Retention of Methylene Blue on an Agro-Source Material

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Abstract—The present work reports the characterization and the effectiveness of a vegetable origin adsorbent. Shells of the walnuts of Argan tree (SAR). SAR was characterized in terms of apparent and absolute densities and humidity rate. The thermal stability of the SAR material was determined by thermogravimetry analysis (TGA) and differential thermal analysis (DTA). The effect of different parameters such as contact time, mass of adsorbent, pH of the solution, temperature, and the concentration of pollutant on the adsorption of Methylene Blue (MB) on the SAR were studied. From this study it can be concluded that the adsorption of MB on SAR is an endothermic and spontaneous. The adsorption phenomenon involved follows a pseudo second-order kinetics described by the Langmuir isotherm

Keywords: Argan, Adsorption, Environment, Methylene blue, Water treatment.

I. INTRODUCTION

The textile, colorants, paper and plastic industries generate considerable amount of water loaded with 10 % to 15 % of dye [1]. These pollutants are the first identifiable even with naked eye in the wastewater [2]. They are stable in nature and absorb sunlight, which will affect the intensity of light absorbed by phytoplankton and hydrophytes, reducing photosynthesis and concentration of dissolved oxygen in the aquatic environment which causes an increase of the chemical oxygen demand (COD) level [3].

These pollutants may interact by adsorption on various substrates natural: mineral, animal or vegetable (clay, wool, wood, waste of the olive grain pits ...) [4]. This property allowed using the adsorption in large areas of separation (extraction, purification, decontamination, etc...), in particular the use of activated carbon, which has been the subject of many studies [5, 6, 7, 8]. This technique has been proved very effective, but the commercial activated carbon is very expensive [8, 9], hence the search for new adsorbent materials from plant waste with cost effective are of high interest.

In this context, we are interested in a natural origin material: Shells of the walnuts of Argan tree (SAR) to promote firstly a simple, efficient and effective method

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capable of reducing pollution from industrial dye, and on the other hand, a valorisation of the material used.

II. MATERIALS AND METHODS

A. Materials

1) Preparation of polluting solution

The pollutant chosen in this study was the methylene blue (MB): a cationic organic dye belonging to the family of Xanthines [10], with the molecular formula: $C_{16}H_{18}CIN_3S$ and named according to IUPAC 3, 7-bis (Dimethylamino)– phenothiazin–5-ium chloride. This dye is widely used in the textile industry and especially to give the blue colour in articles such as jeans. It is stable in sunlight, natural oxidants, and resistant to biodegradation [11]. The solutions used were prepared by serial dilutions, from a mother solution with the concentration of 1 g/l. The wavelength of maximum absorption $\lambda max = 661$ nm is determined from scanning of the absorption spectrum of MB from 900 nm to 300 nm using a UV-visible spectrophotometer (UV 2300).

2) Preparation of adsorbent

Shells of the walnuts of Argan tree used are from the 2012 harvest in Agadir region (southern Morocco). These shells are sorted to remove impurities, and then ground in a grinder "Retsch SM 100" equipped with a 1mm sieve. The ground material is sieved through a series of sieves with diameters [1 mm; 500 μ m; 315 μ m; 100 μ m; 80 μ m; 50 μ m; 0 μ m] to distribute according to their diameter. These sieve pass are kept in glass bottles closed.

B. Experimental methodology

1) Measuring the residual concentration

In order to determine the residual concentration after adsorption, we take 15 mL of each sample solution, and then allowed to settle for 24 hours. Finally, the concentration is calculated using the absorbance measured by a UV-Visible spectrophotometer "UV-2300" set to the appropriate wavelength λ max = 661 nm, determined previously, and using the Beer-Lambert law.

2) Calculating yields and quantities adsorbed

The amounts adsorbed per mass unit of adsorbent and the equilibrium yields are respectively calculated using (1) and (2):

$$Q_{ads} = \frac{(\mathcal{C}_0 - \mathcal{C}_{eq})}{m} * V \tag{1}$$

 $R(\%) = \frac{(C_0 - C_{eq})}{C_0} * 100$ (2)

Where:

- C₀: initial concentration of the adsorbate (mg/L).
- Ceq: residual concentration of the adsorbate (mg/L).
- m: mass of adsorbent used (g).
- V: the volume of solution (L).
- Qads: the amount of pollutant adsorbed per mass unit of adsorbent (mg/g).
- R: the yield of adsorption (%).
- 3) Mass effect

This study helps us to determine the optimal mass of adsorbent used in the following work. It is performed by adding various masses of adsorbent to MB solutions with a concentration of 128 mg/L, while keeping the volume of the solution fixed to 50 mL and the temperature $T = 24\pm1$ °C.

