

Desorption of Methylene Blue Adsorbed on Activated Carbon from Cocoa Pod Shell

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Abstract

Environmental protection has become a concern for the world. For this reason, the objective of this work is to remove methylene blue adsorbed on activated carbon. The coal used comes from cocoa pod shells. Before pyrolysis, the shells were ground, sieved and impregnated with orthophosphoric acid. Before desorption, the activated carbons were initially saturated with MB. These saturated coals were brought into contact with a sodium chloride (NaCl) solution and then stirred. The evolution of the resorbed MB concentration was monitored by spectrophotometry. The desorption tests showed a remarkable elimination from the first 10 minutes. The desorption kinetics comprises two phases: a rapid kinetics between 0 and 30 minutes and a slow kinetics between 30 and 60 minutes. The desorption of the dye reaches a concentration equal to 0.84 mg/l at pH = 4 at temperature = 80°C. For modeling, the coefficient of the Langmuir II model is greater than or equal to 0.9893. The model of Langmuir III is less than or equal to 0.9373. The Freundlich model coefficient is 0.9842 or less. The desorption is therefore carried out on energy-homogeneous adsorption sites and without any interaction between the adsorbed cations of the dye. Experimental parameters such as pH, temperature and concentration of sodium chloride (NaCl) solution influence the desorption of MB. And the model of Langmuir II describes well the process of desorption of the MB.

Keywords

Desorption, Activated Carbon, Methylene Blue, Isotherm, Sodium Chloride

1. Introduction

Pollution and environmental protection are major concerns for society. They are therefore included in research programs and in economic and political decisions [1]. Human activities cause enormous ecological disasters. These include over-exploitation of natural resources, burning of fossil fuels, pollution of drinking water supplies, etc. [1]. This environmental pollution is due to chemical pollutants such as dyes. These come from the paper, plastic, textile, wood and mineral processing industries [2]. Even at low concentrations, these substances cause serious health problems [3]. In order to preserve the environment, the reduction of the pollutant load in the water required several techniques and processes. This is the case for adsorption.

A process in which molecules (adsorbates) attach to the surface of a solid (adsorbent) activated carbon. It will have fewer sites available. This therefore results in a loss of the adsorption capacity. As a result, the saturated adsorbent is destroyed by incineration or deposited in a landfill. Unfortunately, both disposal techniques are economically and environmentally costly [4]. In addition, the deposition of adsorbents in landfills is similar to the movement of pollutants from one site to another. A major concern in the management of the adsorbents used is the risk of leaching adsorbates (adsorbed pollutants) into the environment [5]. Therefore, this material needs to be regenerated. Regeneration or reactivation consists in desorbing and/or destroying the molecules picked up by the activated carbon. It is increasingly common due to environmental responsibility [6]. The importance of the process has led to the introduction of various techniques for regenerating activated carbon [7]. For example, Kim *et al.* (2013) [8] propose the regeneration of surface modified activated carbon with iron by oxidation with hydrogen peroxide.

It is in this context that this work is carried out to remove methylene blue adsorbed on activated carbon from the shells of cocoa pods. To carry out this study, the following specific objectives have been defined:

- To investigate the influence of time and temperature on the desorption of BM from activated carbon.
- To investigate the influence of pH and NaCl concentration on the desorption of BM from activated carbon.
- Model the desorption isotherms of the BM of activated carbon.

2. Materials and Methods

2.1. Presentation of Biological and Laboratory Material

Equipment includes laboratory glassware, equipment and agricultural waste. The glassware consists essentially of Beakers, Erlenmeyer, calibrated burette, volumetric flask, shovel, pipette, sieve, crucible, etc. The glassware consists of: OHAUS/Scout Pro precision analytical balance of ± 0.01 g, memmert type oven, Magnetic heating stirrer, Digital, LBX H20D, ceramic plate, 20 L, UV-Visible absorption spectrophotometer type DV UV5600 and SIGMA brand centrifuge. The biomass

used for the preparation of the coals consists essentially of the shell of cocoa pod of the Forastero type.

The reagents used are: ortho-phosphoric acid (H_3PO_4) of purity 85%, sodium hydroxide (NaOH) of purity 98% and molar mass 40 g/mol, potassium iodide (KI) of purity 99% and molar mass 166.01 g/mol, diode (I_2) of purity 99.8%, density 4.83 and molar mass 253.81 g/mol, sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) of molar purity 99% and molar mass mass area 248.18 g/mol, Methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$) of purity 82% and molar mass 318.85 g/mol, Acid chloride (HCl) of purity 37%, density 1.19 and molar mass 36.5 g/mol.

