Elimination of a cationic dye in aqueous solution by adsorption on activated carbon: Optimization of analytical parameters, modeling and thermodynamic study

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Abstract
Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. The aim of this study was to evaluate the adsorption of Methylene Blue (MB) dye onto activated carbon from aqueous solutions was realized in a batch system. However, some examined factors such as contact time, pH solution, initial concentration of MB, adsorbent dosage and temperature were found to have significant impacts on the adsorption capacity of AC. The AC was characterized by BET surface area measurement, Point of Zero Charge (pH\text{pzc}), FTIR spectroscopy and X-ray diffraction analysis. Batch studies were conducted in order to determine the optimal parameters required to reach the adsorption equilibrium. The maximum adsorption capacity of the AC for MB at 298 K was determined to be 170.357 mg/g. The adsorption kinetic data were analyzed employing several kinetic models: pseudo-first order, pseudo-Second order, Elovich equation, and intraparticles diffusion model. It was established that the adsorption process obeyed the pseudo-second-order kinetic model with a determination coefficient (R\text{2}) equal to 0.999. The evaluation of thermodynamics parameters such as the Gibbs free energy $\Delta G^\circ (-7.856 \text{ to } -6.142 \text{kJ/mol})$, positive enthalpy $\Delta H^\circ (13.384 \text{kJ/mol})$ and the change of entropy (63.46 J/mol K) indicated a spontaneous and endothermic nature of the reaction with a chemisorption process. Comparative tests by the heterogeneous photocatalysis of MB in the presence of a semiconductor will be the subject of the rest of this study.

Keywords
Kinetic, isotherm, adsorption, thermodynamic, activated carbon, Methylene Blue, modeling

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Introduction
The dyes production plants are increasing by the day with the technological advancement. Colored waste waters are the result of extensive dyes production, they come mainly from the textile industries and cause hazards to the aquatic environment due to presence of acids, bases, toxic organic, inorganic, dissolved solids and color. In recent years, the quality of water in the world has deteriorated considerably because of uncontrolled industrial discharges, the intensive use of nitrogenous organic compounds, dyes in
several areas and the disorderly exploitation of water resources. Among the nitrogenous organic compounds, the amino acids may be responsible for coloring the water, odors, bad taste and, moreover, they can contribute to the formation of many disinfection by-products during the chlorination of water potable. The effluents from the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of pollution. Many dyes and their break down products may be toxic for living organisms, particularly methylene blue (MB). Therefore, the discoloration of dyes is an important aspect of the wastewater treatment before their discharge in the aquatic environment. It is difficult to remove the dyes from such effluents, because they are not readily degradable and are not removed generally from the sewage by conventional techniques. The great visibility of dyes, even at trace concentrations, is generally related to less-dissolved oxygen in aquatic habitats, decreasing the penetration of sunlight along with photosynthetic activities. In this way, ecological harm may spread downstream to agricultural or aquaculture regions, affecting aquatic flora and fauna. It is, therefore, obligatory for some places to exercise proper treatment before the disposal of such wastewater.

MB products include a group of dye compounds which have many uses, namely, biological staining, dermatological agent, veterinary medicine, and inhibitor. Global demand for coatings and paints is predicted to rise 3.7% per year to 54.7 million metric tons in 2020. The growing consumer demand for dye compounds in various end-use segments is projected to act as a major growth factor for the global market over the following few years. MB, a widely used dye, travels to incorporate itself in aquatic systems (highly soluble, 50 g/L) and in the atmosphere. It has many uses, for example, dermatological agent, biological stain, veterinary medicine, to inhibit mold propagation in poultry feed, fungus, and intestinal parasites. MB dye is toxic when injected into humans and animals. Common harmful effects of MB on humans are irritation to the gastrointestinal tract with long-term exposure resulting in organ damage. Activated carbon is a versatile adsorbent which has been used widely for the adsorption process, but remains relatively expensive. Consequently, many authors have studied the feasibility of low cost and abundantly available substances that are used for the synthesis of activated carbon. This has prompted a growing research interest in the production of activated carbons from renewable and cheaper precursors which are mainly industrial and agricultural byproducts, for the wastewater treatment. However, the activated carbons available in the commerce are relatively expensive and their production and regeneration constitute limiting factors. Hence, many researchers have focused on the search on new low-cost precursors issued from agricultural wastes such as oil palm biomass, date palm, olive stones, sawdust, rice husk, apricot stone, clean laccase, cationic polymeric, core-shell magnetic, titania nanoparticle, and modification of activated carbon. The remarkable adsorption capacity of activated carbons is due to their well-developed porous structure and pore size distribution, as well as the surface functional groups. For this purpose, we carried out a parametric study of the adsorption by studying the effect of several significant parameters on the decolorizing power of the material used particularly the contact time, the concentration of the adsorbent, the pH, and temperature. The objectives of this study are summarized below.

