



## Kinetic and thermodynamic study of the adsorption of methylene blue on activated carbon based on corn cobs

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### Abstract

In the present study, adsorption experiments were carried out to investigate the removal of methylene blue (MB) from aqueous solution using activated carbon from corn cobs which is a cheaper adsorbent. The characteristics of carbon were determined using X-ray diffraction (XRD), SEM, iodine number,  $\text{pH}_{\text{ZCN}}$  and the Boehm method. The results show that the prepared activated carbon is amorphous, microporous and generally acidic in surface. The adsorption performance Activated carbon was evaluated using MB as the model adsorbate. Adsorption kinetics was studied and the rate of sorption was found to conform to pseudo-second-order kinetics with 30 min as equilibrium time. Langmuir, Freundlich and Dubinin–Radushkevich models were investigated and all of them were in good agreement. The surface of the carbon is heterogeneous and the interaction MB-activated carbon is mainly chemisorption type. The pH and temperature also influence this phenomenon. Maximum monolayer adsorption capacity for MB removal was found to be 37.45 mg/g at temperature 50°C and pH 6.2. Moreover, thermodynamic parameters suggested that the adsorption of MB onto corn cobs activated carbon was a spontaneous and exothermic process. The results demonstrated that corn cobs are a suitable precursor for the preparation of efficient adsorbent for dye removal from wastewater.

## 1. Introduction

Eliminating pollutants is a major issue in the fight against environmental pollution, in particular water pollution. These pollutants are of all kinds: pesticides; heavy metals; PAHs and dyes. Dyes reduce photosynthesis and inhibit plant growth [1]. They also create aesthetic pollution due to the unpleasant view they give as a messy appearance. The high toxicity of organic dyes can cause hazards such as cancer. In addition to health problems, these dye effluents constitute sources of danger for aquatic life and also a real source of pollution for the soil. As a result, the issue of textile effluents discharged into the environment appears to be a major issue in water treatment. To fight against this pollution, several treatment methods are proposed by researchers depending on the nature and composition of the effluents to be treated.

Although there are several modes of water treatment, among which the biological method [2], photocatalysis [3], precipitation [4], membrane filtration [5], etc., adsorption on activated carbon [6,7], is a more promising means, easier to achieve and technically efficient [8]. Activated carbons have been used effectively for the removal of dyes from wastewater [7-8].

However, the cost of this technique is still high. This is why for years several agricultural wastes including banana peels [9], coconut shells [10], ricinodendron heudolotii shells [11], olive fruit shells [12] and rice husks [13] have been used for the production of activated carbon.

In this study, activated carbon based on corn cobs was evaluated as a adsorbent for removal of a dye model, methylene blue from aqueous solution.

The objective of this work is to carry out the thermodynamic and kinetic study of the adsorption of methylene blue on activated carbon based on corn cobs in order to explain the mechanism of transport that takes place at the solid-liquid interface in the adsorption process of a dye on activated carbon. Thermodynamic parameters such as enthalpy ( $\Delta H^\circ$ ), free energy ( $\Delta G^\circ$ ) and entropy ( $\Delta S^\circ$ ) were evaluated to determine the adsorption process. As for the kinetic parameters, they allowed us to know the rate constant and to explain the diffusion phenomenon of methylene blue. The applicability of the isotherm models, that is, Langmuir isotherm, Freundlich isotherm and Dubinin–Radushkevich isotherm, was analyzed to determine which isotherm gives the best correlation to experimental data. In addition, the effect of pH solution and effect of temperature were evaluated.

## 2. Methodology

### 2.1 Preparation of activated carbon

The preparation and activation of the carbon was carried out thermally and chemically using phosphoric acid at 500 ° C. For this, the corn cobs crushed into small pieces were washed in tap water to remove dust, then washed with distilled water and dried in an oven at 105 ° C for 24 h before drying. After this step, the corn cobs were impregnated at room temperature and at atmospheric pressure with magnetic stirring in a solution of H<sub>3</sub>PO<sub>4</sub>. The carbonaceous material is carbonized at 500 ° C in an OBERSAL brand oven. The carbon obtained is washed thoroughly, after cooling, with distilled water until the pH of the rinsing water is between 6 and 7. The carbon thus obtained is dried in an oven at 105 ° C for 24 h, then crushed and sieved (size  $\leq 125\mu\text{m}$ ).

### 2.2 Characterization of activated carbons

The specific surface area was determined by adsorption of acetic acid in aqueous medium [14]. The iodine number was determined by adapting the CEFIC 1989 method and the standard AWWA B 600-90 [15]. To do this, 100 mL of a 0.1N iodine solution is treated hot and in an acidic medium for 30 seconds with a quantity of activated carbon. The treated solution is filtered and 50 mL of the filtrate is titrated with 0.1N sodium thiosulfate solution with starch as an indicator of end of reaction.

The surface functions were determined and quantified using the Boehm titration method by the action of activated carbon on NaHCO<sub>3</sub>, CaCO<sub>3</sub>, NaOH and HCl [16].

The determination of the pH<sub>pzc</sub> was carried out by adding 0.15 g of CA to 50 mL of NaCl solutions (0.01 M). The pH of each mixture is adjusted between 2 and 12 by adding 0.1 M NaOH or HCl solution. Stirring is maintained for 48 hours, at a temperature of 25 ° C. The final pH of each mixture is then measured. We draw the graph  $\Delta\text{pH} = f(\text{pHi})$ . The pH<sub>pzc</sub> is the point of intersection of the curve with the axis that passes through zero.

