



# Evaluation of Adsorption Capacity of Methylene Blue in Aqueous Medium by Two Adsorbents: The Raw Hull of *Lophira Lanceolata* and Its Activated Carbon

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**Abstract:** The purpose of this study is to evaluate the adsorption capacity of two adsorbents from the lignocellulosic residues of *Lophira Lanceolata*. The raw hull of *Lophira Lanceolata* and its activated carbon produced by chemical activation with orthophosphoric acid ( $H_3PO_4$ ) at 50% ( $V_{acid}/V_{water}$ ) of the said hull. The ratio of impregnation to orthophosphoric acid used is 4.5. Activation and carbonization were carried out at 400°C. The physicochemical properties of the prepared activated carbon were determined and methylene blue adsorption tests were performed. On the basis of the results obtained, the iodine test revealed that the activated carbon produced had a microporosity of 646.81 mg/g, a density of 0.3156, a moisture content of less than 15% and ash content equal to 2%. Regarding the adsorption, results showed that methylene blue (100 ppm) adsorbed more easily on the activated carbon produced than on the crude residues with respective contact time of 10 minutes and 40 minutes. The removal rate was of the order of 100% for the activated carbon and of 83.56% for the raw hulls. Furthermore, an influence of the mass of the support, of the initial concentration and of the pH on the kinetics and on the adsorption capacity was observed. Kinetics obeyed to the pseudo-second order model; the diffusion was intra-particular and the Freundlich and Langmuir models satisfactorily described the adsorption of methylene blue respectively on the crude residues and on the produced activated carbon.

**Keywords:** Adsorption, Activated Carbon, *Lophira Lanceolata*, Methylene Blue, Microporosity

## 1. Introduction

Each year, large quantities of by-products from agricultural exploitation are released into the environment. In addition, there are industrial releases loaded with synthetic dyes and chemicals that lead to the pollution and degradation of water resources [1]. These influence the pH of water and can lead to serious public health hazard (cholera, diarrhea, reprotoxic effects, blue disease in children and cancer risks. Consequently, research has been carried out to establish methods for water and wastewater treatment (2 to 3 references). Most of research work carried out mainly focuses on the combination of physical treatments

(coagulation, flocculation etc.) and chemical (ozonation, chlorination tec.) [2]. But these methods are often secondary sources of pollution and prove to be too costly. Moreover, the most recent physical methods such as anodic oxidation and electrooxidation require technical means such as high-voltages, which are too expensive. In view of these difficulties, it is necessary to find alternative methods which simultaneously solve the problems linked to the degradation of the environment and water quality. In this context, several studies have highlighted the adsorption capacities of industrial dyes as well as heavy metals in water by residues

of coconut, wood, sunflower stems, sugar cane which have been shown to be effective when converted into activated carbons (2 to 4 references). Activated carbon is a polyvalent material commonly used as an adsorbent due to its internal and external surface, as well as its extremely high microporous volumes [3]. It is also endowed with high adsorption capacities, fast adsorption kinetics, and relative ease of regeneration (references). Because of these properties, it arouses great covetousness in many fields (water treatment, manufacture of gas masks, etc). Precursors of activated carbon generally come from two sources: fossil (lignite, peat and coal) and vegetal. In order to reduce the cost of production of this material, research is now oriented towards agricultural lignocellulosic raw materials or from their processing industries. accordingly, previous research work in our laboratory has indicated that the fruits of *Lophira Lanceolata* release 33% of hulls that are rich in lignins (30%) and can be used for the depollution of wastewater by adsorption of micropollutants [4]. On this basis, the general objective of this work aims at making a comparative study of the capacity of eliminating methylene blue by the hull of *Lophira Lanceolata* and its activated carbon. Specifically, it was:

- to evaluate the adsorption kinetics of methylene blue on the crude residues and on the activated carbon of the shells of *Lophira Lanceolata*.
- to elucidate the process of adsorption by adsorption isotherms of the dye by the residues and by the activated carbon.

## 2. Materials and Methods

### 2.1. Vegetal Material and Conditioning

*Lophira Lanceolata* fruits were harvested in Boribansifa, in the commune of Toucountouna, in the North-West of Benin. They were sorted, separated in order to remove the allogenic material and then shelled; the hull obtained were grinded and then sieved (mesh size of 1.18 mm). The grinded hull of *Lophira Lanceolata* obtained were washed with tap water, rinsed with distilled water and then dried in an oven at 110°C for 24 hours. After drying process, the latter were stored at room temperature in the laboratory for adsorption tests and for activated carbon preparation.

### 2.2. Swelling Test

The swelling test was performed by taking 11 mL of powdered material which was completed with water to obtain a total volume of 20 mL. 24 hours later the volume of the powdered material was raised.

### 2.3. Methodology for the Production and Characterization of Activated Carbon

The preparation of the activated carbon can be carried out from any precursor containing carbon. The precursor used in this study was the hull of *Lophira Lanceolata*. Activated carbon, after production, was used to remove methylene blue

in an aqueous medium.

#### 2.3.1. Production of Activated Carbon

Activated carbon was prepared from the hull of *Lophira Lanceolata* in four stages: pretreatment, chemical activation, pyrolysis and washing (Balogoun and al., 2015).

#### 2.3.2. Treatment with Orthophosphoric Acid ( $H_3PO_4$ )

The grinded hull of *Lophira Lanceolata* were impregnated with orthophosphoric acid diluted to 50% ( $H_3PO_4/H_2O$ : V/V) with an impregnation ratio (RI) of 4.5.

$$RI = \frac{m_{H_3PO_4}}{m_{precursor}} \quad (1)$$

The mass of the precursor was that of the pretreated biomass. At the end of this impregnation operation, the mixtures (hull +  $H_3PO_4$  solution) was dried at 110°C. In a Leader Engineering Widnes Cheshire UK for at least 24h [5, 8].

#### 2.3.3 Carbonisation of Activated Carbon Precursors

The carbonization was carried out in a furnace (400°C) programmed at a temperature gradient of 10°C/min. After a stay of 2 h at the final temperature (400°C), the activated carbon obtained was removed from the furnace and then cooled in a desiccator, this method is similar to that of Balogoun and al. (2015) [5].

#### 2.3.4. Washing of Activated Carbon

The prepared activated carbon was washed with an amount of hydrochloric acid solution and then distilled water. In each case, the experiment was held in a water bath (warm water for no more than 24 hours) before the solution or washing water was renewed continuously for at least two months. This operation made it possible to reorganize the sheets of the activated carbon and to remove residues of the activating agent which clogs the pores. After washing, the activated carbon was dried at a temperature of 110°C. Until a dry activated carbon was obtained [5].

