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Study of the Power Adsorbing the Powder Nutshells for Elimination of the Methylene Blue

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Abstract: *In this work, the adsorption of a cationic dye to an aqueous solution with an adsorbent prepared from the shell walnuts has been demonstrated. Different effects as the adsorbent dosage, initial dye concentration, contact time and the particle size were studied. The adsorption isotherms were analyzed using the Langmuir model and Freundlich and the thermodynamic and kinetic parameters were assessed to predict the nature of the adsorption.*

Keywords: *Nut shells, Methylene blue, Static regime, Modeling, Kinetics, Isotherms*

I. Introduction

The rejections of the textile industry constitute a major problem for the human health, in particular the various coloring agents, which are used in excess to improve the dye [1]. Therefore, waters rejected in the nature strongly concentrated in coloring agents the low biodegradability of which returns their difficult treatment, what establishes a source of important degradation of the environment. A wide variety of physical, chemical and biological techniques were developed and tested in the treatment of effluents containing dyes.

These methods include coagulation-flocculation [2], precipitation, ion exchange [3, 4], membrane filtration, irradiation, ozonation and oxidation [5, 6]... However, these methods are expensive and result in the generation of large amounts of sludge or derivatization.

Among the treatment processes of liquid discharges, adsorption stays a technique relatively used and easy to implement [7].

The present work aims at studying a practical and economical method for removal of methylene blue dye from the water by adsorption on walnut shells used as a new natural adsorbent.

The influence of several parameters on the adsorption of the methylene blue on it bio adsorbing was studying, in particular the time of contact, the mass of him adsorbing used, the size grading and the initial concentration of the dye.

To understand better the mode of fixation of the coloring agent, we were particularly interested to study the kinetics, the thermodynamics and the adsorption isotherms.

II. Materials and Methods

During this research, the used absorbent is a material a residue of the nut shells the elaboration of this support spent by several stages since the wash with the distilled water, the drying in the steam room at a temperature of 110°C for 18 hours, the grinding, until the obtaining of the particles of size gradings characterized by following diameters: $D \leq 80$ .mum; $80\mu m \leq D \leq 850\mu m$; $D \leq 850\mu m \leq 2mm$.

All the experiences have been realized in discontinuous reactors (static system), by setting in contact a mass (m) of walnut shells of granulometry given with an aqueous solution of concentration C0 (mg/l) of (MB), then the mixture is shaken in temperature well defined during all the manipulation to assure a good homogenization of the solution, and a better contact between the adsorbate (MB) and all active sites of adsorbing it.

After a time of agitation, the samples collected are settled throughout a sufficient time, and also the residual concentration in the equilibrium (Ce), It's determined by an UV-visible spectrophotometer (type UV-3100PC) with the maximal wavelength (λ=664nm). The yield of elimination of the coloring agent (MB) was calculated by using the following formula:

$$R(\%) = \left(\frac{C_0 - C_R}{C_0}\right) * 100 \qquad (1)$$

The solution of (MB) was prepared by mixing a crystallized product and distilled water, while pH controlling constantly during the manipulation.

III. Results and Discussion

1- Contact time

The obtained results are represented on the figure 1. In the first minutes the kinetics of adsorption are very fast, what can be explained by the availability of the active sites on the surface of adsorbing it. Then it becomes slower until reach the balance after the occupation of the majority of sites by the ions of MB.
During work, a time of contact of 60 minutes seems widely sufficient to reach the balance.

2- Optimization of the influencing parameters

➢ **Effect of the concentration of adsorbate**

When analyzing the results represent on the figure 2, we notice that the absorbed quantity increases with the increase of the initial concentration of MB. After sixty minutes, it reached a constant value regardless of the first concentration; this shows that the equilibrium time is independent of the initial concentration of the dye.

➢ **Effect of the mass of the nut shells**

The analysis of the results which represents in the figure 3 showing that the fixed quantities of coloring agent owe being one agreement with the doses of adsorbing in solution; to assure an equivalent number of sites of adsorption.

➢ **Effect of the size grading of the nutshells**

In this study, we used the various fractions of size. The kinetics of adsorption of methylene blue are represented on the figure 4. The capacity of adsorption is preferable for a range of lower size of 80 µm, because the adsorption depends on the external surface of the adsorbing material increased with the fineness of its particles.

3- The adsorption kinetics

In the literature, different kinetic models were used to evaluate the adsorption process [8]. In the same context to model, the kinetics involved in the adsorption of MB on walnut shells and to determine certain parameters kinetic as the constant of speed and the quantity adsorbed in the balance, two models were studied: pseudo-first order and the pseudo-second order.