The ash content of the coals was determined by referring to the ASTM (American Standards Technology Method), ASTM D 2866-94 [17]. A mass of carbon is placed in a crucible and then placed in an oven at 650 ° C until there is no more detectable loss of mass. This happens after 7h.

The morphology of activated charcoal was determined by scanning electron microscope (SEM) using a Tescan LYRA 3 XMH.

The crystal structures were analyzed by an X-Ray diffractometer (D8 Advance Bruker, Germany) with a germanium detector for angle  $2\theta$  between  $20\text{--}120^\circ$  with scan rate of  $0.01^\circ/\text{s}$ .

### 2.3 Spectrophotometric determination of samples

Methylene blue is a cationic dye of index CI-52015 with the formula  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$ . It is used as a model molecule in the adsorption of dyes on activated charcoal. The Hach 3900 spectrophotometer was used to determine the concentrations of the methylene blue dye solution. The maximum wavelength corresponding to the adsorption of the dye is  $\lambda_{\text{max}} = 662 \text{ nm}$ .

### 2.4 Kinetic adsorption study

The study of the kinetics of adsorption of Methylene blue was carried out at room temperature on activated carbon. The aim is to determine the time required to reach equilibrium carbon adsorption and kinetic order. For kinetic adsorption study, 0.1 g of activated carbon was mixed with 25 mL of 100 mg/L, 150 mg/L, 200 mg/L and 250 mg/L of Methylene blue solution in a 100 mL conical flask. These mixtures were shaken on magnetic agitator at 150 rpm for intervals time of 5 and 60 minutes. After each contact time solutions were filtered and the initial and final concentrations of Methylene blue were determined by spectrophotometer Hack 3900. The amount of Methylene blue adsorbed onto carbon is calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t)}{m} \times V \quad \text{Eqn. 1}$$

Where  $q_t$  is the amount of Methylene blue adsorbed by activated carbon (mg/g);  $C_0$  and  $C_t$  are respectively the initial and the final concentration of Methylene blue at time after filtration (mg/L);  $V$  is the initial solution volume (L);  $m$  is the mass of the activated carbon (g).

### 2.5 Adsorption isotherms

For equilibrium adsorption study, 0.1 g of activated carbon was mixed with 25 mL of different Methylene blue concentrations: 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L and 300 mg/L in 100 mL conical flasks. Then reaction mixtures were shaken on magnetic agitator at 150 rpm for equilibrium time (30 min) at room temperature. After equilibrium time, samples were filtered and spectrophotometer Hack 3900. The amount of Methylene blue adsorbed per unit mass of activated carbon at equilibrium,  $q_e$ , was calculated by:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad \text{Eqn. 2}$$

Where  $C_0$  and  $C_e$  are the concentrations of Methylene blue at initial and equilibrium times, respectively;  $V$  is the volume of the (L); and  $m$  is the mass of activated carbon used (g).

## 3. Results and Discussion

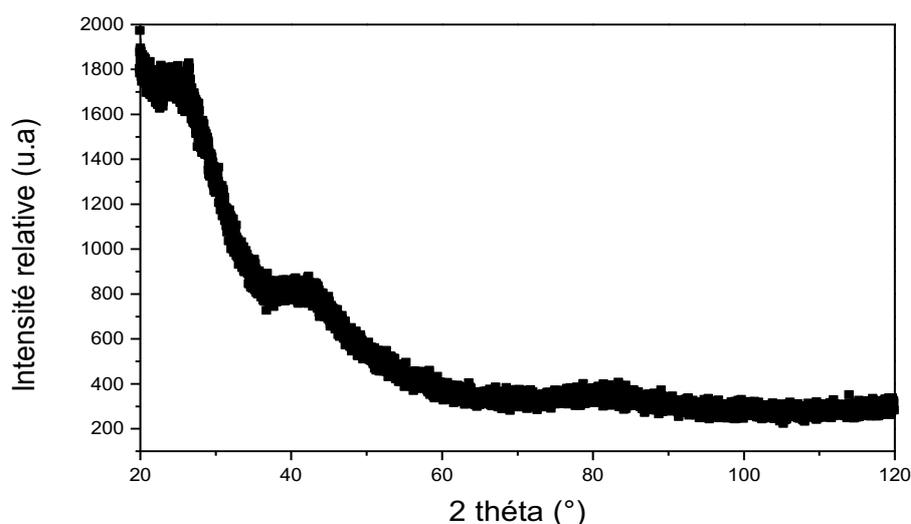
### 3.1 Characterization of activated carbon

The characteristics of activated carbon are given in [Table 1](#). The low ash content reflects a low fraction of mineral compounds and therefore good preparation of the carbon with a large carbonaceous fraction [18]. The iodine number gives an estimate of the relative area of the sample and is generally used to measure the porosity of pores larger than 1.0 nm in diameter. In this study, the iodine number is 674 mg/g. This result is in the typical range of 500 to 1200 mg/g, reflecting the microporous character of this carbon. So, this activated carbon could be excellent in the adsorption of molecules in the liquid phase [19, 20]. The pH of zero charge ( $\text{pH}_{\text{ZPC}}$ ) of carbon, the point which the net charge of adsorbent

is zero was measured using the acid/base titration method. The  $pH_{ZPC}$  was found to be 5.3. The carbon has a generally acidic surface dominated by the phenolic, lactonic and carboxylic functions. Alexandro M.M. Vargas also obtained activated carbons based on flamboyant pods with similar surfaces functions [21]. Surface areas were measured using the adsorbed acetic acid method. The value of the specific surface of the prepared carbon is  $613 \text{ m}^2/\text{g}$ . This value is greater than the specific surface area of activated carbons produced with Solid olive waste by Hamouz et al. [22]. The X-ray diffraction (XRD) pattern of the Activated is illustrated by Figure 1. Appearance of broad diffraction background and the absence of a sharp peak reveal a predominantly amorphous structure [23].