### 2.4. Some Physicochemical Properties of Activated Carbon

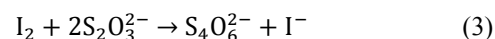
#### 2.4.1. Determination of the Mass Yield

The yield  $r$  of the prepared activated carbon was estimated from the following equation [5]:

$$r = \frac{\text{mass of activated carbon (g)}}{\text{mass of impregnated crushed hull (g)}} * 100 \quad (2)$$

#### 2.4.2. Determination of Iodine Value

The iodine value of the produced activated carbon was determined using the American Society for Testing and Materials D4607-94 (ASTM D4607-94, 2006). The amount of iodine adsorbed (mg) per gram of activated carbon with a residual iodine concentration of 0.02 N, represented the iodine value [6]. The titration with sodium thiosulphate of a volume  $V_f = 25$  mL of the filtrate made it possible to demonstrate the capacity of adsorption of iodine by the activated carbon. The equation of the reaction is as follows:



From the stoichiometric relationship of the reaction equation between iodine and sodium thiosulphate, the amount of iodine adsorbed by the activated carbon is deduced. Let  $X'$  be the quantity of iodine adsorbed:

$X'$  = amount of initial iodine - amount of iodine remaining after 30s of contact. The amount of residual iodine is determined by the relationship:

$$X' = V_1 N_1 - \frac{(V_1 + V_{HCl}) N_2 V_{th}}{V_f} \quad (4)$$

With:

$N_1$  = 0.1 N normality of the iodine solution;  $N_2$  = 0.1N normality of the sodium thiosulfate solution;  $V_1$  = 50 mL the volume of iodine treated;  $V_{HCl}$  = 5 mL; Volume of hydrochloric acid;  $V_f$  = 25 mL the volume of iodine titrated.

The iodine value of the activated carbon is then calculated using the equation of the curve

$$\frac{x}{m} = f(Cr) \quad (5)$$

With:  $m$  the mass (g) of activated carbon;  $Cr$  concentration of residual iodine

$X$  is the quantity in mg of adsorbed iodine given by the relationship:

$$X \text{ (mg)} = 126.90.X' \quad (6)$$

#### 2.4.3. Determination of Density

To determine the density we weighed mass  $a$   $m$  of a volume of 50 mL of activated carbon; The equivalent mass  $m_0$  of the same volume of 50 mL of the distilled water was also weighed; then, the calculation of the density was done by the relation:

$$d = \frac{m}{m_0} \quad (7)$$

#### 2.4.4. Determination of Ash Rate

The ash rate (% C) was calculated as follows [7]:

$$\%C = \frac{m_3 - m_2}{m_1} * 100 \quad (8)$$

$m_1$ : initial mass of the AC used in (g).

$m_2$ : mass of the crucible before carbonization in (g).

$m_3$ : mass of the crucible filled after charring in (g).

#### 2.4.5. Determination of Moisture Content

The moisture content (% H) can be calculated by the following formula [7]:

$$\%H = \frac{m_3 - m_2}{m_1} \quad (9)$$

$m_1$ : initial mass of the AC used in (g).

$m_2$ : mass of the crucible filled after drying (g).

$m_3$ : mass of the crucible filled before drying (g).

### 2.5. Methodology of Adsorption Tests

#### 2.5.1. Kinetic Study of Adsorption: Contact Time

Adsorption kinetics were studied to determine the amount

of dye adsorbed at different time intervals (equilibrium time is one of the most economically important factors for polluted water treatment systems) [8]. A volume of 200 mL of dye-laden solution (methylene blue) of the concentration of 100 ppm was stirred at 200 rpm. 2 mL samples were collected at intervals of time (5 min for crude residues and 1 min for activated carbon) are filtered on Wattman filter papers N°1 and analyzed by UV/visible absorption spectrophotometry. The residual concentration of the dye was determined by the Beer-Lambert law. The quantity  $Q_t$  of the dye adsorbed at time  $t$  is given by the equation:

$$Q_t = (C_0 - C_e) \frac{m}{V} \quad (10)$$

$Q_t$ : amount of adsorbed dye per gram of adsorbent (mg.g<sup>-1</sup>);

$C_0$ : initial dye concentration (mg.L<sup>-1</sup>);

$C_e$ : residual concentration at equilibrium (mg.L<sup>-1</sup>);

$V$ : volume of the solution (L);

$m$ : mass of the adsorbent (g).

#### 2.5.2. Influence of Some Parameters on Adsorption

##### i. Effect of Mass of Adsorbent

This study consisted in following the effects of the mass of the adsorbents (the crude hull and the activated carbon) on the adsorption. To this end, we have introduced into several erlenmeyers variable masses of adsorbent, the same volume of pollutant solution at the same concentration and at free pH. The whole was stirred under the same conditions for a period greater than or equal to that of the adsorption equilibrium and the residual concentration of the pollutant was determined. The mass effect was studied at room temperature, at a rate of 200 rpm<sup>-1</sup> and 100 ppm of methylene blue. The chosen adsorbent masses vary between 0.1 and 2 g.

##### ii. Influence of pH

This consists in following the effects of pH on the various parameters of the adsorption. For this purpose, the same mass of adsorbent and the same volume (2000 mL) of pollutant solution of the same concentration, but whose pH values are variable (pH varying from 2 to 12), have been introduced into several Erlenmeyer plants. The whole was stirred under the same conditions for a period longer than the equilibrium time previously determined. After the equilibrium time, the solutions containing the adsorbent were filtered and the residual pollutant and control concentrations were determined. The initial pH values of the dye solutions were adjusted using the NaOH (0.1 N) and HCl (0.1 N) solutions for the different pH values studied (2; 4; 6; 8; 10; 12).

##### iii. Influence of Initial Solution Concentration

This study consisted in following the effects of the concentration on the various parameters of the adsorption. For this purpose, the same mass of adsorbent and the same volume (50 mL) of pollutant solution of variable concentrations and at free pH of the solution were introduced into several erlenmeyers. The whole was stirred under the same conditions for a period longer than the equilibrium time, we have filtered and the residual concentration of the

pollutant was determined. The effect of the initial dye concentration was studied by stirring at a rate of 200 rpm<sup>-1</sup>, 200 mL of dye solutions, the concentrations used varying from 5 to 150 ppm.

