Kinetic and thermodynamic studies adsorption of Methylene Blue (MB) in aqueous solution on a bioadsorbent from *Cucumeropsis mannii* Naudin waste seeds

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ABSTRACT

The aim objectives of present study were to prepare a bioadsorbent from the seeds of *Cucumeropsis mannii* Naudin (BCM) and to examine its effectiveness in the removal of methylene blue (MB) from aqueous solution by adsorption process. The process of adsorption of MB onto BCM was optimizing by varying different parameters such as contact time, initial dye concentration, and temperature. The kinetic of adsorption was analyzed using pseudo-first-order and pseudo-second-order kinetic models. The experimental equilibrium data were examined using Langmuir and Freundlich isotherms. Thermodynamics parameters were also determined. The results show that the maximum adsorption percentage is 89% and the maximum adsorption capacity is 47 mg g\(^{-1}\) at 308 K. Isotherms studied showed that Freundlich model is the best model to describe adsorption of BCM onto MB. Kinetic studies show that the adsorption process follows pseudo second-order-kinetic model. The thermodynamic study indicated a negative value of \(\Delta H^\circ\) (\(-41 \text{ kJ mol}\(^{-1}\)) and shows that adsorption of MB on BCM is exothermic and essentially a chemical process. BCM is a potential bioadsorbent for the removal of MB from aqueous solution and can therefore be used for water purification process.

Keywords: *Cucumeropsis mannii* Naudin, methylene blue, adsorption, bioadsorbent, isotherms, kinetics and thermodynamics.

INTRODUCTION

The use of organic dyes in many industrial activities such as dyeing of leather, paper, textiles, wood, silk, plastics, in cosmetic, food and pharmaceutical industries is the basis of many inconveniences (Alouani et al., 2018). The presence of organic dyes in effluents has many impacts on ecological receptor environment and on humans. Madhura et al. (2014) indicate that wastewater from processes using organic dyes has high biological oxygen demand (BOD) and chemical oxygen demand (COD). Other researchers (Mauyra et al., 2008; Vanessa et al., 2017) report that organic dyes are the basis of several effects on human health. Some dyes are carcinogenic, mutagenic and teratogenic and are likely to cause several ailments such as nausea, hemorrhoids, skin and mucous ulcers, severe irritation of the respiratory system (Alouani et al., 2018).
Almost 5% to 25% of dyes applied on tissues are not fixed, and thus found in wastewater and likely to pollute waters, aquatic species, including fauna and flora. Organic dyes are persistent pollutants. Therefore, the removal of organic dyes from waste effluents becomes environmentally very important.

Several techniques for removing dyes especially methylene blue from wastewater are used and include biological, chemical, and physicochemical methods such as precipitation, coagulation and flocculation, membrane filtration, ion exchange, ozonation, irradiation and adsorption (Li et al., 2009; Zidane et al., 2011; Sun et al., 2012; Kassale et al., 2015; Miyah et al., 2017; Oliveira et al., 2017). Most of these methods are costly, require a lot of energy, produce huge amounts of sludge or generate derivatives that are sometimes more toxic than the initial products themselves (Masson et al., 2015; Tchuifon et al., 2015). Of all these methods for water treatment, adsorption is proving to be the most. Activated carbon is one of the most used adsorbents on this subject (Kifuani et al., 2012; Sark et al., 2015; Maazou et al., 2017). However, the cost of producing activated carbon is quite often very high. Many scientists worldwide are working on the preparation of low costs adsorbent materials from cheap and locally available precursors, found in renewable natural sources, such as agro-industrial wastes (Laximi et al., 2010; Yao et al., 2015; Kifuani et al., 2018).

Methylene Blue is one of the most used dyes in the dyeing of several products, especially silk, cotton and wood, and for temporary coloring of papers. It is used as a colored redox indicator, histologic dye, or antiseptic for superficial wounds treatment (Atef et al., 2009). By contact, MB is likely to cause eye burns in humans or animals. Inhalation induces respiratory difficulties and oral ingestion causes nausea, vomiting, sweating and abundant cold sweats (Kifuani, 2013).

This manuscript is a continuation of the work done by Kifuani et al. (2018), from which they made a preliminary study of MB adsorption onto BCM in different conditions of pH, time of contact, initial concentration and mass of adsorbent.