**Table 1.** Characteristics of activated carbon in this study

Parameters	Values
Ash content	6%
Surface area ( $\text{m}^2/\text{g}$ )	613
Iode number ( $\text{mg}/\text{g}$ )	674
$pH_{ZC}$	5.3
Carboxyl ( $\text{mmol}\cdot\text{g}^{-1}$ )	1.48
Lactonic ( $\text{mmol}\cdot\text{g}^{-1}$ )	1.90
phenolic ( $\text{mmol}\cdot\text{g}^{-1}$ )	2.02
Acidic ( $\text{mmol}\cdot\text{g}^{-1}$ )	5.40
Basic ( $\text{mmol}\cdot\text{g}^{-1}$ )	2.05

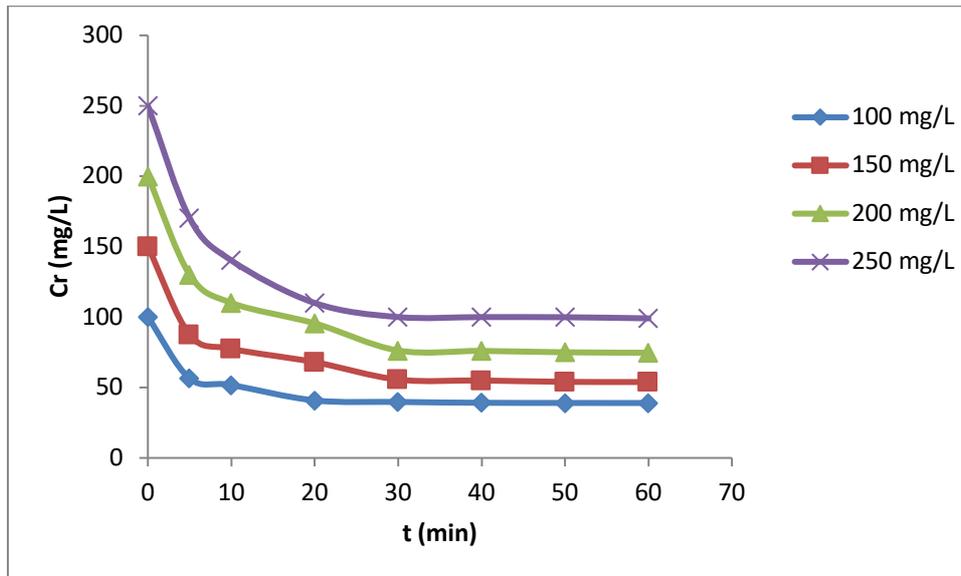


**Figure 1.** The X-ray diffraction pattern of corn cobs activated carbon (CCAC).

### 3.2 Adsorption of methylene blue

#### 3.2.1 Kinetic study of adsorption

The study of the kinetics of adsorption of MB on activated carbon was carried out with different concentrations. The curves in Figure 2 show that the concentration of MB decreases as a function of time. From the figure, it is clear that the adsorption process is rapid in the first 10 minutes. After saturation of these active sites, the MB entered the pores of the adsorbent with a slower rate to reach the equilibrium time [24]. Equilibrium is reached after 30 min. As the time becomes longer, there is desorption of methylene blue in the medium. This carbon therefore rapidly adsorbs methylene blue. 30 min was therefore taken as the equilibrium time for the rest of the study.



**Figure 2.** Kinetic of Methylene blue on CCAC.

In order to determine the mechanism of adsorption, 3 kinetic models were applied under different experimental.

### 3.2.2 Pseudo first order model

The pseudo first order model equation is known as the Lagergren equation and has the expression:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{Eqn. 3}$$

Where  $k_1$  is the first-order reaction rate constant of adsorption of MB on activated carbon in ( $\text{min}^{-1}$ ),  $q_e$  is the amount of MB adsorbed at equilibrium in ( $\text{mg/g}$ ),  $q_t$ , the quantity of MB adsorbed at time  $t$  in ( $\text{mg/g}$ ) and  $t$ , the contact time in ( $\text{min}$ ).

The linearization and integration of the previous equation gives us

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Eqn. 4}$$

The application of this model consists in plotting the curve  $\ln(q_e - q_t) = f(t)$  represented by Figure 3a. The parameters values of this model are summarized in Table 2. The linear regression coefficients suggest that this model does not apply very well to the adsorption of BM on the carbon studied. These results are confirmed by the difference between the values of  $q_{e, \text{exp}}$  and  $q_{e, \text{cal}}$ .

### 3.2.2 Pseudo-second-order model

Ho, et al established an equation to describe the kinetics of adsorption called the pseudo second order model whose linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Eqn. 5}$$

Where  $q_t$  is the amount adsorbed at time  $t$  ( $\text{mg/g}$ ),  $k_2$  is the rate constant of the pseudo 2nd order model and  $q_e$ , is the amount adsorbed at equilibrium. The application of this model consists in plotting the curve  $\frac{t}{q_t} = f(t)$  represented by Figure 3b.