- Contribution for the conservation of the natural environment.
- Valorization of activated carbon for the elimination of organic pollutants in static mode.
- Elaboration of adsorbents at low economic cost comparable to activated carbons.
- Valorization of the low cost adsorption method compared to other methods in water treatment.
- Possibility of switching from static mode (at the laboratory scale) to dynamic mode (column mode) at the industrial scale.
- Provide theoretical models for the simulation of the phenomenon.
- Regeneration of adsorbent for other uses.

**Materials and methods**

The spectrophotometer is a technique which owes its development to progress in the quantum mechanics allowing, among other things, to identify a chemical substance and to determine the concentration of a solute in solution, by using the Beer-Lambert’s law where the absorbance (A). Ten millimeter quartz cell was used and the reproducibility is 0.1 nm. Two light sources were used: a visible tungsten halogen and UV deuterium lamps; the scanning speed was set at 1200 nm/min. The blanks were carried out in a quartz cell identical to the previous one with ultra pure water. Measurements of the residual concentrations were obtained by linear interpolation using a previously calibration graph.

The pH of the solutions was accurately measured using a microprocessor-based pH meter of the HANNA HI 8521 type. The instrument was calibrated with commercial buffers of pH 4, pH 7, and pH 10. The pH was adjusted to by using H$_2$SO$_4$ and NaOH respectively for acidic and basic media.

**Materials**

The adsorbent used in this study is a commercial activated carbon. Then they were ground to have particles smaller than 50 mesh, and placed in brown bottles for future use. The Methylene blue MB of chemical formula C$_{16}$H$_{18}$ClN$_3$S whose molecular weight is 319.852 g/mol is
provided by Merck Company (purity 99.998%) and the absorbance peaks at at $\lambda_{\text{max}}$ of 662 nm. IUPAC Name [7-(dimethylamino) phenothiazin-3-ylidene]-dimethylazanium; chloride. Chemical structure and properties of the Methylene blue are given in Table 1. Dye stock solutions were prepared at 1000 mg/L concentrations by dissolving dye powders at required amounts in distilled water. By diluting the dye stock solutions with distilled water, the solutions at required concentration were adjusted for adsorption experiments.

**Characterization of activated carbon**

Nitrogen (N$_2$) adsorption–desorption experiments were performed at liquid nitrogen temperature by means of Micromeritics Tri Star II 3020. To remove volatile contaminations, degassing processes were completed for EACs at 90°C for 0.5 h and immediately after, at 300°C for 2 h under vacuum before measurements. By using the Brunauer–Emmett–Teller (BET) method, specific surface areas were determined, and total pore volumes were calculated through nitrogen adsorption at $P/P_0 = 0.984$.

The Fourier Transform Infrared spectroscopy (FTIR) is used to identify the characteristic functional groups of AC. Five milligram of AC are mixed with dry KBr of spectroscopy quality and pressed under a pressure of 4500 psi to form thin disk. Then, the FTIR spectrum was plotted with a Perkin Elmer 2000 infrared spectrometer. The sample was scanned from 4000 to 400/cm for 16 times to increase the signal to noise ratio.

The X-ray diffraction (XRD) pattern of the activated AC are obtained with a Philips X-ray diffractometer (PW 1890 model) 40kV, 40 mA, $\lambda = 1.54 \text{Å}$. The patterns are obtained with CONIT T-2T scan mode at 0.17°/step of step width and 8°/min of scan speed.