Methylene blue and its characteristics:

Methylene blue is an organic compound whose systemic name is 3,7-bis-phenazathionium, soluble in water and more slightly in alcohol. Methylene blue is a nitrogen derivative, the most commonly used in the dyeing of cotton, wood and silk, and is a dark blue crystal-line powder. It can cause eye burns that can permanently injure the eyes of humans and animals. Its inhalation can give rise to respiratory difficulties, leading to cases of anaemia after prolonged adsorption. Its characteristics are listed in the following **Table 1**.

2.2. Solution Preparation

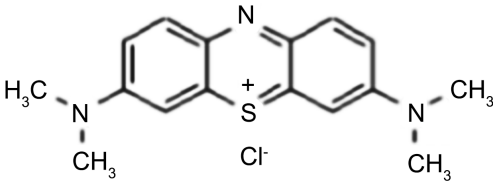
- Methylene blue

500 mg or 0.5 g of methylene blue is introduced into a 1 L flask. A little distilled water is added until the blue is completely dissolved and then the mixture is made up to the mark.

- Sodium chloride (1 M)

It is weighs and introduce into a 1 L flask 58.5 g of sodium chloride. A little distilled water is added; then stirring is carried out until the sodium chloride grains completely dissolve. Finally, distilled water is added up to the mark.

Table 1. Characteristics of Methylene blue.

Dye	Methylene blue
Structure	
Chemical formula	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$
Molecular weight (g/mol)	319.85
Peak wavelength λ max (nm)	662
Solubility in water	40 g/mol à 20°C
degree of purity	82%
Smell	odourless

- Hydrochloric acid (0.1 M)

4.1 mL of the commercial hydrochloric acid solution is introduced into a 500 mL flask. The mixture is made up to the mark with distilled water.

- Soda (0.1 M)

It is weighed and introduced into a 1 L flask 4.081 g of soda. A little distilled water is added and then stirred until the sodium hydroxide grains completely dissolve. Finally, distilled water is added up to the mark.

2.3. Implementation of Desorption

The desorption tests for methylene blue were carried out in the same device as the adsorption. A mass of the charged carbon pollutant is contacted with a desorption solution (NaCl). The effect of several parameters was examined:

- Effect of pH (pH = 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12) at optimum temperature.
- Effect of contact time.
- Effect of NaCl concentration.

2.4. Spectrophotometry UV/Visible

The evolution of the BM concentration is monitored by spectrophotometry in the UV-Visible domain. And this follow-up is done by applying the Beer Lambert law. This law relates the absorbance of light by a compound to its concentration:

With: Abs: Absorbance, I_0 : the intensity of the incident ray, I : the intensity of the transmitted ray, ε : the molar extinction coefficient at the wavelength at which the measurement is made (l/mol-cm).

l : optical path length (cm) and C : solute concentration (mol/L).

The spectrophotometer used is a UV-Visible spectrophotometer of the Hach DR. 1900 type.

2.5. Method of Assessing Desorption Capacity: Kinetics and Desorption Rate

2.5.1. Desorption Capacity

Desorption was performed as a function of time to determine the amount of desorbed dye at different time intervals. 0.1 g of coal containing methylene blue following adsorption were brought into contact with 100 ml of 1 M molarity sodium hydrochloric acid (NaCl) solution. The mixture was stirred at times ranging from 0 to 60 min. The amount of dye desorbed during the time of the experiments is given by the following relation:

$$q_{des} = v(C_i)/m \quad (1)$$

$$q_{ads} = q_i - q_{des} \quad (2)$$

With; q_{des} is the amount of methylene blue desorbed at any given time t .

q_{ads} is the amount of methylene blue adsorbed at any given time t .

$$q_e = q_i - VC_e/m \quad (3)$$

With:

V : volume of NaCl solution.

C_e : concentration desorbed at equilibrium.

C_0 : the initial concentration of BM in the NaCl solution.

m : the mass of coal.