The values obtained after application of this model are recorded in Table 2. It is noted that all the linear correlation coefficients are greater than 0.99. This model is therefore applicable. In addition, it can be

seen that the adsorbed quantities calculated by this model are closer to the quantities adsorbed experimentally. The applicability of this model suggests that the limiting step in the BM adsorption process on this carbon could be chemisorption [25]. The adsorption rates ( $k_2$ ) decrease when the dye concentration increases these amounts to the increase in competition on the adsorption sites on the other hand the competition decreases on the active sites of the adsorbent for low concentrations [26]. This result is consistent with the adsorption of methylene blue on kaolin and methylene blue [25], on graphene oxides and carbon nanotubes [27] and on wheat hulls [28].

### 3.2.3 Intraparticle diffusion

Generally, three steps are involved during the adsorption process on a porous adsorbent such as activated carbon: i) transfer of the adsorbed molecule from the breast from the solution to the outer surface of the adsorbent (external diffusion), ii) penetration of the molecule adsorbed inside the pores of the adsorbent (intraparticle diffusion, in the pores), iii) adsorption of the molecule on the internal pore surface [29]. To assess the influence of the stage of intraparticle diffusion, Weber and Morris [30] established an equation given by:

$$q_t = k_i t^{1/2} + c \quad \text{Eqn. 6}$$

Where  $q_t$ , is the quantity adsorbed at time  $t$  (mg/g),  $c$ , the intersection of the line with the axis of ordinates provides information on the thickness of the boundary layer, because the greater the value the intercept is large and the effect of the boundary layer is greater [30] and  $k_i$  is the intraparticle diffusion constant (mg/gmin<sup>1/2</sup>). The plot of the curve  $q_t = f(t^{1/2})$  is represented by Figure 3c. Note that there are two different stages. The first part of the curve, which is the first step, represents the diffusion of molecules in the solid. Usually, this is the longest step. The second step represents the adsorption equilibrium where the reaction takes place. The values of the parameters of this model are recorded in Table 2.

The values of the linear correlation coefficient suggest that this model is not applicable for the absorption kinetics of methylene blue. However, the value 0.95 for 10 mg/L, seems to indicate that diffusion into the pores is part of the absorption mechanism but that it is not kinetically determining [31].

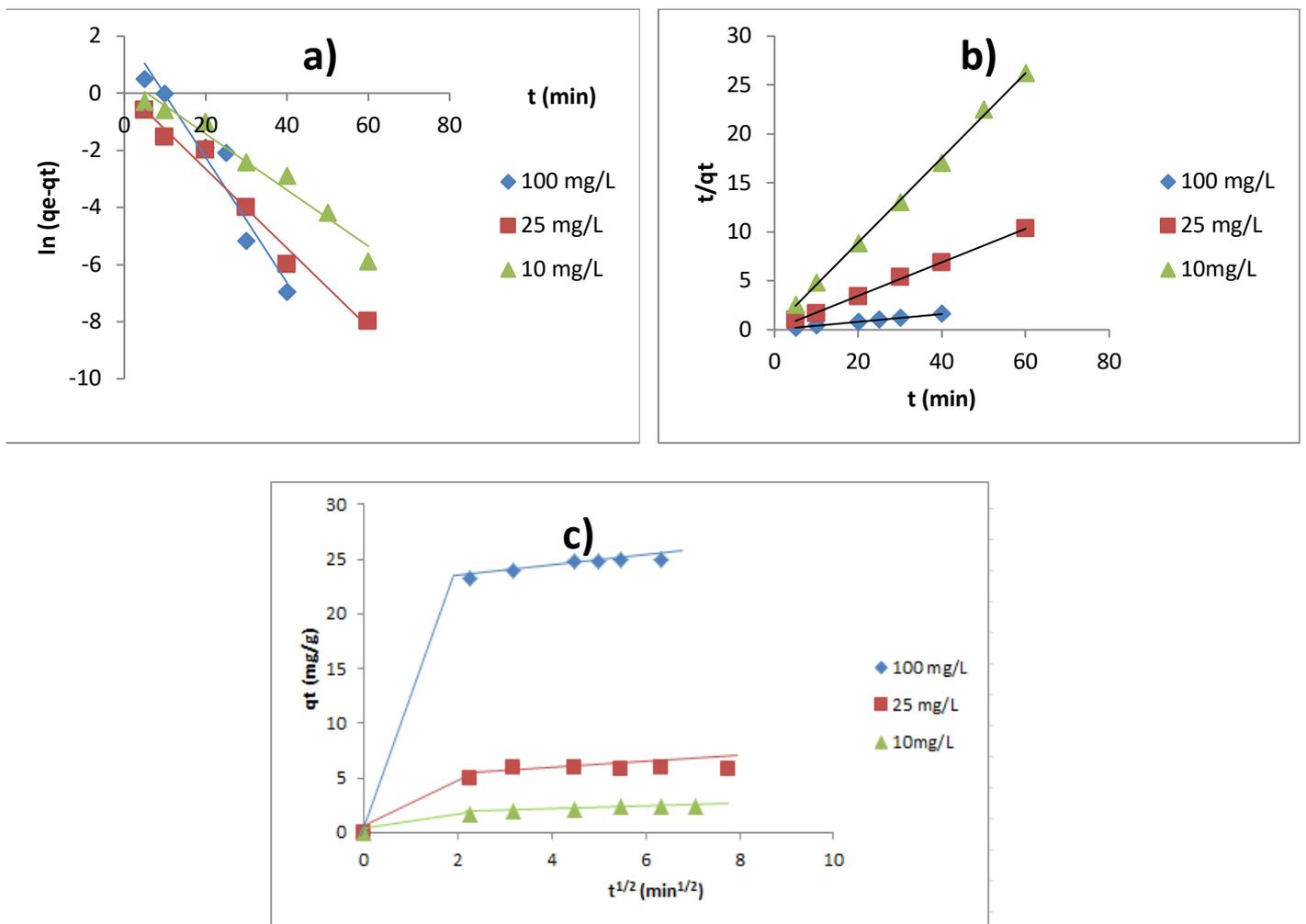
## 3.3 Study of the Influence of Some Factors on the Removal of MB