The aim objectives of present study were to prepare a biosorbent from seeds of Cucumeropsis mannii Naudin and to examine its effectiveness in the removal of MB from aqueous solution by adsorption. In this context, the effect of various parameters such as, contact time, initial dyes concentration and temperature on the adsorption efficiency of MB was evaluated. The adsorption kinetic was analyzed using the pseudo-first-order and pseudo-second-order kinetic models. The experimental equilibrium data were examined using Langmuir and Freundlich isotherms. Thermodynamics parameters were also determined.

MATERIALS AND METHODS

Preparation and characterization of the biosorbent

Biosorbent samples were prepared from seeds of Cucumeropsis mannii Naudin. The seeds were washed with tap water and then with distilled water. Washed, crushed and sieved barks (sieve with a mesh size ≤ 1 mm), the powder were dried at laboratory temperature and then in an oven (DEPATCH Oven Co) for 48 h at 45 °C. The resulting powder was stored in an airtight container. The preliminary characterization of Cucumeropsis mannii Naudin biosorbent (BCM) is presented in Table 1.

Preparation and analysis of dye solution

Adsorption capacity was determined using methylene blue as organic dye model; a commercial product was used without purification. Methylene blue is the prototype of medium-sized dyes. Different solutions were prepared by successive dilutions with distilled water of initial solution (1000 mg L⁻¹) to obtain 1 L of each of diluted solutions of concentrations ranging from 1 mg L⁻¹ to 100 mg L⁻¹. These solutions were analyzed, before and after adsorption, by UV-Vis spectrophotometry (Spectrophotometer HACK, model 1115) at λ_max= 662 nm. The
concentrations of the solutions were calculated using Beer-Lambert equation. The chemical structure of methylene blue is given in Figure 1.

**Batch adsorption tests**

The adsorption tests were carried out in discontinuous process, in hermetically sealed adsorber (LACOPE ADS X-3) containing 100 mL of MB solution 50 mg L$^{-1}$ and 800 mg of BCM bioadsorbent and the mixture was stirred gently with speed of 150 rpm at different times ranging from 0 min to 450 min, different concentrations (1 mg L$^{-1}$ to 100 mg L$^{-1}$) and different temperatures (308 K, 313 K, 318 K, 323 K and 328 K) to examine the effect of various parameters such as, contact time, initial dyes concentration and temperature on the adsorption efficiency of MB. The stirring time was set at 180 min, within the equilibrium field, for all experimental temperatures. After stirring, the suspension was centrifuged (centrifuge LABOFUGE 200 HERAEUS) at 3000 rpm for 30 minutes. After centrifugation, the filtrates were analyzed at 662 nm using a HACK 1115 spectrophotometer, and the adsorption capacity of BCM bioadsorbent was determined from the following equation (Kassale et al., 2015):

$$Q_e = \frac{(C_o - C_e)V}{m_B}$$  \[1\]

Where $Q_e$ is the adsorption capacity of bioadsorbant (mg g$^{-1}$), $C_o$ the initial concentration of MB solution (mg L$^{-1}$), $V$ the solution volume (L), $C_e$ the equilibrium concentration of adsorbate (mg L$^{-1}$) and $m_B$ the bioadsorbent mass.

The percentage of adsorption (%Ads) of MB on the BCM bioadsorbent is given by the following equation (Saeed et al., 2010):

$$% Ads = \frac{C_o - C_e}{C_o} \times 100$$  \[2\]

**Modeling the kinetic of the adsorption**

The modeling of MB adsorption kinetics on BCM bioadsorbent was done using pseudo-first-order and pseudo-second-order kinetic models. The kinetic models commonly used for surface reaction are Lagergren pseudo-first-order and Lagergren pseudo-second-order. The equations usually used are as follows (Saeed et al., 2010):

**Pseudo-first-order -Lagergren kinetic model:**

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$  \[3\]

$$\ln(q_e - q_t) = \ln q_e - k_1t$$  \[4\]

**Pseudo-second-order-Lagergren kinetic model:**

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$  \[5\]

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2t$$  \[6\]

In this study, the kinetic models were applied using kinetic equations developed by Kifuani et al.

**Pseudo-first-order -Kifuani kinetic model** (Kifuani et al., 2012):

$$\ln \left(\frac{q_e}{q_e - q_t}\right) = k_1t$$  \[7\]

Where $q_e$ and $q_t$ are adsorption capacity at equilibrium and at time t, respectively (mg g$^{-1}$), $k_1$ is the rate constant of pseudo-first-order adsorption (min$^{-1}$).

