adsorbent [25]. The pseudo-second order model can be represented in the following form [26]:

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

Where, K_2: Adsorption rate constant of the pseudo-second order model ($g.mg^{-1}.min^{-1}$). If this equation is content, by plotting t/q_t as a function of time t, we must obtain a line of slope $1/q_e$ and order the origin to be equal to $1/(K_2q_e^2)$ (Figure 11).

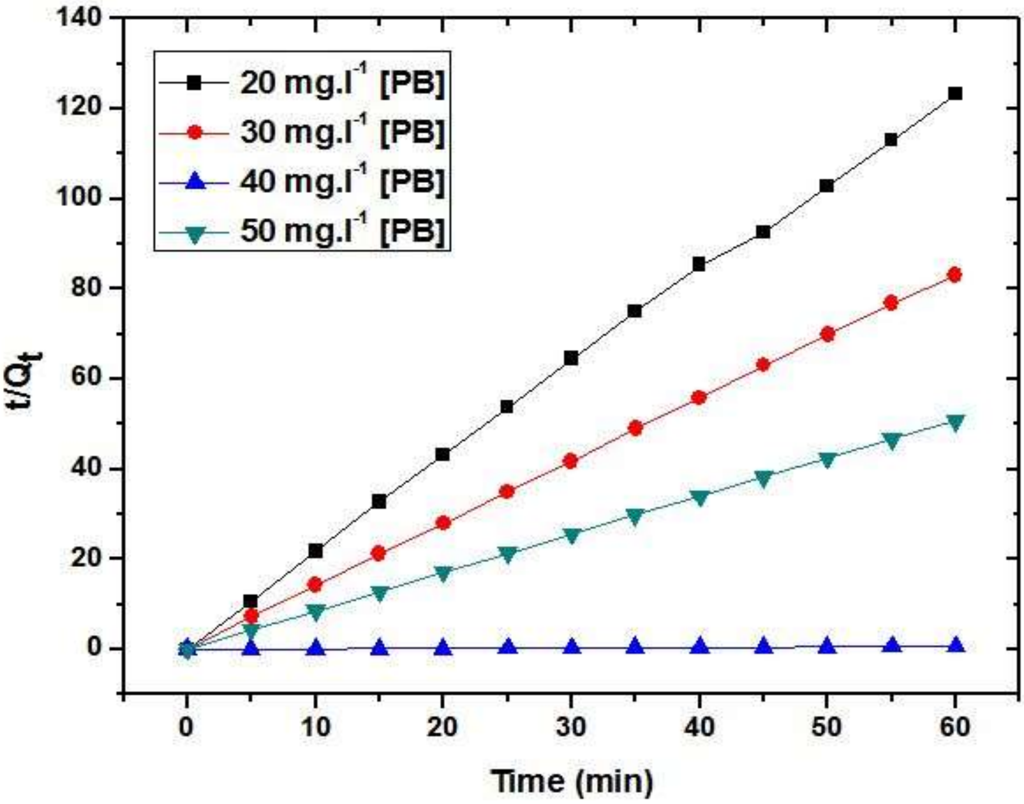

Figure 11: Pseudo-second order model for the adsorption of MB by PB

The calculation of the correlation coefficients of the various parameters shown in Table 1 shows that the values obtained are approximated to the pseudo-second order kinetic model indicating that the experimental results of the adsorption of MB on PB are well described by this latter model.

Table 1: Kinetic constants of the pseudo-second order model

[MB] (mg.l^{-1})	Q_{exp} (mg.g^{-1})	Kinetics of pseudo-second order		
		K_2 (g.mg^1.min^{-1})	Q_{cal} (mg.g^{-1})	R^2
[PB]=20 mg.l^{-1}	0.486742	2.654	0.4887	0.998
[PB]=30 mg.l^{-1}	0.722611	1.7826	0.7193	0.999
[PB]=40 mg.l^{-1}	0.953025	3.3928	0.9523	0.999
[PB]=50 mg.l^{-1}	1.182234	5.580	1.1827	1

Adsorption isotherms

To quantify the adsorption capacity of MB dye on PB, the Langmuir and Freundlich models were used to determine certain kinetic parameters such as equilibrium adsorbed amount and velocity constant.