### 2.5.3. Modeling of Adsorption Kinetics

Several kinetic models have been used to interpret the experimental data to provide essential information for the use of these adsorbents in the adsorption domain. We adopted five (05) kinetic models that are: pseudo-first order (PPO), pseudo-second order (PSO) models, external diffusion, intraparticle scattering and Elovich model. [9, 10]

#### i. Pseudo First Order Model (PPO)

The expression is given by Lagergren:

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \quad (11)$$

$k_1$ : first-order reaction rate constant of adsorption of the dye on the adsorbents (min<sup>-1</sup>).

$Q_e$ : amount of the adsorbed dye at equilibrium in (mg.g<sup>-1</sup>).

$Q_t$ : amount of the dye adsorbed at time  $t$  in (mg.g<sup>-1</sup>).

$t$ : contact time in (min).

After integration with the initial conditions  $q_t = 0$  to  $t = 0$ , the equation becomes:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (12)$$

The linearization of the preceding equation gives:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (13)$$

One plots  $\ln(Q_e - Q_t) = f(t)$ , we obtain a straight line which gives  $k_1$  and  $Q_e$ .

This model makes it possible to describe the phenomena occurring during the first minutes of the adsorption process [11].

#### ii. Pseudo-second Order Model (PSO)

The pseudo-second order model (PSO) is given by the following expression:

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2 \quad (14)$$

where:

$K_2$ : Second order reaction rate of adsorption of the dye on the adsorbents in (g.mg<sup>-1</sup>.min<sup>-1</sup>).

$Q_e^2$ : amount adsorbed at equilibrium in (mg.g<sup>-1</sup>),

$Q_t$ : amount adsorbed at time  $t$  in (mg.g<sup>-1</sup>).

$t$ : contact time (min).

After integration, we obtain:

$$Q_t = \frac{K_2 * Q_t}{1 + K_2 * Q_e * t} \quad (15)$$

The linearization of the preceding equation gives:

$h = k_2 Q_e^2$  is the initial adsorption rate in (mg<sup>-1</sup>.min).

We trace  $t/Q_t = f(t)$ , we get a straight line which gives  $k_2$  and  $Q_e$ .

Unlike the first-order model, the pseudo-second order model is applicable to a wider time interval (generally the

entire adsorption process)

#### iii. External Delivery Model

The external diffusion, through the film surrounding the solid particles of the adsorbent. A model of this phenomenon is represented by the equation:

$$\ln[(C_0 - C_e)/(C - C_e)] = K_3 \times t \quad (16)$$

Where  $K_3$  is the external diffusion constant,  $C_0$ ,  $C_e$  and  $C$ , the initial concentrations in ppm, at equilibrium then at time  $t$  (min), respectively.

#### iv. Intraparticle Scattering Model

The molecules are probably transported in the particles of the adsorbents by an intraparticle diffusion process because of the porosity of the adsorbents. Generally three steps are involved during the adsorption process by the porous adsorbent: i) transfer of the molecule adsorbed from the breast of the solution to the external surface of the adsorbent (external diffusion), ii) penetration of the adsorbed molecule to Adsorption of the molecule on the inner surface of pores [12]. To understand the mechanism of adsorption of the two dyes we use the equation of Weber et al. (1963) [13]:

$$Q_t = k_i * t^{1/2} + c \quad (17)$$

$Q_t$ : this is the quantity adsorbed at time  $t$  (mg.g<sup>-1</sup>),

$c$ : the intersection of the line with the  $Y$  axis or the intercept.

#### v. Model of Elovich

It can be expressed as:

$$\frac{dQ_t}{dt} = \alpha \exp(-\beta Q_t) \quad (18)$$

Where:  $\alpha$ : the initial rate of adsorption (mg.g<sup>-1</sup>.Min) and  $\beta$ : the desorption constant (g.mg<sup>-1</sup>).

To simplify the Elovich equation it has been assumed that  $\alpha \beta t \gg 1$  and that

$Q_t = 0$  to  $t = 0$ , so we get:

$$Q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \quad (19)$$

We trace  $Q_t = f(\ln t)$

The values of  $\alpha$  and  $\beta$  can be determined [14, 15].

#### 2.5.4. Modeling Adsorption Isotherms

We have described the adsorption process using two adsorption isotherms: the linear Langmuir and Freundlich transforms. The isotherm is the curve which represents the relationship between the quantity of methylene blue adsorbed per unit mass of adsorbent  $Q_e$  and the concentration of solute in solution  $C_e$ . We obtained such curves from the results of laboratory tests carried out at 25°C. To this end, known quantities of adsorbent are introduced into volumes of water to be treated and, after a given contact time, the residual concentration of solute in solution is measured. The amount of adsorbed solute is calculated using the equation:

$$Q_e = \frac{(C_0 - C_e) * V}{m} \quad (20)$$

### i. Langmuir Isotherm

This model corresponds to the L-type isotherms (Langmuir, 1918 quoted by Voice & Weber (1983) [18]:

$$Q_e = \frac{Q_{max} * k_L * C_e}{1 + k_L * C_e} \quad (21)$$

$Q_e$ : Content in the adsorbent at equilibrium (M of soil pollutant.M<sup>-1</sup>),

$C_e$ : equilibrium solution concentration (M.L<sup>-3</sup>),

$Q_{max}$ : Maximum content in the adsorbent (M.M<sup>-1</sup> of sol),

$K_L$ : Langmuir Constant (L<sup>3</sup>.M<sup>-1</sup> of pollutant).

### ii. Freundlich's Isotherm

This model establishes a relation between the quantity of impurity (methylene blue) adsorbed and the quantity remaining in the liquid phase, this equation is based on an exponential distribution of the energies of the adsorption sites, it is expressed by the following relation [17]:

$$Q_e = K C_e^{1/n} \quad (22)$$

Equation which is linearized in the following form:

$$\log Q_e = \log K + 1/n \log C_e. \quad (23)$$

$Q_e$ : Amount of adsorbed impurity per unit mass of adsorbent (mg.g<sup>-1</sup>)

$C_e$ : residual concentration of the adsorbate at equilibrium (mg.L<sup>-1</sup>)

$K, n$ : Freundlich constants of the pollutant

It is a line of slope  $1/n$  and of ordered at the origin  $\log K$ . High values of  $K$  and  $n$  indicate a strong adsorption in the range of the studied concentrations. Conversely, low values indicate low adsorption at low solute concentrations. This equation differs from the previous one by the fact that it does not provide for an upper limit to adsorption and that it admits the possibility of interaction between adsorbed particles. The parameters  $K$  and  $1/n$  specific of the pollutant-material torques are of importance in the comparison of the performances of the materials.