The determination of the point of zero charge (pH$_{\text{PZC}}$) was conducted to investigate how the surface charge of (AC) adsorbent depends on pH. pH$_{\text{PZC}}$ of the activated carbon was determined using the procedure described elsewhere.$^{24}$ 0.01M of NaCl was prepared and the initial pH was adjusted between 2 and 12 using HCl or NaOH solution (0.1M). Fifty milliliter of NaCl solution was placed in Erlenmeyer flasks with 0.1 g of adsorbent. The flasks were kept under agitation (150 rpm, 48 h), and the final pH of the solution was measured. The intersection point of the curves pH$_{\text{final}}$ versus pH$_{\text{initial}}$ and the bisector was taken as pH$_{\text{PZC}}$.

**Adsorption experiments**

The adsorption experiments were performed with batch method. In batch adsorption studies, the dye solutions at the desired concentrations were adjusted from dye stock solutions through dilution with water, and placed in Erlenmeyer flasks. After that, adsorbent were put in the Erlenmeyer flasks. They were located into a shaker with thermostat controlled (Wise Bath) and shaken at 250 r/min till adsorption equilibrium was reached at desired temperature. Samples were then centrifuged for 20 min at 4000 r/min to set apart their solid phases from liquid phases, and their remaining dye amounts without adsorbed in solutions were detected using a UV–visible spectrophotometry (Mecasys Optizen POP Series) at 662 nm wavelength for. Using the above method, adsorption experiments were performed to assess the effects of concentration AC (0.0125–0.125 g/50 mL), initial MB dye concentration (200–500 mg/L), and temperature (25–45°C). The amount of MB (mg/g) adsorbed by (AC)q$_t$ was calculated from the relation:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m}$$

Where $C_0$ is the initial MB concentration and $C_t$ the MB concentrations (mg/L) at any time, V the volume of solution (L), and m the mass of AC (g).

**Results and discussion**

**Adsorbent characterization**

BET surface area and pore size. The specific surface area was determined by the BET equation. The external surface area
area, micropore area and micropore volume were calculated by the t-plot method. The total pore volume was evaluated from the liquid volume of N\textsubscript{2} at high relative pressure near unity 0.99. The mesopore volume was calculated by subtracting the micro-pore volume from the total volume. The pore size distribution (PSD) was determined using the density functional theory (DFT) model. All characteristics for the adsorbent (AC) are reported in Table 2.25

| Table 2. Physicochemical characteristics of AC. |
|----------------------------------------------|
| Humidity (%) = 3.7  | Ash rate (%) = 3.4  | pH\textsubscript{pzc} = 2.20 |
| \( S_{\text{BET}} \) (m\textsuperscript{2}/g) | 658.1 | VPT (m\textsuperscript{3}/g) | 0.473 |
| \( S_{\text{EXT}} \) (m\textsuperscript{2}/g) | 79 | \( V_{\text{m}} \) (cm\textsuperscript{3}/g) | 0.158 |
| \( S_{\text{MIC}} \) (m\textsuperscript{2}/g) | 579 | \( V_{\text{mic}} \) (cm\textsuperscript{3}/g) | 0.312 |
| \( V_{\text{mic}} \) (%) | 66.38 | \( V_{\text{mes}} \) (%) | 33.62 |

**FTIR spectrum analysis.** In Figure 1(a), the small band around 1700/cm is attributed to the stretching vibrations of the C=O groups (ketones, aldehydes, lactones or carboxylic groups), the spectra also show a band at 1650–1600/cm due to the vibrations of elongation of C=C bonds in the olefin structure, the bands between 1000 and 1350/cm are assigned to the vibrations of CO bonds.22 We observe a small decrease in the intensity of the peaks 1740/cm of the synthesized materials and disappearance of the others at 2920/cm due to carbonization.

**X-ray diffraction analysis.** Figure 1(b) generally shows an amorphous structure of all the materials and a low crystalline of the samples in the range from 10\(^\circ\) to 43\(^\circ\). For the raw material, the diffraction diagram has a peak at 22\(^\circ\) which is attributed to the presence of native cellulose. The diffraction pattern of activated carbon, show almost the same shape and have the same diffraction peaks at 25\(^\circ\) and 43\(^\circ\) which are attributed respectively to the presence of carbon/graphite and dehydrated hemicelluloses. On the other hand we note that after activation of the raw materials, the main peak moves from 22\(^\circ\) to 25\(^\circ\) and the appearance of a peak at 43\(^\circ\), which shows that the activation process has been successfully completed.