**Pseudo-second-order- Kifuani kinetic model** (Kifuani et al., 2012):

$$\frac{q_t}{q_e(q_e - q_t)} = k_2t$$  \[8\]

Where, $k_2$ is the rate constant of pseudo-second-order adsorption (g mg$^{-1}$ min$^{-1}$).

**Modeling the adsorption isotherms**

Modeling the adsorption isotherms was made using Langmuir and Freundlich equilibrium models.
The Langmuir model

The Langmuir model (Alouani et al., 2018) has been used in its linear form given by the following equation:

\[
\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m . K_L . C_e} \quad [9]
\]

Where \( Q_e \) is the amount of solute fixed per unit mass of adsorbent (apparent adsorption capacity) (mg g\(^{-1}\)), \( Q_m \) represents the maximum amount of solute fixed per unit of adsorbent mass (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of the adsorbate (mg L\(^{-1}\)) and \( K_L \), the Langmuir constant related to rate of adsorption.

The equilibrium parameter (\( R_L \)) is defined by the following equation (Alouani et al., 2018):

\[
R_L = \frac{1}{1 + K_L . C_o} \quad [10]
\]

Where \( K_L \) is the Langmuir constant (L mg\(^{-1}\)) and \( C_o \), the initial dye concentration (mg L\(^{-1}\)).

The Freundlich model

The linear equation of Freundlich (Miyah et al., 2017) is given by the following equation:

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad [11]
\]

Where \( Q_e \) is the amount adsorbed at equilibrium (mg L\(^{-1}\)), \( C_e \) the equilibrium concentration of adsorbate, \( K_F \) the Freundlich constant, a constant related to the adsorption capacity; it is therefore the capacity of adsorption when equilibrium concentration is unitary. The dimensionless constant \( n \) is related to the adsorption intensity.

Thermodynamic parameters

Adsorption tests were performed at five different temperatures: 308 K, 313 K, 318 K, 323 K, and 328 K. The variation of the standard free enthalpy (\( \Delta G^o \)) is calculated according to the equation (Li et al., 2009):

\[
\Delta G^o = -RT \ln K_L \quad [12]
\]

Where \( R \) is the gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the absolute temperature (K) and \( K_L \) is the Langmuir constant (mg L\(^{-1}\)).

The variation standard enthalpy (\( \Delta H^o \)) and the variation standard entropy (\( \Delta S^o \)) were determined using Van’t Hoff equation (Li et al., 2009):

\[
\ln K_L = \left( \frac{\Delta S^o}{R} \right) - \left( \frac{\Delta H^o}{R} \right) \frac{1}{T} \quad [13]
\]

Table 1: Characteristics of the BCM bioadsorbent.

| Parameters    | Values     |
|---------------|------------|
| Particle size | \( \leq 1 \, \text{mm} \) |
| Humidity (%)  | 7.08       |
| Dry matter (%)| 92.92      |
| Ash (%)       | 03.20      |
| pH\(_{ZPC}\)  | 05.02      |
| \( S_{BM} \) (m\(^2\) g\(^{-1}\)) | 251.87     |

Figure 1: Chemical structure of Methylene Blue.
RESULTS
Characteristics of the bioadsorbent
These characteristics are given in Table 1. It is observed that BCM has a high specific surface area (251.87 g cm\(^{-3}\)). The pH\(_{PZC}\) indicates that the surface of the bioadsorbent is zero at pH 5.02. Beyond this value, the surface of the bioadsorbent has a negative charged surface and below that pH, the surface is positively charged. All experiments were conducted at auto-equilibrium pH (6.67).

Effect of time on adsorption
The effect of time on adsorption was studied by mixing a solution of BM 50 mg L\(^{-1}\) with 800 mg of bioadsorbent. The adsorption time was varied from 0 min to 450 min and the temperature was varied from 308 K to 328 K. The results obtained are presented in Figures 2 to 4. The results of Figure 2 show a decrease in residual concentration with mixing time, and after a given time, the reduced concentration remains constant. The apparent adsorption capacity (\(Q_e\)) and the apparent adsorption percentage capacity (%Ads) increase with the contact time BCM-MB at different temperatures, until a maximum value which remains constant despite the increase in time (Figures 3 and 4). This maximum value corresponds to maximum adsorption capacity or the maximum adsorption percentage (Table 2).