The  $k_F, k_L, R_L, Q_{max}$  and  $n$  parameters characterizing the Langmuir and Freundlich models for the adsorption of methylene blue on activated carbon and crude residues were determined from the slopes and ordinates at the origin Linear transformations of Freundlich and Langmuir.

## 3. Results and Discussion

### 3.1. Swelling Test

After 24 hours in the water, no significant change in the volume of the powdered product was observed. We therefore continued the test over a period of 48 hours and then 72 hours. We found that the initial volume of powder had not undergone any variation. This insensitivity to water would be due to its chemical composition more precisely in lignin. Indeed, lignin is known to provide vascular plants with

rigidity and waterproofness, as well as high resistance to decomposition. It can therefore be deduced that this material cannot be used as a filter bed.

### 3.2. Production Yield and Physical-chemical Characteristics of Activated Carbon

#### 3.2.1. Production Efficiency

The production yield of activated carbon is an important parameter in the feasibility study of the production of activated carbon from a given precursor and under specified conditions. It is one of the performance indicators of a method of preparing this material for industrial production. The production yield of the activated carbon was 75.17%.

#### 3.2.2. Physico-chemical Characteristics of Activated Carbons

##### i. Ash Content

The ash content obtained is equal to 2% and is therefore very low. According to some authors, the lower the ash rate, the better the active carbon (at least 2 references).

##### ii. Density

This is the density of activated carbon for a densified bed, for gas storage applications, activated carbon is often densified to obtain more storage capacity in the same volume. The density of the produced activated carbon is 0.3156.

##### iii. Moisture Content

We assessed the amount of water physically linked to activated carbon by determining the moisture content. The value obtained in this study for our material was less than 15% by weight.

##### iv. Indice of Iodine

It has been reported by numerous groups of researchers [18] that the iodine value is an indication of the adsorption capacity in micropores. There is therefore a proven correlation between the iodine value and the specific surface area. The isotherm of adsorption of iodine by activated carbon:

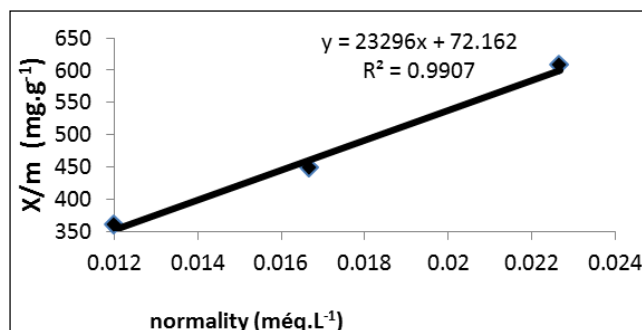


Figure 1. Isotherm of Adsorption of Iodine by Activated Carbon.

It is deduced that indice of iodine value of activated carbon was 646.81 mg.g<sup>-1</sup>.

### 3.3. Spectrophotometric Properties of Methylene Blue

#### 3.3.1. Determination of the Maximum Absorption Wavelength

The analysis of the dye studied was carried out by spectrophotometry in the visible range (380 -750 nm). When determining the absorbance of methylene blue as a function of wavelength, a peak was observed at a wavelength between 660 nm and 670 nm (Figure 2). We have therefore chosen as the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) 665 nm to perform the spectrophotometric analyzes of the solutions of methylene blue.

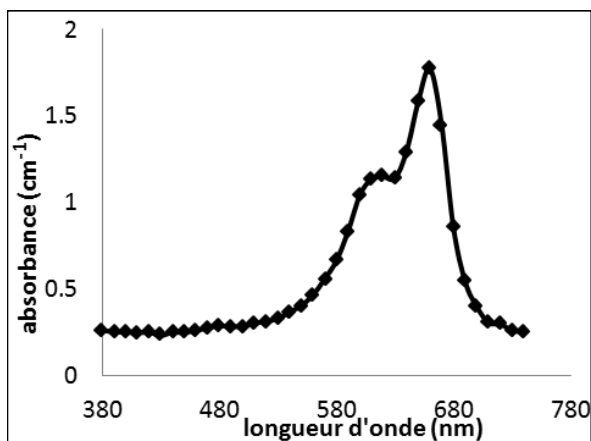


Figure 2. Absorption Curve of Methylene Blue as a Function of Wavelength.

#### 3.3.2. Verification of the Beer Lambert Law by the Plot of the Calibration Curve

The calibration curve is established from the diluted solutions of methylene blue, Figure 3 showed that the line has a regression coefficient ( $R^2 = 0.9998$ ) which is very close to unity. Thus, there is a possibility of determining the residual concentrations by the Beer-Lambert law. The absorbance is proportional to the concentration. However, it should be noted that concentrations of the methylene blue solution were taken between 0 ppm and 600 ppm. Concentrations greater than 45 ppm were diluted to remain within the detection limit of the apparatus. The actual values were determined by multiplying the obtained absorbances by the dilution factors.

$$\text{Absorbance} = 0.016 * C \quad (24)$$

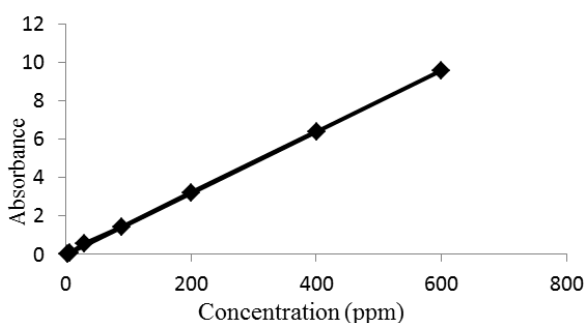


Figure 3. Calibration Curve of the Absorption of Methylene Blue in Aqueous Solution at 25°C.

### 3.4. Adsorption Tests

#### 3.4.1. Evaluation of the Adsorption Capacity of Methylene Blue by the Residues of the Hulls of *Lophira Lanceolata*

In our study, we investigated the adsorption of methylene blue on the hull grinded of *Lophira Lanceolata*, which is a natural adsorbent available in both northern and central Benin. This adsorbent was used in the raw state without prior treatment; The preparation of the sample and the adsorption procedure have already been described previously. In order to optimize the adsorptive power of this material, various parameters were studied: the mass of the adsorbent, the contact time, the initial dye concentration and the pH.