- **Model of pseudo-first order:**

The first model of pseudo-first order [9] is expressed as follows:

$$\frac{d_{Q_t}}{dt} = k_1(Q_e - Q_t) \qquad (2)$$

Qe and Qt ($mg.g^{-1}$) is the quantities adsorbed in the balance and in time t
k_1 (min^{-1}) is the constant of speed of adsorption of the so-called model - first order.
The integration of the equation (2) becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \qquad (3)$$

- **Model the pseudo-second order**

The model of the pseudo-second order [10] is expressed by the following equation:

$$\frac{d_{Q_t}}{dt} = k_2(Q_e - Q_t)^2 \qquad (4)$$

Where:
K_2 is the constant of speed of adsorption of the model the so called second order ($g.mg^{-1}min^{1}$).
Q_t: the capacity of adsorption at the moment t.
Q_e: the capacity of adsorption in the balance.
The integration of the equation (4) gives:

$$\left(\frac{1}{Q_t}\right) = \left(\frac{1}{k_2 app Q_e^2}\right)\frac{1}{t} + \left(\frac{1}{Q_e}\right) \qquad (5)$$

Better linearity was obtained for the pseudo-second-order model, as shown in Figure 9. So the process does not follow the pseudo first order model.
Furthermore, from Table 3, the calculated values of the amount adsorbed to the $Q_{e,callus}$ equilibrium callus pseudo second order model is consistent with experimental data $Q_{e,exp}$ regardless of the initial concentration of MB.

4- Modeling adsorption phenomenon

In order to determine the maximum theoretical capacity and define the model, which obeys this sorption, we applied to the experimental data measured the equations of both models, Freundlich and Langmuir.

The equation of Freundlich model [11] was as follows:

$$Q_e = \frac{X}{m} = K_F C_e^{1/n} \quad (6)$$

The relationship linearized Freundlich is:

$$\text{Ln}\, Q_e = \text{Ln}\, K_F + {}^{1}/_{n}\, \text{Ln}\, C_e (7)$$

The equation of the adsorption Langmuir model [12] is given as follows:

$$Q_e = \frac{a * Q_m * C_e}{1 + aC_e} (8)$$

The linear relation of the equation of Langmuir:

$$\frac{1}{Q_e} = \frac{1}{Q_m a} * \frac{1}{C_e} * \frac{1}{Q_m} \quad (9)$$

The application of equations Langmuir and Freundlich on test results obtained are shown in Figures 5 and 6.

The parameters of these two equations are reported in Tables 1 and 2. According to the results, the Freundlich equation is the most suitable for this sorption than Langmuir.

This context is demonstrated, firstly by the values of the regression coefficients and the values of the theoretical maximum capacities that are better for the Freundlich equation (Tables 1 and 2).

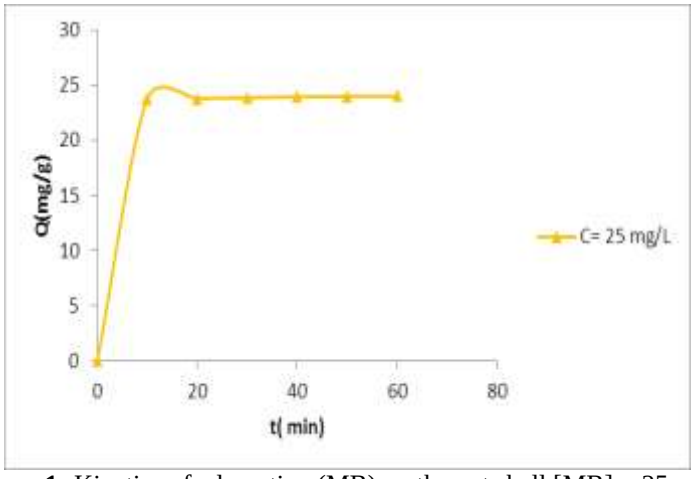

Figure 1: Kinetics of adsorption (MB) on the nut shell [MB] = 25 mg/l; m = 1 g / L; T = 22 ° C, and D <80 µm