**Influence of analytical parameters**

**Influence of the contact time and initial concentration on the adsorption capacity.** The adsorption capacity of MB increases over time to reach a maximum after 60 min of contact time and thereafter tends toward a constant value indicating that no more MB ions are further removed from the solution. The equilibrium times averages 45 min but for practical reasons the adsorption experiments are run up to 60 min.

With raising the initial MB adsorbed increases to at pH 4 (Figure 2) for the range concentration (50–200 mg/L) respectively and from these results, we can deduce that the adsorption of MB onto AC is done in three stages:

i) Adsorption is rapid during the first minutes of the reaction; this can be interpreted by the fact that at the start of adsorption, the number of active sites available on the surface of the adsorbent is much greater than that of the sites remaining after some time.26

ii) For the high contact times the molecule needs time to diffuse inside the pore of the adsorbent.27

iii) For the rest of the quantity not adsorbed is interpreted by the saturation of the surface of the adsorbent (all adsorption sites are occupied).

**Influence of pH on adsorption capacity.** To study the influence of pH on the adsorption of MB by unaccompanied minors and using 50 mL of the dye of concentration 100 mg/L for different pH, a temperature 25\(^\circ\)C and a contact time of
60 min, the quantity of carbon active ingredient used is 50 mg. It is observed that the percentage of MB removal increasing consistently with increasing pH (Figure 3). The pH effect on the MB adsorption onto AC can be explained from the zero point charge \( (pH_{pzc}) \), the surface functions of the material have a significant influence on the adsorption performance. The basic or acidic nature of the adsorbent surface governs its retention capacity vis-à-vis to the pollutant. However, the character and chemical properties of adsorbent are directly linked to the nature of the functional groups located on its surface. The surface charge of the adsorbent, resulting from the acid-base equilibrium, depends on both the pH and ionic strength of the solution with which the material is in contact. This charge can be positive or negative depending on the environmental conditions.

Therefore, an important feature of the surface is the determination of \( pH_{pzc} (=2.20) \) by drift method which defines the pH for which the surface charge, linked to the exchange of protons, cancels out; \( pH_{pzc} \) characterizes the acidity or alkalinity of the surface. Below \( pH_{pzc} \) the surface charge is positive (acidity) where oxygen groups are in the cationic form, which converts to negative above \( pH_{pzc} \) (alkalinity) and tends to decrease when the oxygen content increases. For basic pH, the adsorption capacity of MB decreases when the pH increases, resulting from repulsive electrostatic forces between the adsorbent/pollutant with the same charges.

**Effect of the adsorbent dose.** The first stage of batch experiments on MB and the effect of adsorbent dose on the AC adsorption are examined. Significant variations in the uptake capacity and removal efficiency are observed at different adsorbent dose (1–6 g/L), indicating that the best adsorption is obtained with a dose of 1 g/L (Figure 4). This result was subsequently used in all isotherms adsorption experiments.

**Adsorption kinetic study**

The kinetic study is important since it describes the uptake rate of adsorbate, and controls the residual time of the whole process. Several models were proposed to study the mechanisms controlling the adsorption. The pseudo-first order equation and pseudo second order model are given in equations:

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \cdot t
\]

\[
\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e} + \frac{1}{q_e} \cdot t
\]

Where \( q_t \) (mg/g) is the amount of MB adsorbed on AC at the time \( t \) (min), \( K_1 \) (/min) and \( K_2 \) (g/mg.min) are the pseudo-first order and pseudo-second order kinetics constants respectively. The slope and intercept of the plots \( \ln(q_e - q_t) \) versus \( t \) and \( t/q_e \) versus \( t \) were used to determine the first-order rate constants \( K_1 \) and \( q_e \) and second-order rate constants \( K_2 \) and \( q_e \) respectively. The rate constants, predict the uptakes and the corresponding correlation coefficients for AC summarized in Table 3. For the pseudo-first-order kinetic, the experimental data deviate from linearity, as evidenced from the low values of \( q_e \) and \( C_0 \) and the model is inapplicable for the present system. By contrast, the correlation coefficient and \( q_e_{cal} \) determined from the pseudo-second order kinetic model agree with the experimental data (Figure 5) and its applicability suggests that the adsorption MB onto AC is based on chemical reaction (chemisorption), involving an exchange of electrons between adsorbent and adsorbate. The dye is attached to the adsorbent surface by chemical bond and tends to find sites that maximize their coordination number with the surface.
The Elovich kinetic equation is related to the chemisorptions process and is often validated for systems where the surface of the adsorbent is heterogeneous; the linear form is given by:

\[ q_t = \alpha + \beta \ln t = + \frac{1}{\beta} \ln \alpha + \frac{1}{\beta} \ln t \]  

Where \( \alpha \) (mg/g.min) is the initial adsorption rate, and \( \beta \) (mg/g) the relationship between the degree of surface coverage and the activation energy involved in the chemisorption.