##### i. Study of the Parameters Influencing Adsorption

Effect of mass of adsorbent (figure 4) showed that the amount of adsorbed methylene blue increases as the mass of the adsorbent increases. According to Hameed (2010) [19], this was explained by the increase in the number of adsorption sites. The maximum elimination rate recorded is 83.56% for a mass greater than or equal to 1 g.

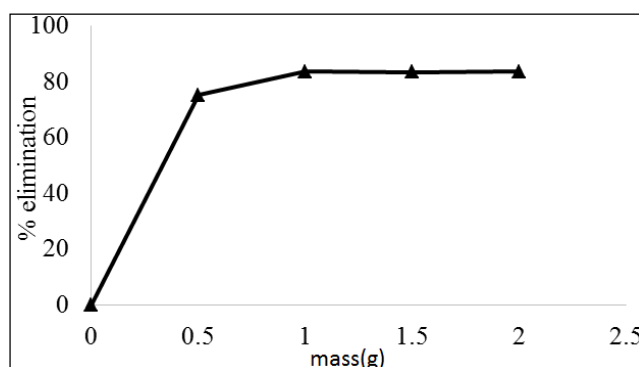


Figure 4. Evolution of the Rate of Removal of Methylene Blue as a Function of the Mass of the Grinded huLLs.

Operating conditions: Temperature = 25°C, stirring speed = 200 rpm and mass = 1 g.

At the concentration of 100 mg.L<sup>-1</sup> of methylene blue, the maximum elimination rate recorded was 83.56% for a mass equal to 1 gram. Above 1g of grinded material, the removal rate becomes constant. The increase in the reduction rate of methylene blue with the increase of the adsorbent mass is due to the availability of a large active surface area. On the other hand, the constancy in the dye removal rate for a mass greater than 1 gram is due to the bulkiness of the solution by the ground media which prevent the molecules of methylene blue from accessing the active sites. As reported by Mane and *al.* (2007) and Hui and *al.* (2011) [20, 21].

##### ii. Effect of Contact Time

The adsorption kinetics studied revealed that the equilibrium was reached after 40 min and the maximum removal rate was 83.56%. It was observed that the adsorption is rapid during the first 30 minutes of the reaction (Figure 5). For high contact times, the molecule needs time to



reach new adsorption sites, Sahnoun (2011) [22] drew the same conclusion. The remainder of the unadsorbed amount is explained by the saturation of the surface of the adsorbent.

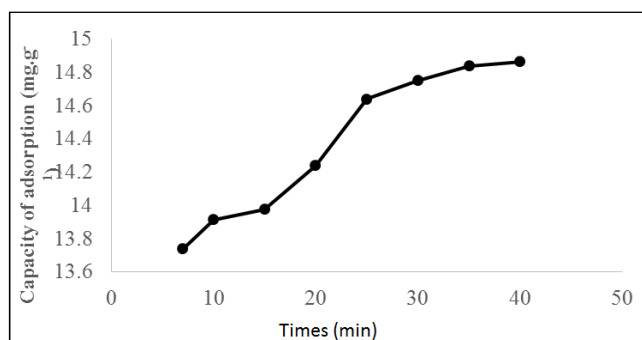


Figure 5. Adsorption Kinetics of the BM on the Grinded Hulls.

Operating conditions: Temperature = 25°C, stirring speed = 200 rpm, and mass = 1 g.

### iii. Effect of pH

According to Figure 6, the adsorption capacity increases slightly as the pH of the solution increases. According to Nonviho (2015) [4], the hulls of *Lophira Lanceolata* contain Cellulose and hemicellulose (hydroxide groups or oxides), which charge negatively in aqueous media. Thus the increase in pH favors the development of the negative electrical charge of the surface. This negative charge exhibits an electrostatic attraction with respect to the cationic dye (methylene blue).

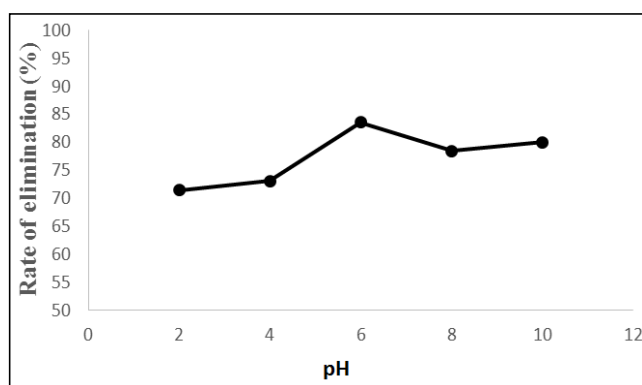


Figure 6. Effect of pH on the Adsorption of bm on Grinded Hulls.

Operating conditions: Temperature = 25°C, stirring speed = 200 rpm and Volume of the methylene blue solution = 200 mL.

### iv. Effect of Initial Concentration of Methylene Blue

The adsorption of methylene blue onto the hulls of *Lophira Lanceolata* was carried out at different initial dye concentrations (25 ppm, 50 ppm, 75 ppm, 100 ppm 150 ppm). The analysis of these results (Figures 8 and 9) revealed that, whatever the initial concentration of methylene blue, the adsorption capacity reached its maximum after 10 minutes.

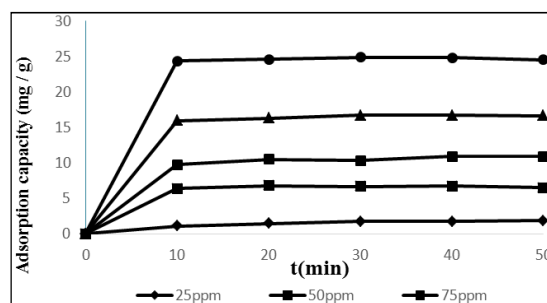
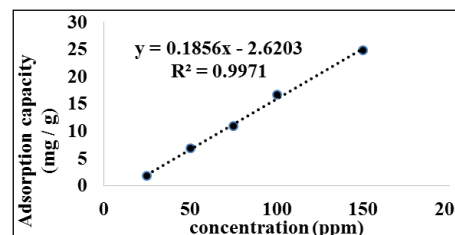


Figure 7. Influence of the Initial Concentration on the Adsorption Capacity of BM on Grinded Hulls.



Operating conditions: Temperature = 25°C, stirring speed = 200 rpm and mass = 1 g.

Figure 8. Influence of the Concentration on the Adsorption Capacity of the BM on Grinded Hulls.