### 3.3.1 Effect of pH solution

The effect of pH solution on adsorption capacity of CCAC was investigated by varying the pH of MB solution from 2 to 12. As shown in Figure 4a, the adsorbed amount of MB depends on pH solution. The quantity of BM adsorbed increases between 3 and 6, then decreases after this value. The interaction between the adsorbent and the adsorbate is low in acidic and basic media. The best adsorption process is obtained at pH 6.2 suggesting that the pH significantly affects the adsorption process.

### 3.3.2 Effect of temperature

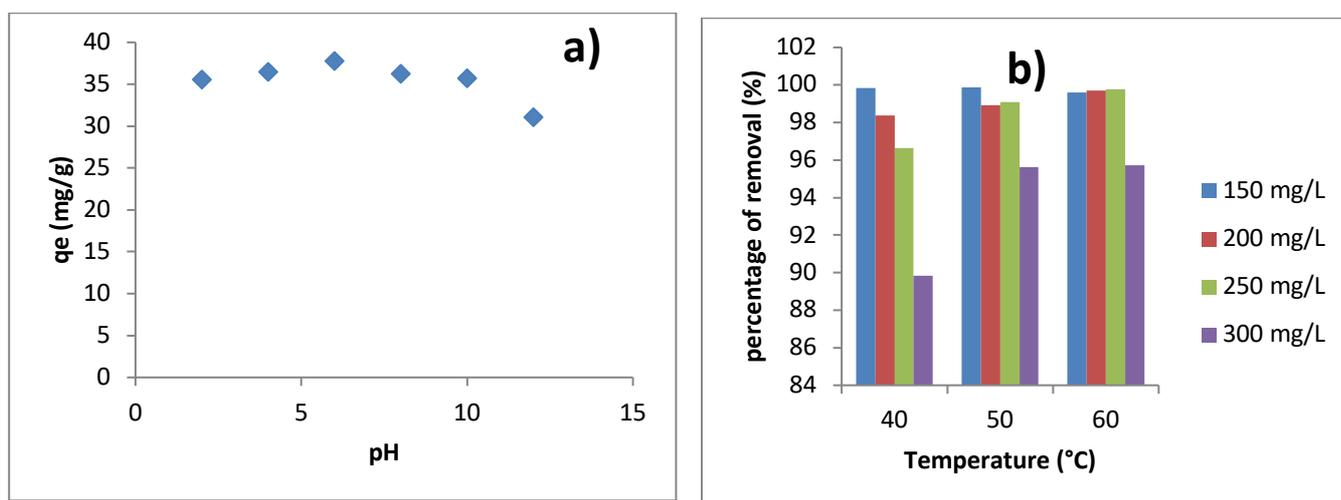
The effect of temperature on adsorption was evaluated. Figure 4b shows the rate of methylene blue removal as a function of temperature. For a concentration of 150 mg/L, elimination is almost 100% regardless of temperature. As the concentration increases, the elimination of methylene blue increases with temperature. Activated carbon does not completely adsorb the molecule at 60 ° C for a concentration of 300 mg / L.



**Figure 3.** Graphical representation of the modeling of MB adsorption kinetics by application of a) the pseudo-first order model, b) the pseudo-second-order model and c) intraparticle diffusion model.

**Table 2.** Values of parameters of the three applied kinetics models for MB.

	C (mg/L)		
	10	25	100
$q_{e,cal}$ (mg/g)	2.46	6.14	24.32
<b>Pseudo-first order</b>			
$k_1$ ( $\text{min}^{-1}$ )	0.0984	0.1386	0.2193
$q_{e,exp}$ (mg/g)	1.725	3.264	8.502
$R_1^2$	0.9645	0.9786	0.9384
<b>Pseudo-second order</b>			
$k_2$ (g/mg.min)	0.676	0.532	0.090
$q_{e,exp}$ (mg/g)	2.31	5.84	24.75
$R_2^2$	0.9984	0.9987	1.0000
<b>Intraparticle diffusion</b>			
$k_i$ (mg/gmin <sup>1/2</sup> )	0.0972	0.1178	0.4215
c	1.5449	5.2435	22.536
$R_i^2$	0.9456	0.718	0.8801



**Figure 4.** Plot of effect of pH on adsorption (a) and Percentage of adsorption of methylene blue as a function of temperature (b)

### 3.4 Study of adsorption at equilibrium

The study of the adsorption of methylene blue on activated carbon was carried out at room temperature. The amount of methylene blue adsorbed at equilibrium per mass of carbon is given in Figure 5a. The amount of methylene blue adsorbed increases with the concentration at equilibrium. This isotherm appears to be type I according to the IUPAC classification, justifying the microporous aspect of the carbon used. To study the adsorption phenomenon, 3 models were used namely the Freundlich model, the Langmuir model and Dubinin–Radushkevich isotherm [32]. The Langmuir equation is :

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad \text{Eqn. 7}$$

With  $b$  the Langmuir thermodynamic constant linked to the free energy of adsorption,  $q_e$  (mg/g) the quantity of solute adsorbed per unit mass of adsorbent at equilibrium and  $q_m$  (mg/g) the quantity of solute adsorbed per gram of solid required to cover the surface of the adsorbent with a monomolecular layer or maximum adsorption capacity.  $C_e$  (mg/L) represents the residual concentration of the solute at equilibrium.