4) Time effect

The study of the kinetics is crucial in the sense that it determines the contact time of adsorbent-adsorbate required to reach the adsorption equilibrium. Also it allows determining the kinetic model describing the adsorption in order to deduce the kinetic parameters to identify the mechanism of retention [12].

The procedure used for this study is to put in flasks 50 ml of MB solution with concentration 128 mg/l and 4 g of adsorbent. The mixtures are stirred at temperature fixed at $T = 22 \pm 1$ °C using a thermostated bath during determined times.

5) Temperature effect

To study the effect of temperature on the adsorption we placed in a thermostatic bath with magnetic stirring for 10 minutes, 6 vials containers 50 mL of solution of given concentration of MB and 4 g of adsorbent.

6) pH effect

It is useful to know the efficiency of adsorption at different pH. In this context we have studied the influence of this parameter on the adsorption of MB on the SAR. This study is carried out by adding 4 g of adsorbent to 50 ml of solution of MB (128 mg/L) whose pH is adjusted by addition of sodium hydroxide (0.1 N) and / or nitric acid (0.1 N) before the contact with the adsorbent. The pH measurements are made using a multi-parameter device "HANNA HI 255" with a combined pH electrode "HI 1332".

7) *Concentration effect*

In order to study the effect of the concentration of pollutant in the adsorption, we used solutions of MB with different concentrations: 25, 50, 75, 100, 128, 150, 200, 250, 300, 350, and 400 mg/L, to these solutions was added 4 g of adsorbent. Agitation is maintained for 10 minutes at a temperature of 24 ± 1 °C.

III. RESULTS AND DISCUSSION

A. Physical and chemical characterization of the adsorbent used

The material used is characterized by determining the bulk density ($\rho_{app} = 0.732 \text{ kg/L}$), the absolute density ($\rho_{abs} = 1.293 \text{ Kg/L}$) and its moisture content (Th = 9.52 %). Also we made a sieve analysis of the crushed SAR used in this study (Figure.1). The sieve analysis shows that SAR is formed principally of particles of diameter comprised between 1 mm and 500 µm. Finally SAR is analyzed by thermogravimetry (TGA) and differential thermal (DTA) (Figure 2).





The analysis of DTA and TGA curves shows that SAR decomposes thermally in four steps [13, 14]:

- *The first* is endothermic, that onset at 65 °C and ends near 120 °C, this corresponds to the step of dehydration of the surface and the structure. During this stage there is a loss of approximately 10% of mass, which is in agreement with the value of moisture content previously determined (Th = 9.52 %).
- *The second* step is also endothermic, between 260 °C and 350 °C which may correspond to the thermal depolymerisation of hemicelluloses [15,16], accompanied by a loss of 60 % of the initial mass.
- *The third* is exothermic, between 350 °C and 450 °C which corresponds to the degradation of cellulose [17], with 10 % of mass loss.
- *The latter* step is between 450 °C and 510 °C which may be due to the decomposition of lignin [18] with a mass loss of nearly 20 %.

B. Study of some parameters influencing the adsorption

1) Contact time effect

The form of the curve shown in Figure 3 is a typical saturation curve. The analysis of this curve shows that the adsorbed amount increases with the stirring time to achieve a plateau which reflects the adsorption-desorption equilibrium.



 $(m = 4 g; C_0 = 128 mg/L; T = 22\pm1 \text{°C}; 0.5 \text{ mm} \le d \le 1 mm).$

This equilibrium is reached after the first 10 minutes with an adsorption capacity (Qads = 1.58 mg/g). The initial rapid absorption is due to the accumulation of MB on the surface of adsorbent which is a rapid step [19]. From these results (Figure 3) it seems that a contact time of 10 minutes is appropriate to be used in the following work.

2) Effect of particle size of adsorbent

The effect of particle size of adsorbent on the adsorption performance was elucidated by studying the adsorption of MB on SAR particles of different diameters. The results (Figure 4) show that the best yields are obtained for the small particle size, which can be explained by the increase of the specific surface area by decreasing the particle size. In further work we used grain diameters between 0.5 mm and 1 mm, firstly because they constitute the major fraction of the ground material, and secondly they provide acceptable yields of adsorption in the order of 93 %.



adsorption yield of MB on SAR. (t = 10 min; m = 4 g; C₀ = 128 mg/L; T = 22±1 C).