The graph plots showing the influence of the concentration on the absorption capacity (Figures 7 and 8) revealed that the amount of methylene blue adsorbed increased with the initial concentration. Indeed, the increase in the concentration of methylene blue accelerates the diffusion of the latter due to the increase in attraction forces of the concentration gradient [23]. Note the formation of bearings, which indicates a rapid saturation of the support following better diffusion of molecules of methylene blue to the adsorption sites which are still free.

### 3.4.2. Modeling of Adsorption Kinetics

#### i. Pseudo First Order (PPO) and Pseudo-second Order (PSO)

Two kinetic models have been applied to the experimental data to understand the mechanism of this discoloration (Figures 9 and 10).

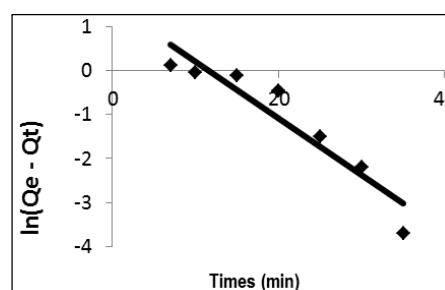


Figure 9. Pseudo-first Order Kinetics.

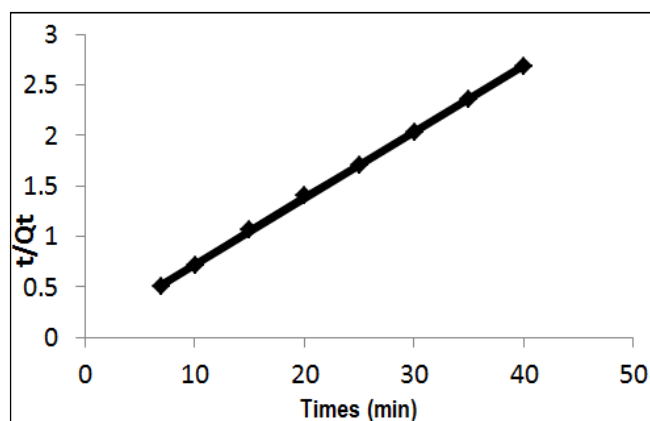


Figure 10. Second-order Pseudo Kinetics.

Table 1. Adsorption Kinetic Parameters.

Equation	R <sup>2</sup>	K <sub>1</sub> (min <sup>-1</sup> )	Q <sub>e</sub> (mg.g <sup>-1</sup> )
<b>Pseudo-first order kinetics</b>			
y = -0.1287x + 1.4838	0.8904	0.1287	30.4649
<b>Second-order pseudo kinetics</b>			
y = 0.0656x + 0.0694	0.9997	16.1269	15.2439

From Table 1, it can be seen that the set of kinetic parameters determined from the two previous straight make it possible to deduce the kinetic model of discoloration. The correlation coefficient ( $R^2$ ) for the second-order model was closer to 1 (i.e 0.9997) than that of the first-order model (0.8904). The second-order model thus gives a better description of the adsorption kinetics compared to the first-order kinetics. Indeed, the equilibrium adsorption capacity calculated using this model was also very close to that found experimentally. The adsorption of methylene blue was thus controlled by the chemical processes that involve the valence forces or the electron exchanges with the biosorbent. The same observation has been previously made by Nonviho [4] with the same material and at the same concentration.

## ii. Type of Broadcast

Table 2. Dissemination Parameters.

Equation	external diffusion		
	R <sup>2</sup>	K <sub>3</sub>	
y = 0.1777x	0.7328	0.1777	
Equation	Intra-particle diffusion		
	R <sup>2</sup>	K <sub>4</sub>	constant
y = 0.34x+12,802	0.9556	0.34	12.802
Equation	Elovich model		
	R <sup>2</sup>	α	β
y = 0.7158x + 12.238	0.9370	4552.76	1.40

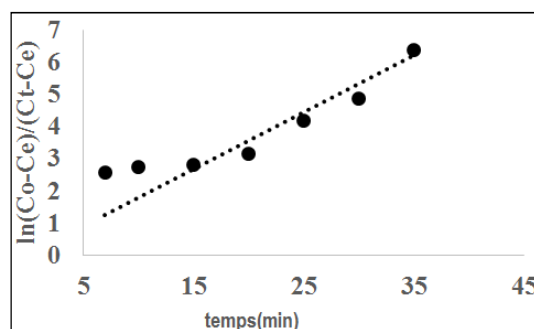


Figure 11. Kinetics of External Diffusion.

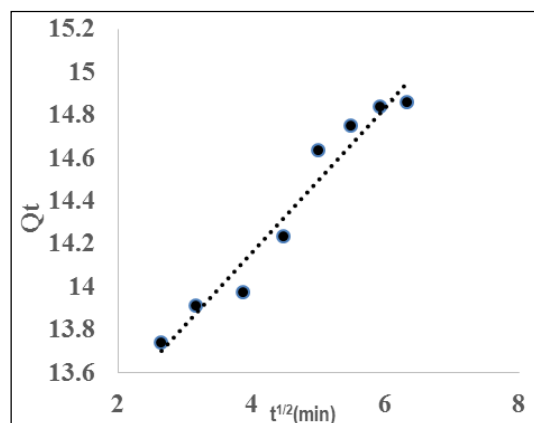


Figure 12. Kinetics Intraparticle Diffusion.

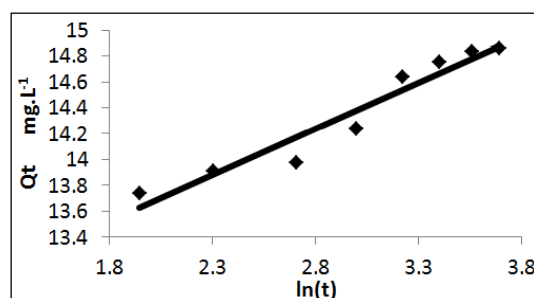


Figure 13. Elovich Model.

The intraparticle diffusion model has a better linearity compared to other models. Indeed, the linear correlation coefficient of the intraparticle model was closer to 1 than those of the other models. The adsorption of methylene blue on the raw hulls (CB) of *Lophira Lanceolata* follows the intraparticle model. It can therefore be deduced that there was formation of chemical bonds between the adsorption sites of the hulls of *Lophira Lanceolata* and the bis-(dimethylamino) 3,7 -phenazathionium ion of methylene blue [4].

## iii. Study of Adsorption Isotherms

To describe the adsorption of the dye, the two most frequently used models were used: the models of Langmuir and of Freundlich.