There are several linear forms of the Langmuir model, one of the most frequently used is:

$$\frac{1}{q_e} = \frac{1}{b q_m} \frac{1}{C_e} + \frac{1}{q_m} \quad \text{Eqn. 8}$$

In Figure 5b, we have represented  $\frac{1}{q_e} = f\left(\frac{1}{C_e}\right)$ . The Langmuir linear correlation coefficient is greater than 0.99 (see Table 3). Langmuir's model can therefore be used to describe the adsorption of methylene blue on this carbon.

The empirical Freundlich equation is written:

$$q_e = K_F C_e^{1/n} \quad \text{Eqn. 9}$$

$C_e$  (mg/L) is the concentration of adsorbate at equilibrium in the residual solution,  $K_F$  [(mg/g)(L/mg) $^{1/n}$ ] et  $n$  (unitless) are Freundlich's constants depending on the adsorption capacity, the bodies present and the temperature.

The linear form of the Freundlich model is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Eqn. 10}$$

The application of the linear form of the Freundlich model made it possible to draw the curve :  $\ln q_e = f(C_e)$  (Figure 5c). The values of the parameters of this curve are grouped together in Table 3. The linear correlation coefficient is greater than 0.99 and n is close to 1. The adsorption is favorable. The Freundlich model can be used to describe the adsorption of methylene blue on this carbon, reflecting the heterogeneity of the surface of this carbon.

One of the more and more popular models is that of Dubinin – Radushkevich. The equation of this model is :

$$q_e = q_D \exp\left(-B_D \left[RT \ln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \quad \text{Eqn.11}$$

$$RT \ln\left(1 + \frac{1}{C_e}\right) = \varepsilon \quad \text{Eqn. 12}$$

The parameter  $\varepsilon$  is called the Polanyi potential

The linear form of the equation for D-R is:

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \quad \text{Eqn.13}$$

With  $q_D$  (mg/g), the constant of the isotherm of D-R, related to the degree of adsorption of the adsorbate per unit area of the adsorbent,  $B_D$  ( $\text{mol}^2/\text{KJ}^2$ ), the constant related to the free energy adsorption,  $R$  (J/mol K) is the gas constant and  $T$  (K) is the absolute temperature.

Figure 5d is the graphical representation by application of the D-R model. The energy  $E$  obtained is 2.357  $\text{KJ} \cdot \text{mol}^{-1}$ . The adsorption process is physical adsorption [33].