2.5.2. Influence of Temperature on Desorption Kinetics

The activation energy measures the magnitude of the forces to be overcome during the desorption process. The rate constants determined for the desorption kinetics could be applied to the Arrhenius equation to determine the activation energy. The relationship between rate constants and solution temperature is expressed as follows:

$$k_r(\text{fast}) \text{ or } k_s(\text{slow}) = k_0 \exp(-E_{des}/RT) \quad (4)$$

where k_0 is the temperature independent factor, E_{dice} is the activation energy (kJ/mol), R is the gas constant (8314 J/mol K) and T is the temperature of the solution (K). Arrhenius Equation could be transformed into a subform:

$$\log(k_r)(\text{fast}) \text{ or } \log(k_s)(\text{slow}) = k_0 \exp(-E_{des}/2.303RT) \quad (5)$$

The activation energy (E_{dice}) was determined from the slope of the Arrhenius diagram, $\log(k_r)(\text{fast})$ or $\log(k_s)(\text{slow})$ as a function of $1/T$.

2.6. Desorption Isotherm Modeling

Several theoretical desorption models have been developed to describe the distribution of the solute between the solvent and the solid phase at equilibrium. Our experimental data were applied to three models: the Langmuir II model, Langmuir III model and the Freundlich model.

2.6.1. Langmuir Isotherm Model

A widely used model is based on reactive assumptions Langmuir (1918). The solid is assumed to have a limited desorption capacity q_m linked to a limited number of desorption sites (monomolecular layer) by the equation:

$$q_e/q_m = \theta = k_L C_e / (1 + k_L C_e) \quad (6)$$

K_L : Langmuir equilibrium constant,

θ : recovery rate.

The linear shape of the Langmuir isotherm:

$$C_e/q_e = C_e/q_m + 1/k_L q_m \quad (7)$$

The essential characteristics of a Langmuir isotherm can be expressed in terms of a constant (dimensionless) separation factor or equilibrium parameter, RL (Hall *et al.*, 1966) which is used to predict whether a desorption system is “favorable” or “unfavorable”. The separation factor, R_L is defined by the following equation:

$$R_L = 1/(1 + k_L C_0) \quad (8)$$

With:

C_0 : maximum initial concentration of phenol ($\text{mg}\cdot\text{L}^{-1}$),

K_L : Langmuir desorption equilibrium constant ($\text{L}\cdot\text{mg}^{-1}$).

The isothermal parameters of this model are determined experimentally by plotting the C_e/q_e curve as a function of C_e .

The isotherm is unfavorable when $R_L > 1$, it is linear when $R_L = 1$, it is favorable when $0 < R_L < 1$ and it is irreversible when $R_L = 0$.

2.6.2. Freundlich Isotherm Model

This model describes desorption on heterogeneous surfaces. It is given by Freundlich (1906):

$$q_e = k_F C_e^{1/n} \quad (9)$$

Using the logarithmic function on this equation, we get the following linear form:

$$\ln q_e = \ln k_F + 1/n \ln C_e \quad (10)$$

where:

k_F ($\text{L}\cdot\text{kg}^{-1}$) and n (dimensionless) experimental constants.

The graph describing $\ln(q_e)$ as a function of $\ln(C_e)$ gives a slope line n , the ordinate of which at the origin is $\ln K_F$. According to this equation, the isotherm initially has an infinite slope and does not have a strict saturation plateau. The n parameter in the Freundlich equation is an indicator of the affinity and capacity of each carbon/pollutant pair: for $n > 1$, the desorption is quantitatively greater and for $n < 1$ it is lower Reffas (2010).

3. Results and Discussion

3.1. Influence of Time and Temperature on Dye Desorption

3.1.1. Dye Desorption Kinetics

Figure 1 is a graphical representation of the desorption kinetics of methylene blue as a function of temperature.