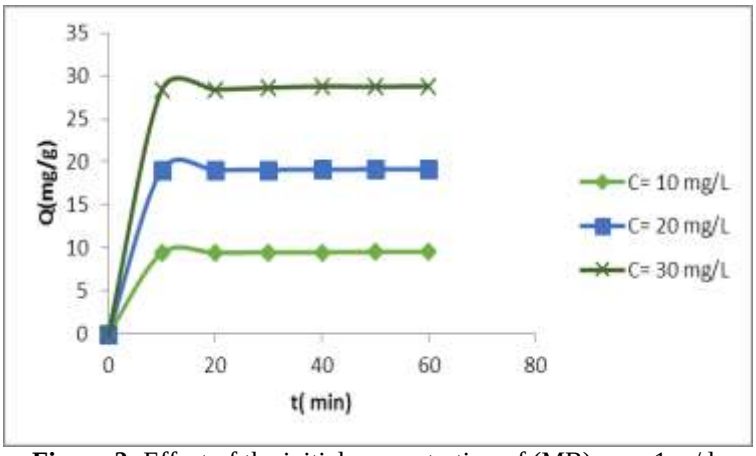

Figure 2: Effect of the initial concentration of (MB), m = 1 g / l; T = 22 ° C and D<80 µm

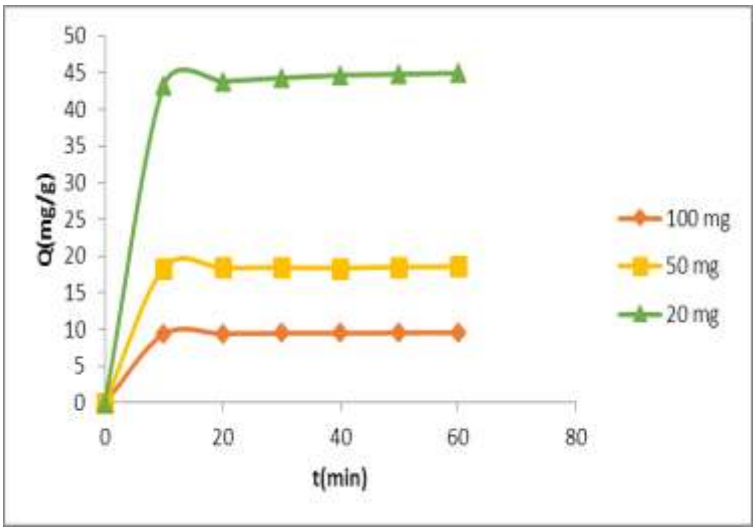

Figure 3: Influence of the mass of the support, [MB] = 10 mg / l;
T = 22 ° C, and D <80 µm

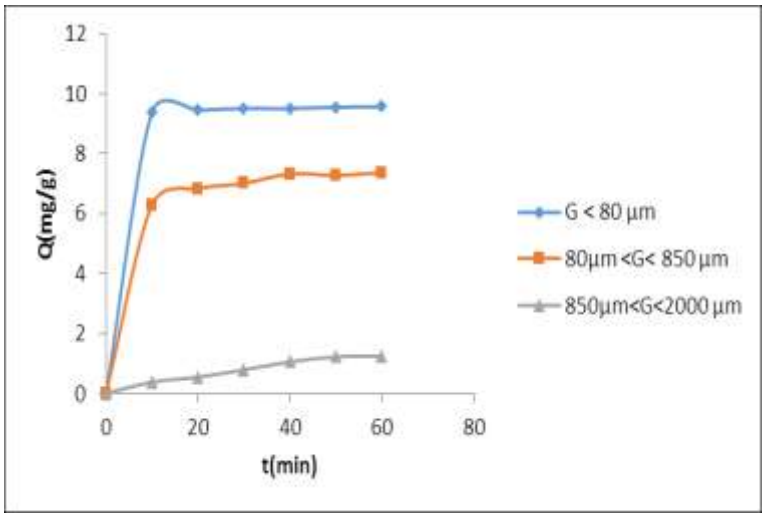

Figure 4: Influence of particle size of the support,m = 1 g / l and T = 22 ° C

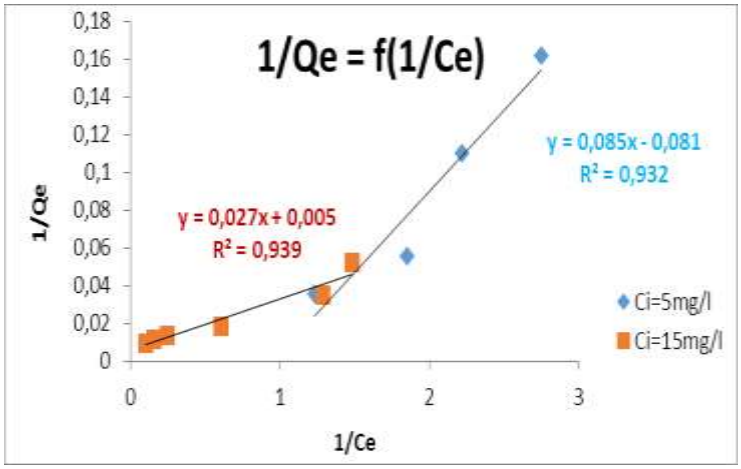

Figure 5: linear Langmuir Model: [MB] = 15 mg / l and [MB] = 5 mg / l,
T = 22 ° C; D<80 µm