Modeling of the adsorption kinetics
Modeling of MB adsorption kinetics on BCM bioadsorbent was done using pseudo-first-order and pseudo-second-order kinetic models for surface reaction. The kinetic parameters of those models are given in Table 3.

The adsorption isotherms of MB
The adsorption isotherms are shown in Figure 5. All isotherms are S-shaped with initial concavity facing downwards (308 K, 313 K and 323 K) or upward (318 K and 328 K).

Modeling the Adsorption Isotherms
Modeling the adsorption isotherms was made using the Langmuir and Freundlich models. The Langmuir and Freundlich parameters and the correlation coefficients are recorded in Table 4.

Effect of adsorption temperature and thermodynamic parameters
Adsorption tests were performed at five different temperatures 308 K, 313 K, 318 K, 323 K, and 328 K. The results in Figures 6 and 7 show a decrease in the maximum adsorption capacity with increasing temperature. The variation in standard enthalpy (\(\Delta H^0\)) and standard entropy (\(\Delta S^0\)) were determined using Van't Hoff relationship, and results on the variations in the standard free energy (\(\Delta G^0\)), standard enthalpy (\(\Delta H^F\)), and standard entropy (\(\Delta S^F\)) of the adsorption process are given in Table 5.

Figure 2: Residual concentration (\(C_r\)) vs. contact time at different temperatures.
(pH: 6.67; \(m_{BCM}\): 0.8 g; \(V\): 100 mL.)
Figure 3: Effect of contact time on adsorption capacity of BCM ($Q_e$) at different temperatures. (pH: 6.67; $m_{BCM}$: 0.8 g; V: 100 mL).

Figure 4: Effect of contact time on the percentage of MB adsorption on BCM at different temperatures. (pH: 6.67; $m_{BCM}$: 0.8 g; V: 100 mL).
Figure 5: The adsorption isotherms of MB on the bioadsorbent BCM at different temperatures. (pH: 6.67; m<sub>BCM</sub>: 0.8 g; V: 100 mL).

Table 2: Maximum adsorption capacity, percentage of adsorption and MB adsorption equilibrium time at different temperatures.

| Temperature (K) | Q<sub>m</sub> (mg g<sup>-1</sup>) | % Ads | ET (min) |
|-----------------|-------------------------------|-------|---------|
| 308             | 5.6                           | 89.00 | 150     |
| 313             | 5.5                           | 88.13 | 150     |
| 318             | 5.4                           | 86.75 | 90      |
| 323             | 5.4                           | 86.75 | 90      |
| 328             | 5.4                           | 85.88 | 150     |

ET: equilibrium time; V: 100 mL; C<sub>i</sub>: 50.0 mg L<sup>-1</sup>; pH: 6.67.

Table 3: Pseudo-first-order and pseudo-second-order parameters for the adsorption of MB onto BCM at different temperatures.

| T (K) | Pseudo-first-order parameters | Pseudo-second-order parameters |
|-------|-------------------------------|--------------------------------|
|       | k<sub>1</sub> (min<sup>-1</sup>) | R<sup>2</sup> | k<sub>2</sub> (g mg<sup>-1</sup> min<sup>-1</sup>) | R<sup>2</sup> |
| 308   | 0.0077                        | 0.9616 | 0.0228 | 0.8397 |
| 313   | 0.0064                        | 0.9690 | 0.0148 | 0.9468 |
| 318   | 0.0030                        | 0.9000 | 0.1595 | 0.9651 |
| 323   | 0.0300                        | 0.9000 | 0.1595 | 0.9651 |
| 328   | 0.0084                        | 0.3599 | 0.0663 | 0.3022 |

V: 100 mL; C<sub>i</sub>: 50.0 mg L<sup>-1</sup>; pH: 6.67.
Table 4: Langmuir and Freundlich parameters for the adsorption of MB onto BCM at different temperatures.

| T(K) | Langmuir parameters | Freundlich parameters |
|------|----------------------|-----------------------|
|      | $Q_m$ (mg g$^{-1}$)  | $K_L$ (L mg$^{-1}$)  | $R_L$ | $R^2$ | $K_F$ | $1/n$ | $R^2$ |
| 308  | 47.9                 | 0.026                 | 0.4308 | 0.9136 | 1.1580 | 0.9549 | 0.9384 |
| 313  | 46.1                 | 0.025                 | 0.4435 | 0.9907 | 1.0543 | 0.9512 | 0.9785 |
| 318  | 44.3                 | 0.029                 | 0.4064 | 0.9600 | 0.8968 | 1.0173 | 0.9661 |
| 323  | 70.6                 | 0.015                 | 0.5785 | 0.9558 | 0.8639 | 1.0276 | 0.9761 |
| 328  | 237.5                | 0.004                 | 0.8419 | 0.9055 | 0.8476 | 1.0077 | 0.9519 |

*K$_F$ unit: (mg g$^{-1}$) (mg L$^{-1}$)$^{-1/n}$; V: 100 mL; C$_i$: 50.0 mg L$^{-1}$; pH: 6.67.