**Intra-particle diffusion equation.** The study of adsorption kinetics is important because the rate of adsorption (which is one of the criteria for determining the efficiency of an adsorbent) and the mechanism of adsorption can both be concluded from kinetic studies. As a standard parameter for studying the behavior of BG dye adsorption at the AC surface is obtained using the Morries-Weber and Morris equation:

\[ q_t = K_i \sqrt{t} + C \]  

Where \( K_{in} \) is the intra-particle diffusion rate constant (mg/g.min\(^{1/2}\)), \( q_t \) the amount of MB adsorbed at time \( t \) and \( C \) (mg/g) the intercept. A plot of \( q_t \) versus \( t^{1/2} \) enables to determine both \( K_{in} \) and \( C \). Figure 5 present a multi-linearity correlation, which indicates that two steps occur during the MB adsorption. The Morris-Weber model reveals an initial linear portion which may be due to the boundary layer effect and a second portion which may be due to the intraparticle diffusion effect. The mechanism of adsorption is complex but the intraparticle diffusion is important in the early stages. The first linear portions could be due to intra-particle diffusion effects. The slopes of the linear parts are defined as rate parameters, characteristic of the adsorption rate in the region where the intraparticle diffusion occurs. Initially and within a short-time period, it is postulated that MB is transported to the Adsorbent external surface through the film diffusion with a high rate. After saturation of the surface, the MB ions enter inside Adsorbent by intra-particle diffusion through the pores and internal surface diffusion until equilibrium is reached which is represented by the second straight lines. The constants of the different models deduced after modeling are grouped in Table 3. The principle of the adsorption process can be summarized into the following four steps.

![Figure 5. Pseudo-second-order model fit for the adsorption of MB dye onto AC.](image-url)

| \( C_0 \) (mg/L) | Second | Order | \( R^2 \) | RSS | \( K_2 \) (g/mg.min) | Pseudo 1 | Order | RSS (%) | \( K_1 \) (min) |
|-----------------|--------|-------|---------|-----|---------------------|----------|-------|--------|--------|
|                 | \( q_{ex} \) (mg/g) | \( q_{cal} \) (mg/g) |         |     |                     | \( q_{cal} \) (mg/g) |         |        |        |
| 50              | 46     | 51.894| 0.9985  | 0.0016| 0.00237            | 38.317   | 0.9563| 0.0842 | 0.0674 |
| 100             | 97     | 101.01| 0.9988  | 0.0004| 0.00306            | 55.398   | 0.9553| 0.0880 | 0.0682 |
| 200             | 174    | 177.62| 0.9999  | 0.0001| 0.0036             | 67.550   | 0.8843| 0.3055 | 0.0763 |

Table 3. Pseudo first-order, Pseudo second-order, Elovich and intraparticles models constants, and correlation coefficients for MB adsorption onto AC.
Transfer of the pollutant from the external layer to the internal (very quick step).

• Displacement of the bound pollutant until contact with the adsorbent (quick step).

• Diffusion in the adsorbent under a concentration gradient (slow step).

• Adsorption in a micro pore (very fast step).

Adsorption equilibrium isotherms

To assess the performance of adsorbent, different equations and isotherms exist, out of which the Langmuir,33 Freundlich,34 Temkin and Pyzhev,35 and Elovich36 isotherms were used that have been presented in Figure 7. Besides, the isotherm models were applied at optimal conditions of the parameters.