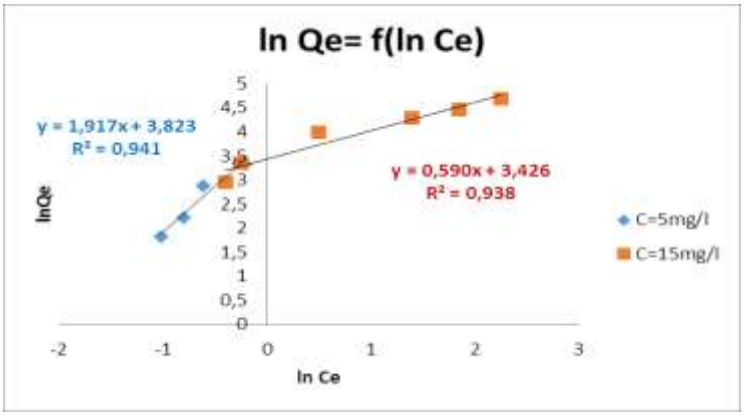

Figure 6: Linear model Freundlich [MB] = 15 mg / l and [MB] = 5 mg / l, T = 22 ° C and D<80 µm

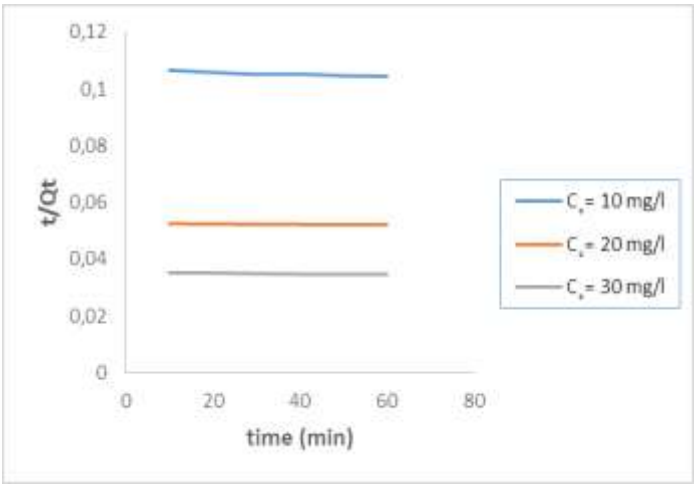

Figure 7: Pseudo-second order model for the adsorption of MB by nutshells

Table 1: The parameters of adsorption of the MB on nutshells for

Modèles	Equation	Q_m(mg/g)	A (L.mg^{-1})	K_F (mg/g)	R (coefficient de corrélation)
LANGMUIR	$\frac{1}{Q_e} = \frac{1}{Q_0 a} * \frac{1}{C_e} * \frac{1}{Q_0}$	12,285	0,952	-	0,9322
FREUNDLICH	$\ln Q_e = \ln K_e + {}^1/_n \ln C_e$	-	-	45,75	0,9419

Table 2: The parameters of adsorption of the MB on nutshells for [MB] =15mg / l

Modèles	Equation	Q_m(mg/g)	A (L.mg^{-1})	K_F (mg/g)	R (coefficient de corrélation)
LANGMUIR	$\frac{1}{Q_e} = \frac{1}{Q_0 a} * \frac{1}{C_e} * \frac{1}{Q_0}$	175,43	0,2088	-	0,9391
FREUNDLICH	$\ln Q_e = \ln K_e + {}^1/_n \ln C_e$	-	-	30,7533	0,9394

Table 3: kinetic Constants of the model of the pseudo-second order

C_i (mg.L^{-1})	$Q_{e,exp}$ (mg.g^{-1})	Modèle de pseudo-deuxième ordre		
		$Q_{e,cal}$(mg.g^{-1})	K_2 (g.mg^{-1}.min^{-1})	R^2
10	9,5698	9,5785	0,4579	0,914
20	19 ,1661	19,1571	0,71706	0,8592
30	28,8262	28,9017	0,1813	0,7916

IV. Conclusion

The study of the process of adsorption of the methylene blue on nutshells was the object of this work. The results showed that the capacity of adsorption of a mass of nutshells increases with the increase of the initial concentration of the coloring agent in the solution.

The modeling of the results of adsorption demonstrated that the model of pen name - the second order offers a better correlation of the kinetic data and that the model of Freundlich describes better the isotherm of adsorption, so the molecules of the coloring agent adsorb in monolayer andsitesare heterogeneous with energies of different fixation.

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