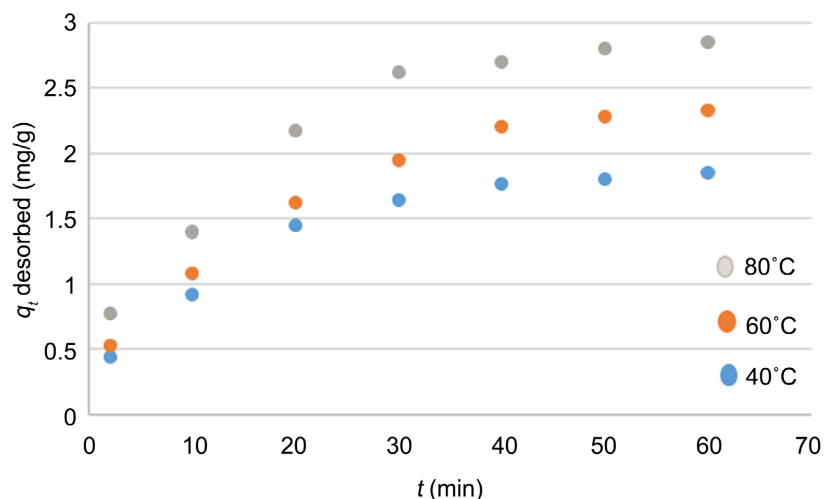


Figure 1. Desorption kinetics of BM as a function of temperature.

The desorption kinetics of methylene blue (**Figure 1**) have two distinct phases whatever the temperature. A first rapid desorption phase ranging from 0 to 30 minutes. A second phase of slow desorption between 40 and 60 minutes. Desorption yield increases over time to reach equilibrium at 60 minutes. It is also noted that desorption intensifies with increasing temperature. Thus, the q_e increases from 1.850 to 2.850 mg/g from 40°C to 80°C.

The removal of methylene blue from our activated carbon is greater than that observed by Bouaziz (2014) [4] on another activated carbon (0.45 mg/g or 0.17% of the total amount of BM), Nyex (0.13 mg/g or 10% of the total amount of BM) and sawdust (7.6 mg/g or 33% of the total amount of BM). On the other hand, our result is less interesting than that observed by Rechache (2019) [1] with thiazole yellow and bright yellow on the SB-Sebacoyl material.

The graphical representation of the kinetic model of desorption of the methylene blue dye is given in **Figure 2**.

The q_t/q_i ratio is independent of temperature and decreases with increasing time to equilibrium. Thus the evolution of desorption with our coal is similar to the observation of Muhammad *et al.* (2011) [9].

The good fit of the experimental points shows that some of this dye is rapidly desorbed and the rest is desorbed more slowly with a somewhat slower rate (**Table 2**). These two speeds are explained by the existence of two types of pores: relatively large pores that would facilitate desorption and thinner pores that are the site of slower desorption [10].

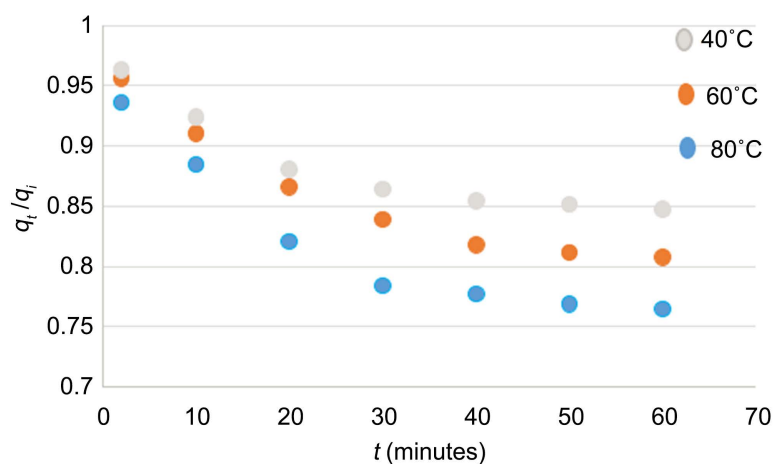


Figure 2. Kinetic model of desorption of methylene blue on activated carbon.

Table 2. Parameters of the desorption kinetics of methylene blue on granular activated carbon.

Temperature °C	q_i mg/g	s	K_r (1/min)	K_s (1/min)	R^2
40	12.13	0.8689	0.004	0.00041	0.8258
60	12.13	0.8389	0.005	0.00063	0.8924
80	12.13	0.7962	0.006	0.00068	0.802

3.1.2. Effect of Temperature on Desorption Kinetics

Figure 3 and **Figure 4** are the Arrhenius graphs for the slow and rapid desorption of methylene blue onto activated carbon.

According to Johnson and Weber (2001) [11], activation energy values are highly dependent on the characteristics of the adsorbent. And these values obtained during the desorption of methylene blue from coal are respectively 119.54 and 439.96 J/mol for the rapid and slow desorption. The fact that the activation energies of Ks are higher implies that diffusion could occur through the micropores. In fact, Wang and Grathwohl (2009) [12] noted that activation energies for diffusion into liquids and gases were greater in micropores than in mesopores or macropores.