The Langmuir model is the best known and most widely applied, it is represented by the non linear and linear forms:

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \frac{1}{q_{\text{max}} \cdot K_L \cdot C_e}
\]  

(6)

Where \( C_e \) is the equilibrium concentration (mg/L), \( q_{\text{max}} \) the monolayer adsorption capacity (mg/g) and \( K_L \) the constant related to the free adsorption energy (L/mg). The applicability to the adsorption is compared by evaluating the statistic RSS, \( R^2 \) values at 25°C. The smaller RSS values obtained for the models indicate a better fitting. The essential features of the Langmuir

\[
R_L = \frac{1}{1 + K_L \cdot C_e}
\]

(7)

\( C_0 \) is the initial concentration of the adsorbate in solution. The \( R_L \) indicates the type of isotherm: Irreversible (\( R_L = 0 \)), Favorable (\( 0 < R_L < 1 \)), Linear (\( R_L = 1 \)), or Un (\( R_L > 1 \)). In

The Freundlich isotherm is valid for non ideal adsorption on heterogeneous surfaces as well as multilayer sorption.

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

(8)

The constant \( K_F \) characterizes the adsorption capacity of the adsorbent (L/g) and \( n \) an empirical constant related to the magnitude of the adsorption driving force. Therefore, a plot \( \ln q_e \) versus \( \ln C_e \) enables the determination of both the constant \( K_F \) and \( n \).

The Temkin isotherm describes the behavior of adsorption systems on heterogeneous surfaces, and is applied in the following form:

\[
q_e = B_T \ln C_e + B_T \ln A_T
\]

(9)

The adsorption data are analyzed according to equation (8). Therefore, the plot versus \( q_e \) versus \( \ln C_e \) enables to determine the constants \( A_T \) and \( B_T \).

The Elovich isotherm is based on the principle of the kinetic, assuming that the number of adsorption sites augments exponentially with the adsorption; this implies a multilayer adsorption described by:

\[
\ln \frac{q_e}{C_e} = \ln(q_{\text{m}} \cdot K_E) - \frac{q_e}{q_{\text{max}}}
\]

(10)

Where \( K_E \) (L/mg) is the Elovich constant at equilibrium, \( q_{\text{max}} \) (mg/g) the maximum adsorption capacity, \( q_e \) (mg/g) the adsorption capacity at equilibrium and \( C_e \) (g/L) the concentration of the adsorbate at equilibrium. Both the equilibrium constant and maximum capacity are calculated
from the plot of \( \ln(q_e/C_e) \) versus \( q_e \). The constants of the different models deduced after modeling are grouped in Table 4.

**Thermodynamic study**

The thermodynamic properties were investigated to determine whether the adsorption process occurred spontaneously. The thermodynamic parameters, namely, Standard enthalpy \( (\Delta H^\circ, \text{kJ/mol}) \), standard entropy \( (\Delta S^\circ, \text{J/mol K}) \), and standard free energy \( (\Delta G^\circ, \text{kJ/mol}) \), were calculated using the following equations:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \\
\Delta G^\circ = -RT \ln K_d \\
K_d = \frac{q_e}{C_e} \\
\ln K_d = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

Where \( R \) is the gas constant (8.314 J/mol K), \( T \) (K) is temperature where \( K_d \) is the distribution coefficient, \( q_e \) (mg/g) is the quantity of BG adsorbed at equilibrium and \( C_e \) (mg/L) is the quantity of MB remaining in solution at equilibrium. The thermodynamic equilibrium constant \( K_d \) for the sorption was determined by plotting \( q_e/C_e \) versus \( C_e \) and extrapolating to zero \( C_e \). The \( \Delta H^\circ \) and \( \Delta S^\circ \) values obtained from the slope and intercept of Von’t Hoff plots of \( \ln K \) versus \( 1/T \) (Figure 8) and the \( \Delta G \) values at various temperatures are summarized in Table 5.