Model of Langmuir

The linear form of the Langmuir isotherm is given by the following Equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (4)$$

Where, C_e: Concentration at equilibrium (mg.l^{-1}); q_e: Amount adsorbed at equilibrium (mg.g^{-1}); q_{max}: Maximum quantity adsorbed at saturation of the monolayer or maximum adsorption capacity (mg.g^{-1}); K_L: Adsorption equilibrium constant, dependent on temperature (l.mg^{-1}). If the Langmuir equation is content, we must obtain by putting our experimental points in $C_e/q_e=f(C_e)$ coordinates a straight line whose slope is ordered at the origin, which allows us to determine q_{max} and K_L. This equation is known as the Langmuir equation. The essential characteristic of the Langmuir isotherm can be expressed by the non-dimensional parameter of Hall, called the equilibrium parameter R_L, which has the form [27]:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (5)$$

Where, C_0: Initial concentration (mg.l^{-1}); K_L: Langmuir adsorbate-adsorbent adsorption equilibrium constant (l.mg^{-1}); R_L: Adsorption isotherm parameter, according to the criterion: favorable if $0 < R_L < 1$ and linear if $R_L=1$ and unfavorable if $R_L > 1$. The results obtained by the Langmuir equation are shown in Figure 12.

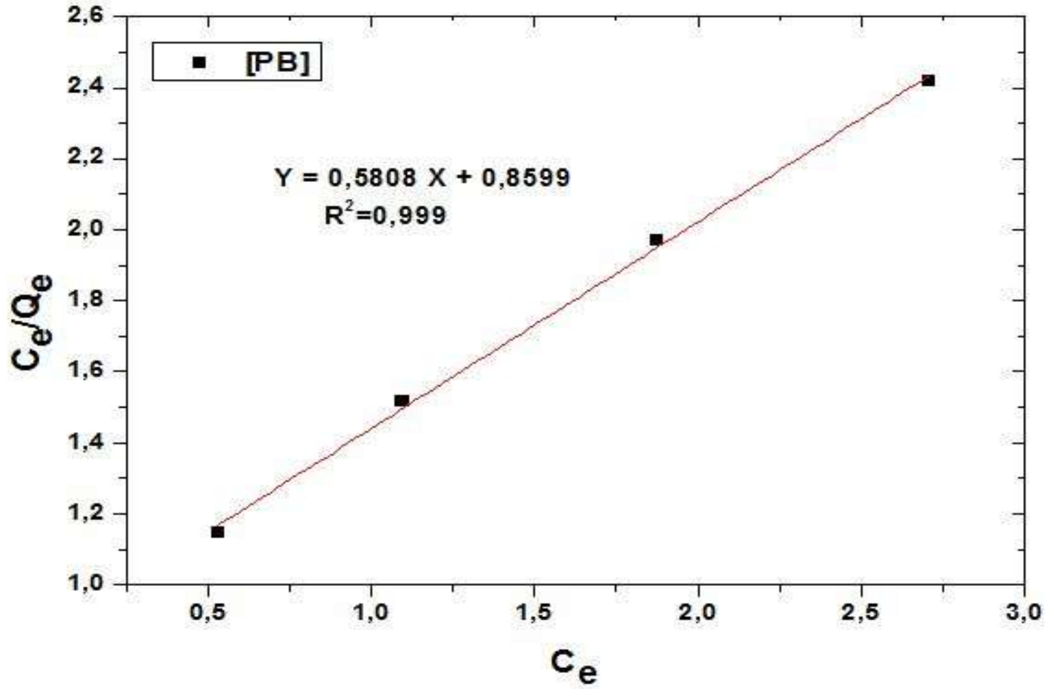

Figure 12: Langmuir isotherm

It is found that the correlation coefficient R^2=0.999 of the Langmuir model is very close to one, this indicates that this model is verified and the adsorption of the MB on the surface of the material PB is monolayer. The calculated Hall parameter value is summarized in Table 2. The results obtained show that the adsorption isotherms of the MB on PB are all favorable.