3) Adsorbent mass effect

The adsorbent mass effect on the adsorption performance is illustrated in Figure 5. The results show that the adsorption performance of MB increases with increasing the mass of adsorbent suspended in the solution and remains constant for a value around 4 g and above.



Figure.5. Effect of adsorbent mass on the adsorption yield of MB on SAR. (t= 10 min; $C_0 = 128$ mg/L; T = 25 ± 1 °C; 0,5 mm $\leq d \leq 1$ mm).

Thus, the mass of 4 g of the adsorbent is sufficient to remove nearly 100 % of the dye, which leading to use this mass in following work.

4) *Effect of concentration of adsorbate*

The effect of the concentration of the adsorbate on the adsorbed amount is shown in Figure 6. The results show that there is a strong increase in the adsorbed amount of MB with increasing the concentration of MB, but beyond 250 mg/L this increase change it intensity towards saturation. This phenomenon may be due to the saturation of free adsorption sites.



Figure.6. Effect of the concentration of adsorbate on MB amount adsorbed on SAR. (t = 10 min; m = 4 g; T = 25 ± 1 °C; $0,5 \le d \le 1$ mm).

5) *Temperature effect*

The curves in Figure 7 correspond to the results of the study of the temperature effect on the adsorption of MB on SAR. We observe that in the range of temperature studied this parameter has a positive impact but low on adsorption [20]. For this reason we chose to work later at room temperature.



Figure 7. Effect of the temperature on the amount adsorbed of MB on SAR. (t = 10 min; m = 4 g; 0,5 mm \leq d \leq 1 mm).

6) *pH effect*

The results of this study are presented in Figure 8. By analyzing theses results it can be noted that an increase in pH has a positive effect on the adsorption. This increase in the adsorbed amount of MB with the pH may be explained by the fact that the addition of cations H^+ neutralizes the negative charge of the SAR, which disadvantages the adsorption of MB cationic in very acid environment. As against, when the pH increases there is a decrease of cations H^+ , therefore the charge of SAR is significantly negative, which favour adsorption of MB [21].



Figure.8. pH effect on adsorption yield of yield of MB on SAR. ($t = 10 \text{ min}; m = 4 \text{ g}; T = 24 \pm 1 \text{ }^\circ\text{C}; 0.5 \text{ mm} \le d \le 1 \text{ mm}$).

C. Study of adsorption kinetics

The order of the reaction is a very important parameter in determining the reaction mechanism. Orders for the adsorption on biomasses the most cited in the literature are:

- *The pseudo-first order* expressed by Lagergren equation [22], which can be linearized in the form of (3):

$$\log(qe - q_t) = \log q_e - \frac{K_1}{2,303}t$$
(3)

- *Pseudo-second order* expressed by (4), linearized in the form of (5) [23]:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

Where:

- q_e and q_t are the amounts of MB adsorbed (mg/g) respectively at equilibrium and at instant t.
- K₁ and K₂ are the rate constants of adsorption pseudofirst-order process (min⁻¹) and pseudo-second order (g.mg⁻¹.min⁻¹).

The results obtained in this study considering the different kinetics orders are shown in Figures 9 and 10. The exploitation of theses curves allowed us to determine the kinetic parameters which are summarized in Table 1.



Figure 9. The Pseudo-First-Order kinetic of MB adsorption on SAR at 22 °C.



Figure 10. The Pseudo-Second-Order kinetic of MB adsorption on SAR at 22 $^{\circ}\mathrm{C}.$

Table 1. Kinetic models parameters for SAR.

pseudo-first order					
$q_e cal(mg/g))$	$K_1 (min^{-1})$	\mathbb{R}^2			
0.219	0.0401	0.7428			
Pseudo-second order					
q _e cal	K_2	\mathbb{R}^2			
(mg/g)	$(g .mg^{-1}.min^{-1})$				
1.575	0.822	0,9993			

The results obtained (Table 1) show that the model the most correlated with experimental results is the pseudo second order, with a correlation coefficient close to 1 (0.9993) and provides an amount adsorbed at equilibrium $(q_e calc = 1.575 \text{ mg/g})$ very close to the experimental value $(q_e exp = 1.580 \text{ mg/g})$. Based on these results it can be concluded that the reaction of adsorption of BM on the SAR follows the kinetic pseudo second order.

D. Adsorption isotherms

Among the most used models in the literature to describe the experimental data of the adsorption isotherms we quote Freundlich model and Langmuir model [24]:

> The Freundlich model assumes the involvement of sorption processes in a heterogeneous surface and active sites of different energies [25]. This model is modelled by (6) that can linearized to the form of (7):

$$q_e = K_F \cdot C_e^{1/n} \tag{6}$$

 $\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$

Where *n* and K_f ((mg/g), (L/mg)^{1/n}) are Freundlich constants related to the favorability of adsorption process and the adsorption capacity of the adsorbate, respectively.