Figure 6: The maximum adsorption capacity ($Q_m$) vs. Temperature. (pH: 6.67; $m_{BCM}$: 0.8 g; V: 100 mL).

Figure 7: The maximum percentage of adsorption vs. Temperature. (pH: 6.67; $m_{BCM}$: 0.8 g; V: 100 mL).

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Table 5: Thermodynamic parameters for the adsorption of MB onto BCM at different temperatures.

| $T$ (K) | $-\Delta S^\circ$ (J mol$^{-1}$) | $-\Delta H^\circ$ (kJ mol$^{-1}$) | $+\Delta G^\circ$ (kJ mol$^{-1}$) | $+\Delta G$ (kJ mol$^{-1}$) |
|--------|---------------------------------|-------------------------------|---------------------------------|--------------------------|
| 298    |                                 |                               |                                 | 2.72                     |
| 308    |                                 |                               |                                 | 6.53                     |
| 313    | 381.03                          | 110.83                        | 2.72                            | 8.44                     |
| 318    |                                 |                               |                                 | 10.34                    |
| 323    |                                 |                               |                                 | 12.24                    |
| 328    |                                 |                               |                                 | 14.15                    |

$V$: 100 mL; $C_i$: 50.0 mg L$^{-1}$; pH: 6.67.

Effect of adsorption time

The increase of adsorption percentage and adsorption capacity with time of contact (mixing time) BCM-MB is due to the availability of free adsorption sites on the surface of the bioadsorbent at the first contact. These sites are gradually saturated. The curves of Figures 3 and 4 show, at the beginning, a rapid increase in adsorption, which is due to the scattering (or external diffusion) of the particles of the adsorbate, characterized by the transfer of the solute through the film located on the geometric surface of the adsorbent. It is also observed a low growth in the percentage of adsorption over time, represented by the tangential part of each curve. This step characterizes an intraparticular diffusion of the matter in which the particles of the adsorbate are transferred through the outer and the inner surfaces of the bioadsorbent (Masson et al., 2015).

The plateau observed represents the surface reaction step, characterized by the fixation of the adsorbate particles on the inner surface at the active sites of micropores, because of the specific or non-specific interactions established between adsorbate particles and active sites of the bioadsorbent. The plateau indicates that the maximum removal rate of 89.00% was achieved at 308 K for pH 6.67 (Table 2). The increase in adsorption capacity as a function of contact time is due to the availability of adsorption sites, as soon as adsorption begins. The resulting plateau indicates the saturation of the available adsorption sites. The maximum adsorption capacity of bioadsorbent ($Q_m$) is then achieved (Hameed et al., 2007).

Adsorption isotherms

The S-shaped isotherms indicate a multilayer adsorption (Ertaş et al., 2010; Kifuani, 2013). The initial downward-facing concavity (at 308 K, 313 K and 323 K) suggests a cooperative adsorption in which the adsorbed molecules favor the fixation of other molecules that are still free at the heart of the solution. This downward-facing concavity also indicates that the solute molecules adsorb vertically to the surface of bioadsorbent. The initial upward-facing concavity (at 318 K and 328 K) indicates the formation of multilayers of solute in solution at low concentrations. This type of isotherms reflects the existence of strong interactions between solute molecules, as compared to the interactions between solute molecules and adsorbent (Kifuani et al., 2013).

Modeling of the adsorption kinetics

The overall correlation coefficient (0.9327) obtained with pseudo-first-order-kinetic model is significantly higher than that obtained (0.9292) for pseudo-second-order kinetic model. This indicates that pseudo-first-order kinetic model is more appropriate to describe adsorption of MB on BCM bioadsorbent (Vasanth et al., 2007). The correlation with pseudo-first-order model shows that adsorption is governed by the surface reaction, characterized by the binding of MB molecules to the surface of bioadsorbent. This correlation coefficient less
than unity does not preclude other adsorption mechanisms.