**Performance of the activated carbon**

It is instructive for a comparative goal to report the adsorption capacity of some adsorbents reported in the literature. In Table 6, it’s given the different values of the Langmuir maximum adsorption capacity \( q_{max} \) of different adsorbent cited in previous works. We can see that the MB adsorption observed in the present study is well positioned with respect to other researches with a maximum adsorption capacity \( q_{max} \) of 170.357 at 298 K, relatively interesting compared to other adsorbents. The differences of the dye uptakes are due to the properties of each adsorbent like the structure, the functional groups and the surface area. AC could be an attractive adsorbent for basic dyes owing to the isoelectric point (\( p\text{H}_{zc} \)). The desorption is an unavoidable process and is an intermediate stage toward the adsorbent regeneration. The latter is an essential tool to estimate the reutilization of any adsorbent for industrial applications, due to ecological concerns and sustainable development needs. For the regeneration of the adsorbent, we opted for chemical regeneration because of its low economic cost. MB desorption of activated carbon was evaluated using three organic solvents methanol, ethanol and acetic acid. The desorption experiments were carried out after adsorption of a MB solution of: 100 mg/L and

### Table 4. Parameters of the adsorption isotherms for MB dye onto AC.

| 25°C | Langmuir | Freundlich | Temkin | Elovich |
|------|----------|------------|--------|---------|
| \( K_L \) | 23.6 L/g | \( 1/n = 0.3999 \) | \( B_r = 34.888 \) | \( K_K = 147.0 \) L/g |
| \( q_{max} \) | 170.357 mg/g | \( n = 2.501 \) | \( A_r = 276.9 \) L/g | \( q_{max} = 57.142 \) mg/g |
| \( K_r \) | 18.378 mg/g | \( \Delta Q^\circ = 49.08 \) J/mol | | |
| \( R^2 \) | 0.9993 | 0.99826 | 0.9973 | 0.9966 |
| RSS | 0.0079 | 0.0196 | 24.288 | 0.0095 |

RSS : residual Sum of Squart; \( R^2 \) : determination coefficient; \( \Delta Q^\circ \) : Temkin energy.
at a temperature of 25°C, the activated carbon was separated from the solution by centrifugation and dehydrated at 40°C for 6 h. The figure shows that only 4.9 and 5% were desorbed using pure ethanol and methanol respectively. On the contrary, with acetic acid, the desorption increased from 0.5% for a concentration of 1 mol/L to 94% for a concentration of 10 mol/L. Three desorption cycles with desorption percentages of 94.91 and 89% were obtained respectively with acetic acid more than methanol and ethanol.

### Conclusion

In this work, an experimental study on the utilization of Activated Carbon (AC) for the removal of Methylene Blue from aqueous solution was investigated. The following conclusions were made based on the results of the present study:

The (AC) was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), and BET techniques. The potential of this adsorbent was studied for decolonization of MB; the influence of the initial pH, dye MB concentration, contact time, adsorbent dose, and temperature on adsorption of MB was investigated. The adsorption capacity of MB increased with increasing the initial dye concentration, while the optimized pH was found to be 6.

The kinetics of MB removal indicated an optimum contact time of 45 min via a two stage of adsorption kinetic profile (initial fast and subsequent slow equilibrium). The MB adsorption AC follows a pseudo-second order kinetic model (R² = 0.999). That relies on the assumption that the chemisorption may be the rate-limiting step and where the MB ions are attached to the adsorbent surface by forming chemical bonds and tend to find sites that maximize their coordination number with the surface.

The equilibrium adsorption data for MB on AC were analyzed by various models. The results indicate that the Langmuir isotherm provides the best correlation (q_max = 170.357 mg/g at 299 K).

The negative ΔG° and positive ΔH° indicate that the adsorption of MB onto AC is spontaneous and endothermic over the studied temperatures range. MB is strongly bonded to the adsorbent surface while the positive entropy states clearly that the randomness increases at the solid-solution interface during the MB adsorption and some structural exchange between active sites and MB ions.

The comparison of the adsorption capacity of our adsorbent with others showed its attractive properties from both industrial and economic interests. This study has given

### Table 5. Thermodynamic functions ΔG°, ΔS°, and ΔH° of MB adsorbed on the AC.

| T (K) | 1/T (1/K) | ln(qe/Ce) | Kd | ΔH° (kJ/mol) | ΔS° (kJ/K.mol) | ΔG° (kJ/mol) |
|-------|-----------|-----------|----|-------------|--------------|-------------|
| 298   | 0.003355  | 2.222     | 9.2073 | –7.856      |              |             |
| 308   | 0.003247  | 2.433     | 11.358 | –6.142      |              |             |
| 318   | 0.003145  | 2.575     | 13.131 | 13.384      | 0.06346      | –6.796      |
| 328   | 0.003049  | 2.725     | 15.256 |             |              | –7.431      |