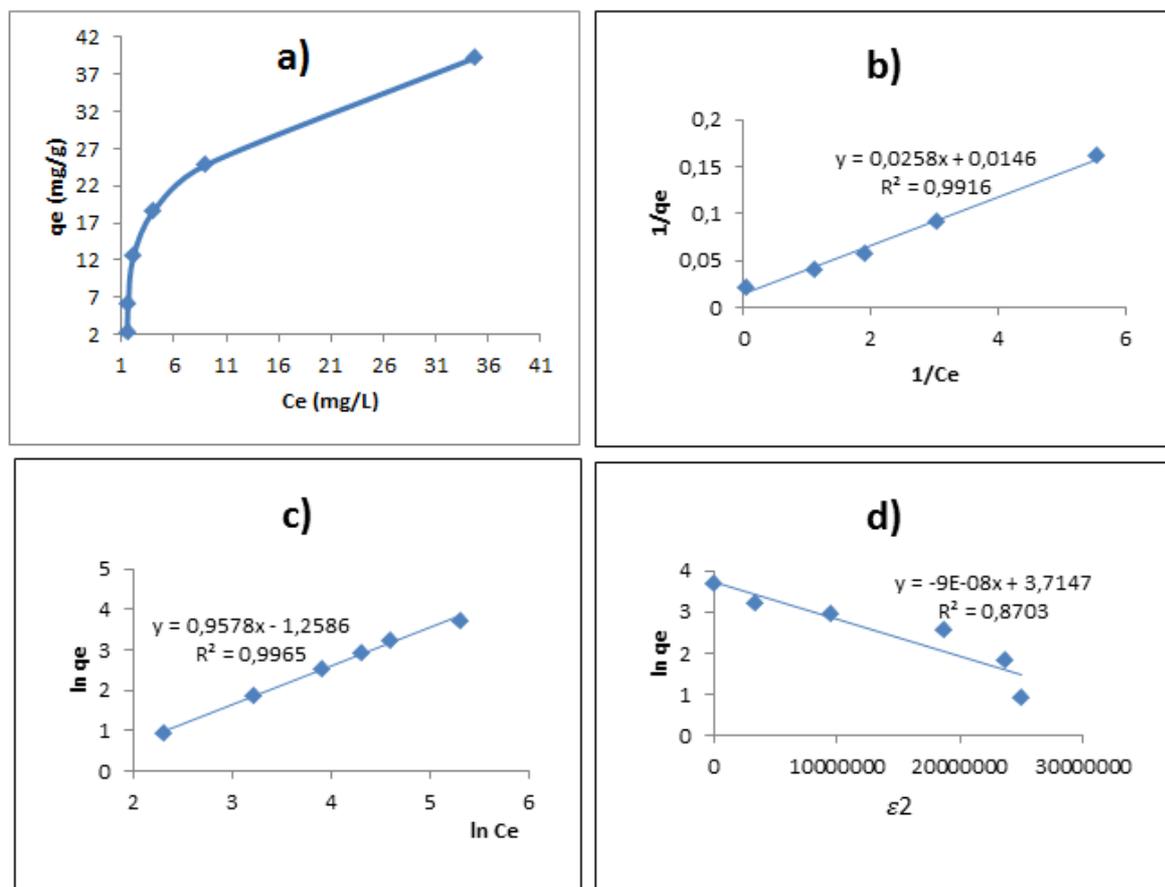


Figure 5. MB adsorption isotherm on activated carbon (a), plots of MB adsorption onto AC with Langmuir model (b), Freundlich model (c) and Dubinin–Radushkevich model (d).

**Table 3.** Equilibrium adsorption isotherm parameters for MB sorption onto CCAC.

Model	R <sup>2</sup>	qm (mg/g)	b	lnk	1/n	B <sub>D</sub> (mol/kJ) <sup>2</sup>
Langmuir	0.9916	68.49	0.5659			
Freundlich	0.9965			-1.2586	0.9578	
Dubinin– Radushkevich	0.8703	41.05				9.10 <sup>-8</sup>

### 3.5 Determination of thermodynamic parameters

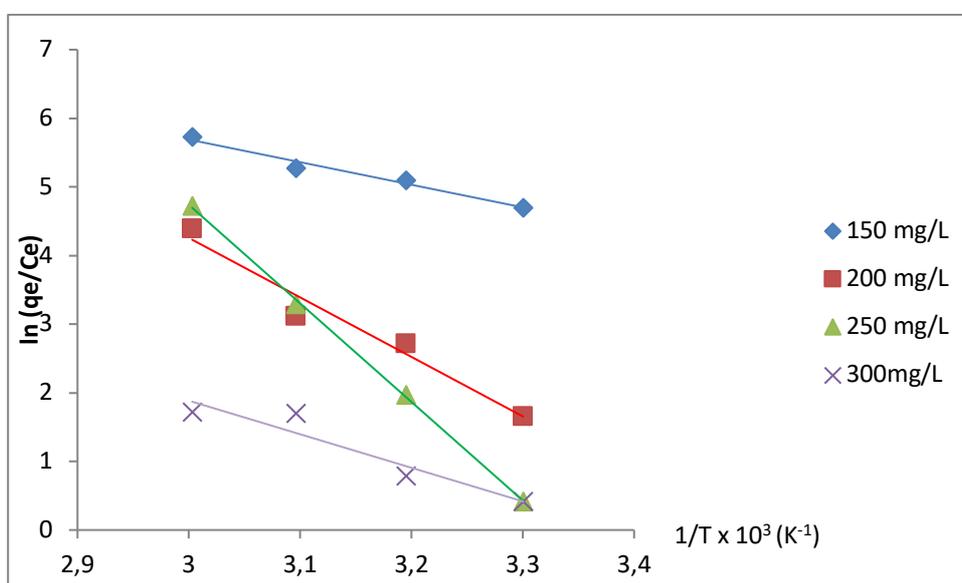
The main criterion for knowing the nature of the adsorption phenomenon is the determination of the thermodynamic parameters. For the determination of the free enthalpy ( $\Delta G^\circ$ ), the enthalpy ( $\Delta H^\circ$ ) and the entropy ( $\Delta S^\circ$ ) of adsorption of BM on activated carbon, the following equations were used [34]:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{T} \quad \text{Eqn. 14}$$

$$\Delta G^\circ = -RT \ln\left(\frac{q_e}{C_e}\right) \quad \text{Eqn. 15}$$

Where  $q_e$  (mg/g) is the amount of BM adsorbed at equilibrium,  $C_e$  (mg/L) is the concentration of BM at equilibrium,  $T$  is the temperature and  $R$  (8.314 J.mol<sup>-1</sup>K<sup>-1</sup>) is the ideal gas constant.

The curve  $\ln\left(\frac{q_e}{C_e}\right)$  as a function of  $1/T$  is represented in Figure 6. The use of the data of these lines made it possible to determine the thermodynamic parameters and the entropy ( $\Delta S^\circ$ ) of adsorption grouped together in Table 4.



**Figure 6.** Effect of temperature on adsorption of BM on activated carbon.

These values show that the maximum amount of methylene blue adsorption ( $q_m$ ) increases with temperature. The free enthalpy ( $\Delta G^\circ$ ) is negative, which reflects the spontaneity of the absorption phenomenon. There is therefore a good affinity between activated carbon and BM [35]. For  $\Delta G^\circ$  greater than  $-20$  kJ.mol<sup>-1</sup>, we have physisorption, while a value below  $-40$  kJ.mol<sup>-1</sup> means that we have

chemisorption. Also, a free enthalpy value between -40 and -20 kJ.mol<sup>-1</sup> suggests that physisorption and chemisorption are both responsible for the adsorption phenomenon [36]. At low concentrations, there is cohabitation of the two adsorption phenomena, while when the BM concentration increases, the adsorption tends to be exclusively of the chemisorption type. The enthalpy ( $\Delta H^\circ$ ) is positive. The adsorption process is therefore endothermic. The values of  $\Delta H^\circ$  are all greater than 60 kJ.mol<sup>-1</sup> showing that the forces involved in this adsorption process could be chemical in nature [37]. The positive value of entropy ( $\Delta S^\circ$ ) could be related to an increase in the disorder at the adsorbent / adsorbate interface [38].