**Modeling the adsorption isotherms**

The experimentally calculated values of Langmuir and Freundlich isotherm parameters are presented in Table 4. From the Table 4, it could be seen that Freundlich isotherm with a global correlation coefficient value, $R^2$, of 0.9622 is the most suited isotherm rather than Langmuir isotherm ($R^2$: 0.9451) to describe the adsorption of MB dye onto BCM bioadsorbent. The correlation with Freundlich model implies formation of multilayer on bioadsorbent surface (Laximi Gayatri et al., 2010; Saeed et al., 2010; Alouani et al., 2018).

The $1/n$ Freundlich parameter is related to the adsorption intensity, or to the strength of the adsorption interactions. It also indicates the relative distribution of energy sites for adsorption and depends on both nature and strength of the adsorption process (Sugana et al., 2010; Kifuani, 2013). It is reported that if the value of $1/n$ is equal to 1, the adsorption is linear. If it is greater than 1, the adsorption is physical; and, if its value is less than 1, adsorption is a favorable chemical process. Values of $1/n$ obtained are less than 1 (at 308 K and 313 K), thus indicating that the adsorption of MB on the BCM is favorable and corresponds to a process of chemical adsorption. At higher temperatures the values of $1/n$ are greater than 1, suggesting an unfavorable adsorption at these temperatures. This corroborates the decrease in adsorption capacity observed with increasing temperature (Table 2).

The equilibrium parameter (or separation parameter), $R_L$, represents the nature of adsorption phenomenon, which can be favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$) or irreversible ($R_L = 0$) (Kifuani et al., 2012). The values of $R_L$ (Table 4) between 0 and 1 obtained in this work indicate that the adsorption is a favorable and a chemisorption process. The calculated maximum adsorption capacities (Table 4) indicate that BCM is a potential bioadsorbent for the removal of methylene blue from aqueous medium and can therefore be used for water purification treatment.

**Effect of adsorption temperature**

The decrease of the maximum percentage capacity and the maximum adsorption capacity with increasing temperature is explained by desorption of BM molecules with temperature due to the decrease in interactions between superficial functions of the bioadsorbent and those of the adsorbate (Alouani et al., 2017). The increase in temperature increases the mobility of adsorbate molecules, resulting in a decrease in adsorption.

**Thermodynamic parameters**

The negative values of $\Delta H^\circ$, higher than 41 kJ mol$^{-1}$ (Table 5) show that the adsorption of MB on BCM is exothermic and essentially a chemical process (Miyah et al., 2017). A negative value of entropy, $\Delta S^\circ$, indicate that the disorder of the molecules decrease in the interface between MB dye and BCM bioadsorbent. From Table 5, it could be seen that the standard free enthalpy have a positive value, which indicate a non-spontaneous adsorption process (Li et al., 2009).

**Conclusion**

Adsorption of Methylene Blue onto BCM at five temperatures was investigated. Adsorption tests were carried out in discontinuous process. Results obtained in this work show that, at different temperatures, adsorption capacity and percentage of adsorption increase with time of adsorption until a maximum value which remains constant despite the increase in time. This increase is due to the availability of free adsorption sites at bioadsorbent surface at the first contact. All isotherms obtained in this study are S-shaped, with initial concavity facing downwards (308 K, 313 K, and 323 K) or upward (318 K and 328 K) and suggest a multilayered adsorption. The kinetic studies indicate that pseudo-first-order model is better to describe adsorption of MB onto BCM. The negative value of standard enthalpy of adsorption, $\Delta H^\circ$, and its
magnitude (-41 kJ mol\(^{-1}\)) shows that the adsorption of MB on BCM is exothermic and essentially a chemical process. Therefore, the adsorption under study is more efficient at low temperatures. Values of 1/n less than unity indicate that the adsorption of the BM on BCM is chemically favored at 308 K and 313 K. The maximum adsorption capacities indicate that BCM is a potential bioadsorbent for the removal of methylene blue from aqueous environment and might be used as a water treatment technique.

**COMPETING INTERESTS**
The authors declare that they have no competing interests.

**CONTRIBUTIONS OF THE AUTHORS**
KMK. and AKKM are the main investigators of this study and have participated in all the stages of the research. BIL, GEB, TMO, JML and PNB have contributed to data processing and discussion of results.

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