### Table 6. Comparison of maximum adsorption capacities for MB dye with literature data.

| Adsorbents | T (K) | Q_max (mg/g) | t_eq (min) | Dose (g/L) | pH | Ref                  |
|------------|-------|--------------|------------|------------|----|---------------------|
| Bamboo dust carbon | 298   | 143.20       | 35         | 35         | 10 | Kannan and Sundaram37 |
| Grounde palm kernel coat | 298   | 277.77       | 60         | 60         | 9  | Oladoja et al.38    |
| Raw clay   | 298   | 50.0         | 50         | 0.2        | 10 | Benguella and Yacouta Nour39 |
| Purified clay | 298   | 65.5         | 50         | 0.2        | 10 | Benguella and Yacouta Nour39 |
| Carbon nano tube | 290   | 103.62       | 60         | 0.2        | 10 | Shahryari et al.40   |
|          | 300   | 109.31       | 60         | 0.2        | 10 | Shahryari et al.40   |
|          | 310   | 119.71       | 60         | 0.2        | 10 | Shahryari et al.40   |
| Strychnos potatorium | 298   | 100          | 120        | 1          | 9  | Jerald Antony Joseph and Xavier41 |
| AC diatomaceous silica | 298   | 126.6        | 120        | 1          | 9  | G et al.42          |
| Defatted Carica papaya seeds | 298   | 769.23       | 70         | 1          | 10 | Voula et al.43      |
| Steam activated bituminous coal | 298   | 580          | 60         | 0.05       | 11 | Weber and Chakravorti44 |
| Jute fiber carbon | 298   | 225.65       | 50         | 1          | 10 | Suteu and Bilba45    |
| Sawdust    | 293   | 142.36       | 50         | 1          | 7  | Stephenson and Duff46 |
| Crushed brick | 293   | 96.36        | 50         | 1          | 7  | Stephenson and Duff46 |
| Apricot stone | 298   | 46.03        | 35         | 1          | 10 | Nandi et al.5       |
|            | 343   | 88.50        | 35         | 1          | 10 | Nandi et al.5       |
| Activated Carbon | 298   | 170.36       | 40         | 1          | 10 | This study          |

| Adsorbents               | T (K) | Q_max (mg/g) | t_eq (min) | Dose (g/L) | pH | Ref                  |
|--------------------------|-------|--------------|------------|------------|----|---------------------|
| Bamboo dust carbon       | 298   | 143.20       | 35         | 35         | 10 | Kannan and Sundaram37 |
| Grounde palm kernel coat | 298   | 277.77       | 60         | 60         | 9  | Oladoja et al.38    |
| Raw clay                 | 298   | 50.0         | 50         | 0.2        | 10 | Benguella and Yacouta Nour39 |
| Purified clay            | 298   | 65.5         | 50         | 0.2        | 10 | Benguella and Yacouta Nour39 |
| Carbon nano tube         | 290   | 103.62       | 60         | 0.2        | 10 | Shahryari et al.40   |
|                          | 300   | 109.31       | 60         | 0.2        | 10 | Shahryari et al.40   |
|                          | 310   | 119.71       | 60         | 0.2        | 10 | Shahryari et al.40   |
| Strychnos potatorium     | 298   | 100          | 120        | 1          | 9  | Jerald Antony Joseph and Xavier41 |
| AC diatomaceous silica   | 298   | 126.6        | 120        | 1          | 9  | G et al.42          |
| Defatted Carica papaya seeds | 298   | 769.23       | 70         | 1          | 10 | Voula et al.43      |
| Steam activated bituminous coal | 298   | 580          | 60         | 0.05       | 11 | Weber and Chakravorti44 |
| Jute fiber carbon        | 298   | 225.65       | 50         | 1          | 10 | Suteu and Bilba45    |
| Sawdust                  | 293   | 142.36       | 50         | 1          | 7  | Stephenson and Duff46 |
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|                         | 343   | 88.50        | 35         | 1          | 10 | Nandi et al.5       |
| Activated Carbon         | 298   | 170.36       | 40         | 1          | 10 | This study          |
encouraging results, and we wish to carry out column adsorption tests under the conditions applicable to the treatment of industrial effluents and to test the heterogeneous photo degradation of MB on the SnO$_2$, TiO$_2$ semiconductors is the future objective of this work.

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