To verify the correlation between the theoretical model and experimental results we plot ln (qe) versus ln (Ce).

The Langmuir model is based on hypotheses imposing a phenomenon monolayer on a surface energetically homogeneous [26]. This model is modelled by (8) that can be linearized in various forms. Among the most used is this form in (9) [27]:

$$\frac{Q}{Q_m} = \frac{K_L C_e}{1 + K_L C_e}$$
(8)

$$\frac{c_e}{Q_e} = \frac{1}{\kappa_L Q_m} + \frac{c_e}{Q_m}$$
(9)

Where $Q_m\ (mg/g)$ and $K_L\ (L/mg)$ are related to the maximum adsorption capacity and Langmuir constant, respectively.

By tracing $\frac{1}{Q} = f(\frac{1}{C_e})$ we obtained a line with slope $\frac{1}{K_L Q_m}$ and y-intercept $\frac{1}{Q_m}$, which allows determining the two equilibrium parameters Q_m and K_L . The essential feature of the Langmuir model can be expressed by R_L , which is a dimensionless constant named "separation factor" and defined by (10):

$$\mathbf{R}_{\mathrm{L}} = \frac{1}{1 + K_{\mathrm{L}} C_0} \tag{10}$$

Where R_L is the Langmuir dimensionless constant separation factor.

By studying this equilibrium four cases are possible [28]:

- For $0 < R_L < 1$, the adsorption is favorable.

- For $R_L > 1$: the adsorption is unfavorable.

- For $R_L = 1$: Linear adsorption.

- For $R_L = 0$: the adsorption is irreversible.

The different results obtained for the two models are summarized in Table 2.

Table 2. The values of parameters for each isotherm model used in the Studies.

Langmuir						
K _L (L/mg)	$q_m (mg/g)$	R _L	R ²			
0.54	3.94	between 0,0241 and 0,00613	0,9988			
Freundlich						
K _F (mg/g)	1/n		R ²			
1,54	0,218	3	0,9829			

The analysis of these results shows that the adsorption of MB on the SAR is best described by the Langmuir model ($R^2 = 0.9988$) than the Freundlich model ($R^2 = 0.9829$). Thus, the MB molecules could be adsorbed in monolayer without adsorbate-adsorbate interactions [29].

E. Thermodynamic Study

The thermodynamic parameter such as (ΔH° , ΔG° and ΔS°) provides information on the heat of reaction, spontaneity, and the affinity between adsorbate-adsorbent. These parameters are calculated from (11), (12) and (13) according to previous studies [30, 31]:

$$K_{d} = \frac{C_{ads}}{Ce}$$
(11)

$$\Delta G^{\circ} = -RTLn(K_d) \tag{12}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S \tag{13}$$

Where:

- C_{ads} is dye concentration on the solid support.

- C_e the residual concentration of this dye in solution.

- K_d is the distribution coefficient of adsorption.

The results obtained are summarized in Table 3. The analysis of these results shows that in the fields of temperatures and concentrations studied the adsorption of MB on the SAR is a phenomenon endothermic ($\Delta H^{\circ}>0$), this finding was consistent with the results obtained where the uptake of MB increased with increasing the solution temperature. The negative value of ΔG° indicates spontaneous nature of adsorption process, while positive ΔS° revealed the strong affinity between the sorbent and the MB [12, 32].

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T(k)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J.mol ⁻¹ .k ⁻¹)	R²
293	-9.74			
298	-11.09			
303	-11,47	60.88	240,56	0,9502
313	-14.70			

Table 3. Thermodynamic parameters calculated for the adsorption of MB on SAR.

IV. CONCLUSION

In this work, we used a natural origin material, the Argan nut shells (SAR), to evaluate its effectiveness in reducing the pollution engendered by the industrial dye such as methylene blue which could be cost effective on one hand and on the other hand, to valorise the SAR material strongly produced in our region (Agadir, southern Morocco).

This study has allowed us as a first step to characterize the mash used as adsorbent by determining its absolute and apparent densities as well as its thermal stability. In a second time this study allowed us to determine the effect of various parameters influencing the adsorption such as the particle size of adsorbent, contact time, temperature, pH of the solution, the initial concentration of MB, the mass adsorbent, and at the end the kinetic and the thermodynamics study showed that the process follows the pseudo-second order kinetic model, and that it is spontaneous and endothermic.

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