3.2. Influence of pH and NaCl Concentration on Dye Desorption

3.2.1. Study of the Influence of pH on Dye Desorption

For this study, a mass of 0.1 g of the carbon charged with polluting was introduced into a volume of 100 ml of a sodium chloride solution. During the study, the pH was adjusted from 3 to 12 at a temperature of 80°.

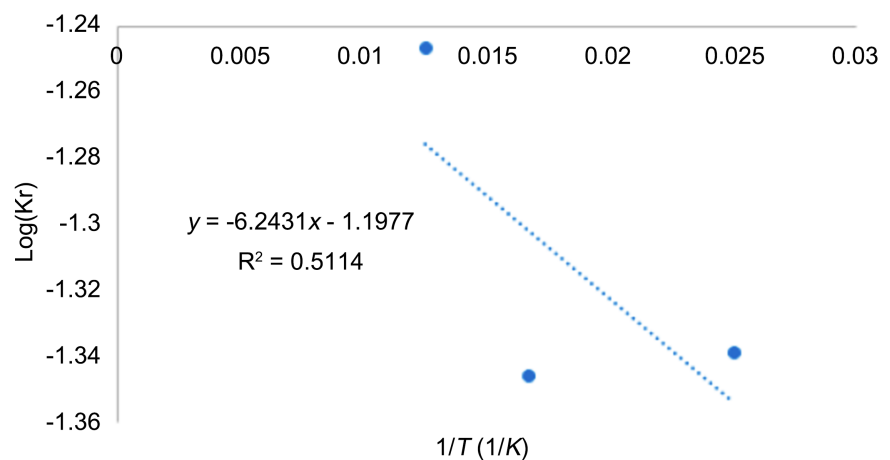


Figure 3. Arrhenius graph for the slow desorption of coal methylene blue active.

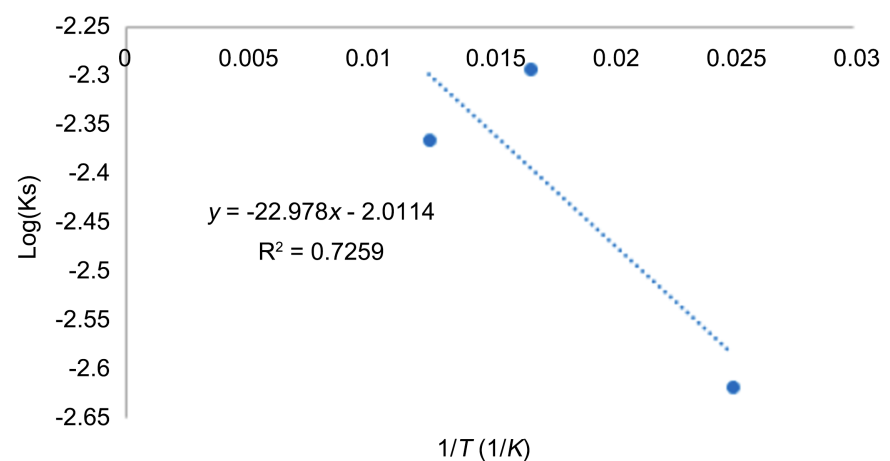


Figure 4. Arrhenius graph for the fast desorption of coal methylene blue active.

Figure 5 show that the desorbed quantity is maximum at pH equal to 4 ($q_e = 4.903$ mg/g). And from pH 4 to 12, the amount desorbed decreases slightly. In both this study and the one by Kavitha and Namasivayam (2007) [13], it is observed that the amount desorbed remains relatively small despite the variation in pH. Thus, ion exchange does not appear to be predominant in the desorption process. In contrast, chemisorption is more likely to be the mode of adsorption [13] [14].

3.2.2. Influence of NaCl Concentration on Dye Desorption

For the influence of the concentration of the desorption solution, a mass of 0.1 g of the polluting coal was added to 100 ml volumes of a sodium chloride solution. And the concentration ranges from 0.1 to 1 M at the temperature of 80°C.

Figure 6 shows that the amount desorbed is all the greater with the increase in the concentration of the sodium chloride solution. The amount desorbed increases from 1.439 g/l to 2.85 g/l from 0.1 to 1 M. The author [14] made the same observation. In addition, it observed the presence of an optimal concentration of desorption agent [14]. This finding was not observed with NaCl, despite the large variation in concentration.