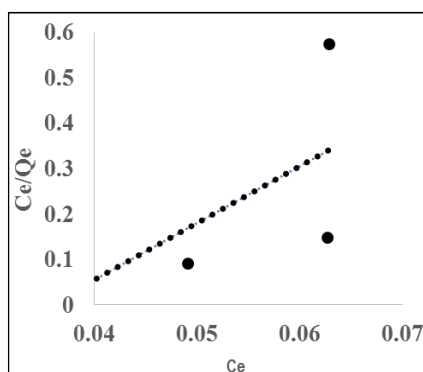


Figure 14. Langmuir Model.

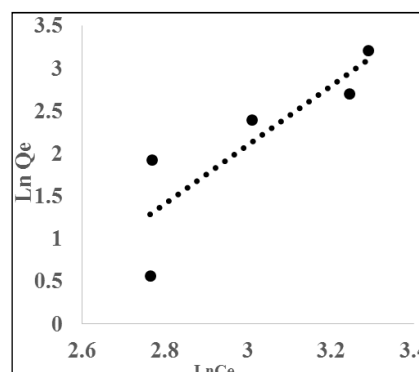


Figure 15. Freundlich Model.

Table 3. Characteristics of the Different Models.

	Equation	R <sup>2</sup>	Constants
Langmuir	$y = 12.557x - 0.4471$	0.5015	$Q_{\max} = 14.40 \text{ mg/g}$
Freundlich	$y = 3.4466x - 8.2417$	0.7414	$n = 0.29$

The Freundlich model better describes our experimental results because the value of its correlation coefficient ( $R^2$ ) was closer to unity. The adsorption sites therefore increased with adsorption, which implies multilayer adsorption. The maximum adsorption capacity was about  $14.4 \text{ mg.g}^{-1}$  and then Since  $n < 1$  therefore the adsorption is chemical (Table 3).

### 3.4.3. Evaluation of the Adsorption Capacity of Methylene Blue on Activated Carbon

#### i. Study of Some Parameters Influencing Adsorption

##### 1. Mass effect of activated carbon on adsorption capacity

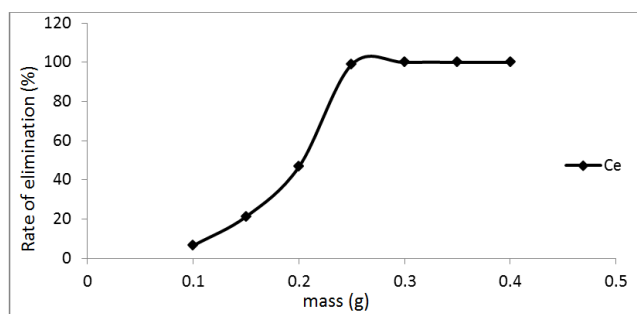


Figure 16. Evolution of the MB Elimination Rate According to the Mass of the AC.

Operating conditions: Temperature =  $25^\circ\text{C}$ , stirring speed = 200 rpm and mass = 0.25 g.

Figure 16 showed that the percentage of elimination increases with the mass of activated carbon. The maximum removal rate recorded is of the order of 100% for a mass  $\geq 0.25 \text{ g}$ . The increase in the mass of activated carbon increases the specific surface area and hence the number of adsorption sites, hence the increase in the amount of adsorbed dye [19]. Otherwise, the constancy in the rate of removal of the dye by activated carbon for a mass greater than 0.25 gram is due to the high elimination rate which is close to 100%, so the variation is no longer noticed.

#### 2. Adsorption kinetics

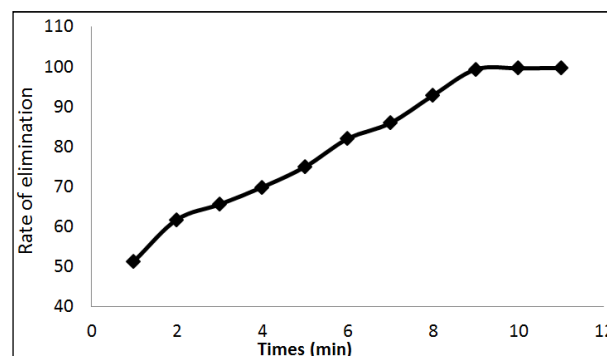


Figure 17. Kinetics of adsorption of the BM on the AC.

Operating conditions: Temperature =  $25^\circ\text{C}$ , stirring speed = 200 rpm,  $C = 100 \text{ ppm}$  and mass = 0.25 g.

The equilibrium was reached after 10 min with a removal rate which is of the order of 100% (Figure 17). We noted the rapidity of adsorption during the first 5 minutes (60% of elimination), this can be interpreted by the fact that, at the beginning of adsorption, the number of active sites available on the surface of the adsorbent was greater than that of the remaining sites After 5 minutes [24].

#### ii. Modeling of Adsorption Kinetics

##### 1. Pseudo first order (PPO) and pseudo-second order (PSO)

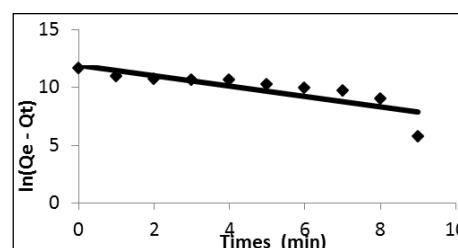


Figure 18. Kinetics Pseudo First-order.

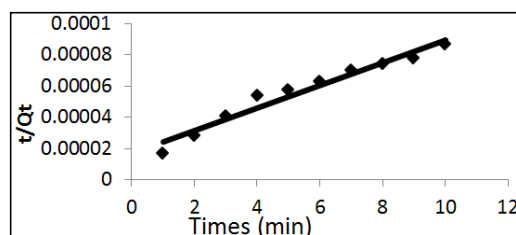


Figure 19. Kinetics Pseudo Second-order.

Table 4. Characteristics of the Different Models.

Lagergren first order pseudo reaction			
Equation	R <sup>2</sup>	K <sub>1</sub> (min <sup>-1</sup> )	Q <sub>e</sub> (mg/g)
y = -0.4499x + 11.943	0.6997	0.4499	15373.211

Second-order pseudo-reaction of Lagergren			
Equation	R <sup>2</sup>	K <sub>2</sub> (g/mg.min)	Q <sub>e</sub> (mg/g)
y = 7E-06x + 2E-05	0.9584	0.0223	7.5916

The pseudo-second order model is the one that best describes the adsorption process because the value of its correlation coefficient ( $R^2$ ) is closer to 1 (Table 4).