Table 2: Parameters of the Langmuir model

Langmuir				
	Q_{max} (mg/g)	K_L (L/mg^{-1})	R_L (L.mg^{-1})	R^2
[PB]	1.722	0.675	0.068	0.999

Freundlich model

The linear form of the Freundlich isotherm is given by the following Equation:

$$q_e = K_F . C_e^{1/n} \qquad (6)$$

The equation can be linearized as follows:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad (7)$$

K_F (mg.g^{-1} (mg.L^{-1}) $^{-1/n}$) is the Freundlich adsorption constant and n is a constant dependent on the nature of the adsorbate and temperature.

Figure 13 and Table 3 represents the Freundlich isotherm based on the plotting of Ln (Qe) as a function of Ln (Ce).

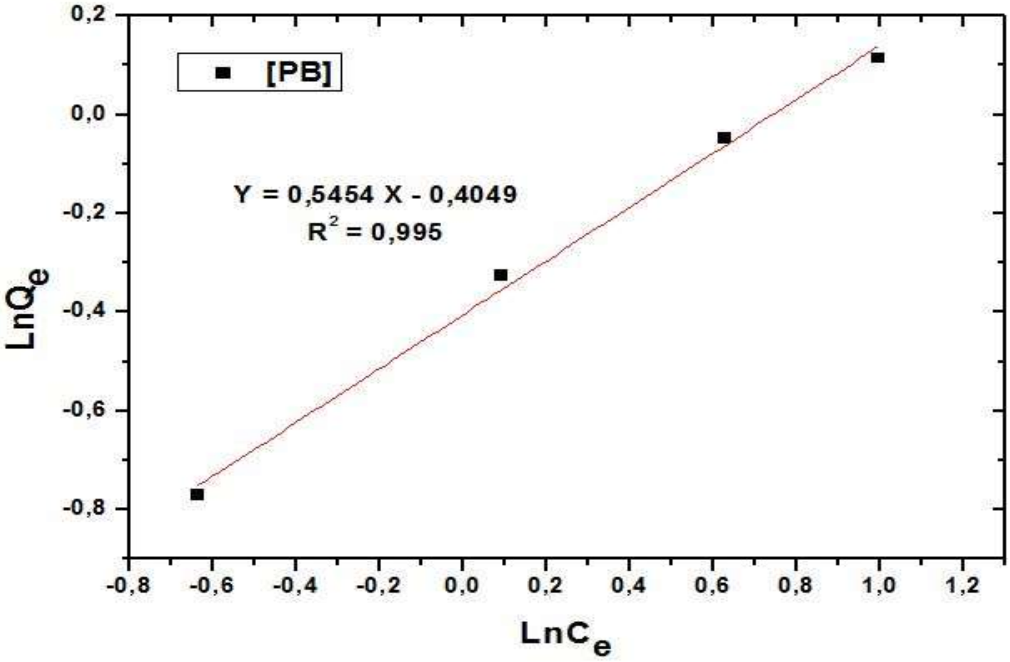

Figure 13: Freundlich isotherm

Table 3: Parameters of the Freundlich model

Freundlich			
	K_f (mg/g)	**n_f**	**R^2**
[PB]	0.667	1.834	0.995

CONCLUSION

To conclude, the optimal adsorption capacity of the PB is of the order of 0.78 mg.g^{-1} with a removal percentage of 96% for a MB concentration of 20 mg.l^{-1}, a adsorbent dose of 2 g.l^{-1}, at a pH=6 and a temperature of 20°C. Besides, the results of the modeling demonstrate that the isotherms are described satisfactorily by the model of Langmuir as much as the adsorption process followed in every case studied the model of the pseudo-second order.

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