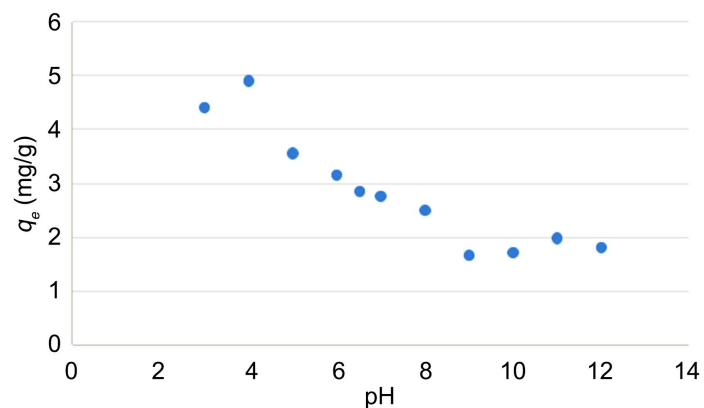


Figure 5. Evolution of the amount of desorbed methylene blue from activated carbon to grain pH function.

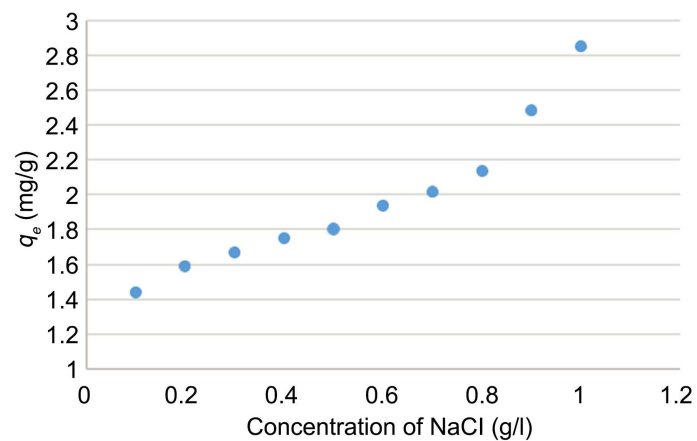


Figure 6. Evolution of BM concentration as a function of NaCl concentration.

3.3. Modeling of Dye Desorption Isotherms

The graphical representations of the Langmuir II, Langmuir III and Freundlich isotherms of the desorption of the dye are given respectively by Figures 7-9. The isothermal constants are listed in Table 3.

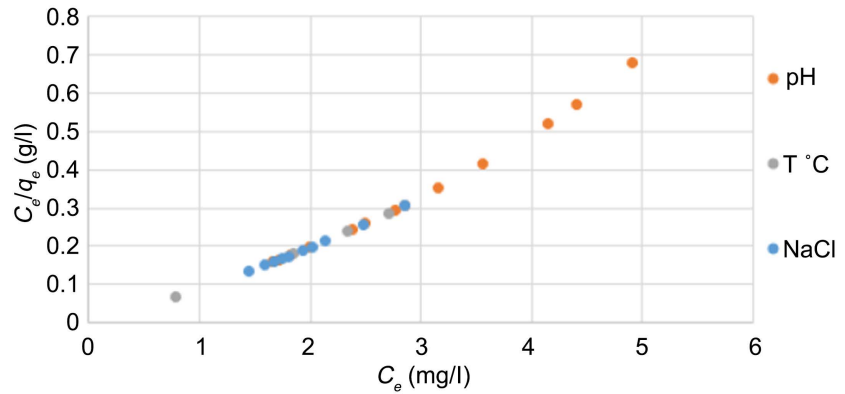


Figure 7. Modeling of Methylene blue desorption isotherm on grain activated carbon using the Langmuir II equation.