## 2. Type of broadcasting

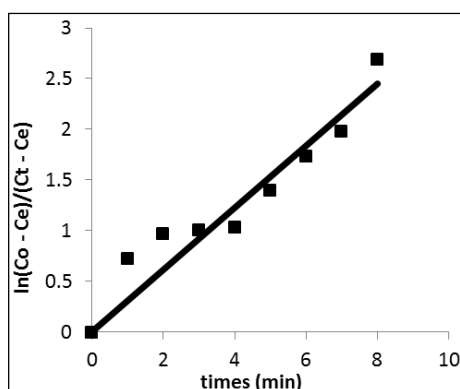


Figure 20. External diffusion model

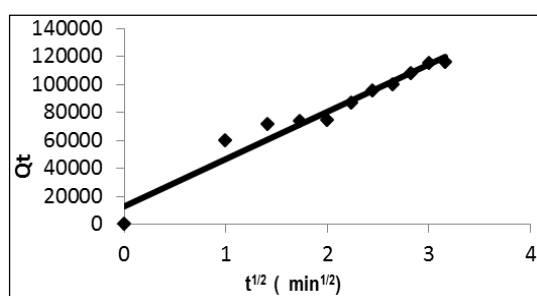


Figure 21. Intraparticle Diffusion Model.

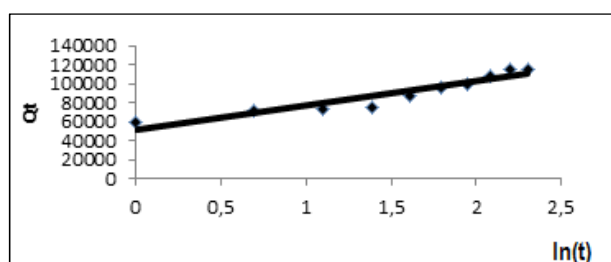


Figure 22. Elovich Model.

Table 5. Characteristics of the Different Models.

Equation	external diffusion		
	R <sup>2</sup>	K <sub>3</sub>	
y = 0.3066x	0.9066	0.3066	

intraparticle diffusion			
	R <sup>2</sup>	K <sub>4</sub>	Constant
y = 33743x + 12891	0.9524	33743	12891

Model of Elovich			
	R <sup>2</sup>	α	β
y = 25427x + 51588	0.8871	193384,1362	3,9328.10 <sup>-5</sup>

The adsorption of methylene blue on activated carbon therefore followed an intraparticle model because its correlation coefficient was higher (Table 5).

## iii. Modeling of Adsorption Isotherms

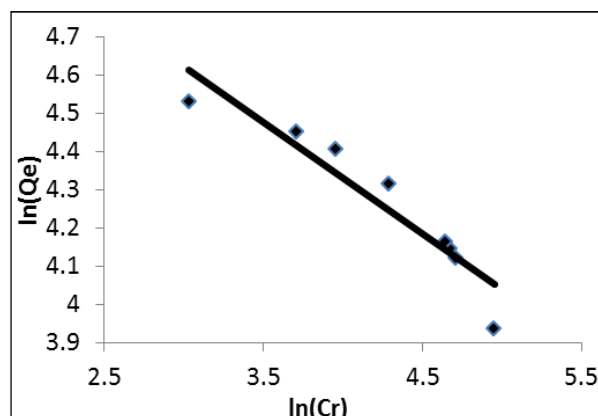


Figure 23. Linear Model of Freundlich.

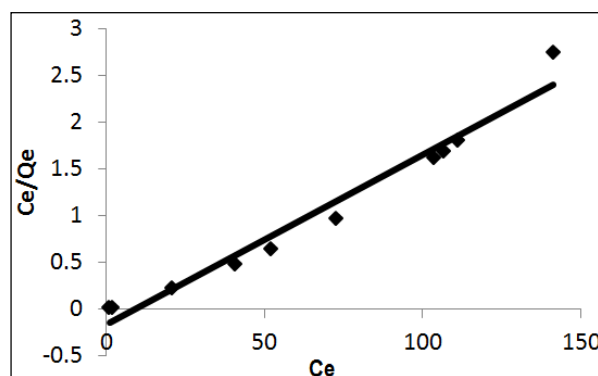


Figure 24. Linear Model of Langmuir.

Table 6. Characteristics of the Different Models.

Langmuir	R <sup>2</sup>	Q <sub>max</sub>	k <sub>L</sub> (g.L <sup>-1</sup> )	R <sub>L</sub>
	0.9657	55mg/g	- 0.11	- 0.10

Freundlich	R <sup>2</sup>	k <sub>F</sub> (mg <sup>1-(1/n)</sup> .L <sup>1/n</sup> .g <sup>-1</sup> )	n <sub>F</sub>
	0.8903	110.39	- 9.21

We found that the Langmuir linear model was the most credible model that best described our experimental results, with  $R^2 = 0.9657$  (Table 6). This shows that the surfaces of

our activated carbon are homogeneous in terms of energy and promotes monolayer adsorption. The maximum adsorption capacity was about 55 mg.g<sup>-1</sup> and then as  $n < 1$  therefore the adsorption was chemical (Table 6).

## 4. Conclusion

The aim of this work was to evaluate the adsorption capacity of two adsorbents from the lignocellulosic residues of *Lophira Lanceolata*. The material consisted of the hulls of *Lophira Lanceolata*, which were rejected in large quantities after extraction of the oil from the fruits. From this material, charcoal was prepared by carbonization at 400°C and activated via chemical activation with orthophosphoric acid diluted to 50%. The result obtained from the iodine test showed that the activated carbon possessed good microporosity. Adsorption tests made it possible to note that the activated carbon was more effective in the removal of methylene blue than the residues of raw hulls. The removal capacities of methylene blue are governed by pseudo second order adsorption speeds. Adsorption isotherms, such as the Langmuir model and the Freundlich model, simulated the adsorption of methylene blue, respectively, on activated carbon and on raw hulls. The  $n_F$  constant of the Freundlich model was less than 1, which makes it possible to say that the adsorption is chemical. Thus, the hull of *Lophira Lanceolata* can be used for the removal of methylene blue in aqueous medium and as a precursor of activated carbon. The activated carbon produced from the hulls of *Lophira Lanceolata* is primarily usable for the removal of the micropollutants (fluoride ions, nitrate ions, phenol, etc.) from the water.

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