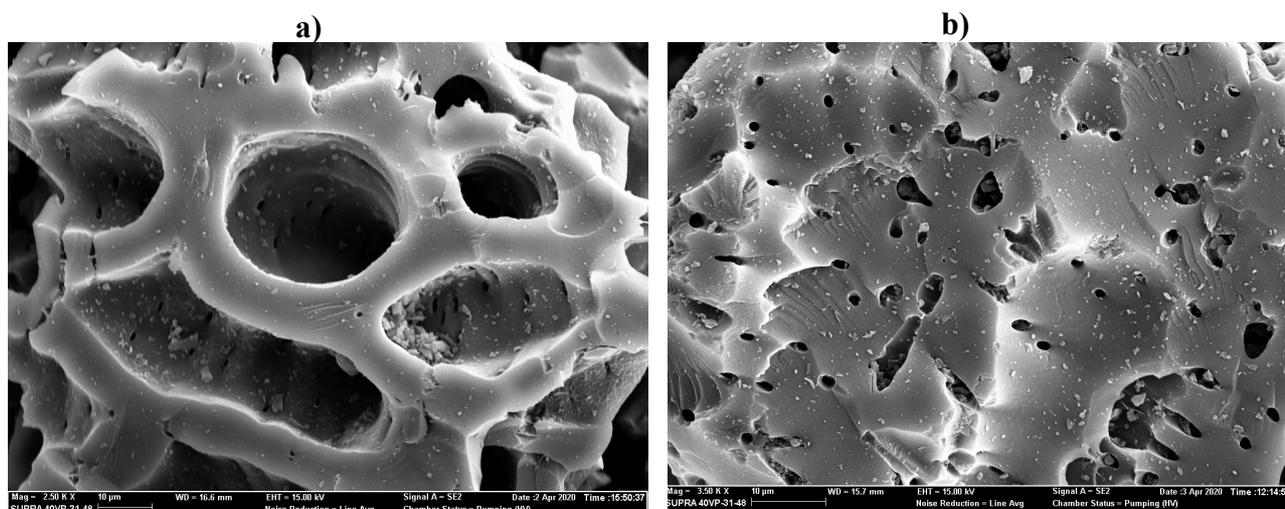
**Table 4.** Values of the thermodynamic parameters of the adsorption of MB on activated carbon.

Concentration	Temperature (K)	(KJ.mol <sup>-1</sup> ) $\Delta G^\circ$	$\Delta H^\circ$ (KJ.mol <sup>-1</sup> )	$\Delta S^\circ$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
150 mg/L	303	-27.27	63.08	298.18
	313	-30.25		
	323	-33.23		
	333	-36.21		
	303	-9.59		
200 mg/L	313	-15.39	166.01	579.55
	323	-21.18		
	333	-26.98		
	303	-3.46		
	313	-12.62		
250 mg/L	323	-21.78	274.05	915.88
	333	-30.94		
	303	-2.65		
	313	-5.81		
	323	-8.97		
300 mg/L	323	-8.97	93.61	316.92
	333	-12.13		

### 3.6 SEM analysis

The SEM images of activated carbon from corn cobs before and after adsorption of methylene blue are shown in Figure 7. The SEM image of activated carbon (Figure 7a) shows open and irregular pores on the surface of the carbon. These pores are the expression of the activation of carbon and its microporous appearance. After adsorption of methylene blue (Figure 7b), BM molecules entered the pores. In

addition, there are some hollows on the surface of the carbon. The BMs after filling the pores are bound to the surface of the carbon giving an almost smooth surface. There was therefore a strong interaction between BM and activated carbon. Adsorption was mainly dominated by chemical interactions [39].



**Figure 7.** SEM image of activated carbon (a) and after adsorption of MB (b).

## Conclusion

The present study shows that Activated carbon from corn cobs has been prepared by chemical activation can be used as an adsorbent for the removal of methylene blue from aqueous solutions. The characterization revealed that the carbon obtained is amorphous and microporous. This carbon was used to remove methylene blue from water. The kinetics studies indicated that the adsorption of MB dye on this adsorbent follows pseudo-second order model better than pseudo-first order model and intraparticle diffusion. The interlayer diffusion is not the rate-determining step in the MB adsorption mechanism. pH and temperature affect significantly the adsorption process. The best adsorption process is obtained at pH 6.2. The elimination of methylene blue increases with temperature. For an initial concentration of 150 mg / L of MB, 99.80% of the adsorbate is removed from 40 ° C. For the study of equilibrium isotherms, the models of Langmuir, Freundlich and Dubinin – Radushkevich were used. All of these models described the adsorption phenomenon well. The surface of the carbon is heterogeneous with non-uniform adsorption. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as  $\Delta G^\circ$ , of  $\Delta S^\circ$  and  $\Delta H^\circ$  adsorption. The results confirmed those of the adsorption models. At concentrations of less than 300 mg/L there is the simultaneous presence of the phenomena of physisorption and chemisorption, while beyond that, the phenomenon of chemisorption is exclusively observed.

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