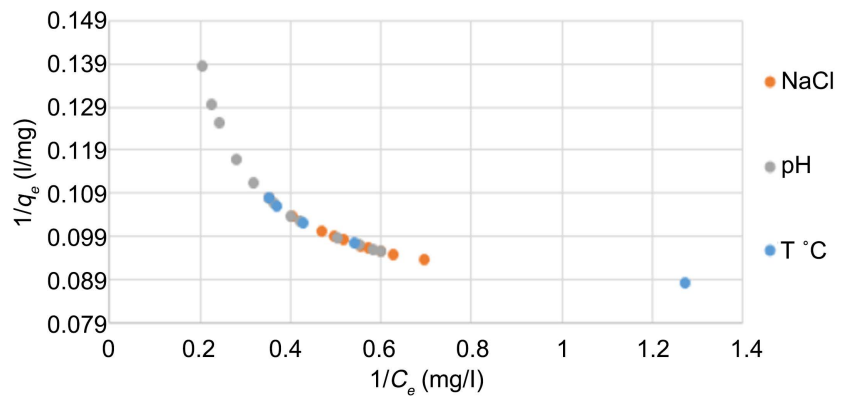


Figure 8. Modeling of Methylene blue desorption isotherm on grain activated carbon using the Langmuir III equation.

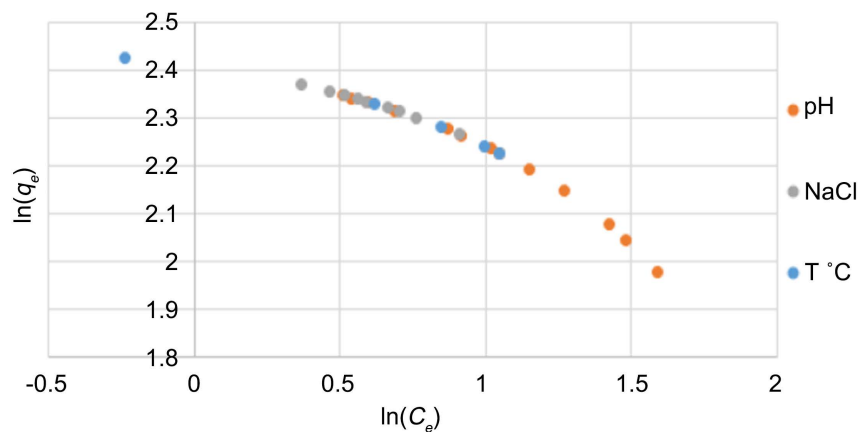


Figure 9. Modeling of Methylene blue desorption isotherm on grain activated carbon by the Freundlich equation.

Table 3. Parameters of the methylene blue desorption isotherm on raw coal in Grain.

		Temperature $T(^{\circ}\text{C})$	pH of NaCl	Concentration of NaCl
	Equation	$y = 0.1148x - 0.0254$	$y = 0.1554x - 0.1188$	$y = 0.1221x - 0.0447$
Isotherm Langmuir II	R^2	0.9967	0.9893	0.9982
	q_m	39.37	6.435	8.190
	K_L	40	1.308	2.731
	Equation	$y = -0.0192x + 0.1116$	$y = -0.0928x + 0.1459$	$y = -0.0403x + 0.1198$
Isotherm Langmuir III	R^2	0.8828	0.8475	0.9373
	q_m	8.961	6.854	8.347
	K_L	466.696	1.572	2.973
	Equation	$y = -0.1508x + 2.4009$	$y = -0.3243x + 2.5413$	$y = -0.2063x + 2.4534$
Isotherm Freundlich	R^2	0.9646	0.959	0.9842
	K_F	11.033	12.696	11.629
	$1/n$	0.1508	0.3243	0.2063

The figures show that the kinetics are the same. Of the three models, the Langmuir II model gives the highest R^2 . It appears that the phenomenon of desorption of methylene blue is better described by the Langmuir II model.

4. Conclusions

This study is part of both the general framework of environmental cleanup and the recovery of agricultural waste. The objective of the study is the removal of methylene blue adsorbed on activated carbon. The study was carried out in three joints:

- Study the influence of time and temperature on the desorption of BM from activated carbon.
- Study the influence of pH and NaCl concentration on the desorption of BM from activated carbon.
- Modeling the desorption isotherms of the BM of activated carbon.

Because of the results, it appears that:

- The desorption kinetics of the methylene blue dye (cationic base) of the coal leads to a 60-minute equilibrium time and a quantity of methylene blue remaining on the coal at equilibrium of 9.28 mg/g at 80°C.
- The amount of blue methylene dye desorbed from coal decreases with increasing pH of the adsorbent solution (NaCl).
- Similarly, the amount of blue methylene dye desorbed increases with increasing NaCl concentration.
- The amount of the desorbed methylene blue dye follows a first order kinetic model with two compartments and three parameters.
- The desorption of methylene blue is done according to the model of Langmuir II.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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