Methylene blue (MB), or tetramethylthionine chloride (fig. 1), is a cationic dye and one of the most widely used pigments in the dyeing industry [19]. It is a water-soluble, dispersible, aromatic, synthetic organic compound with potential applications in industry. From an environmental perspective, the disposal of synthetic dyes is a major concern because some dyes and their breakdown products are carcinogenic and toxic [1, 2]. Furthermore, the discharge of colored effluents into the environment is not only unpleasant but also represents a real danger for humans and their environment, due to their stability and their low biodegradability [3]. Concentrations of these toxic pollutants in wastewater far exceed limits set by the World Health Organization (WHO) and the Environmental Protection Agency (EPA) in many countries [4]. The expansion of industrial activities (pharmaceuticals, cosmetics, textiles, plastics, etc.) is often accompanied by environmental pollution. Pollutants generated by these activities are generally released into the environment without prior treatment and are likely to reach groundwater and pose public health problems. Among these pollutants, is methylene blue, used in wood and paper dyeing and in the pharmaceutical industry. However, methylene blue can cause permanent breathing difficulties, nausea, vomiting, gastritis, mental confusion, tissue necrosis, etc. [5]. To prevent the harmful effects of methylene blue, several physicochemical and biological methods have been developed to remove these dyes, including adsorption, nanofiltration, electrochemical oxidation, precipitation, ozonation, electrocoagulation etc. [6, 7]. Thus, several methods have been used to reduce the harmful effects of effluent discharges, such as biological methods, but the results obtained have often been unsatisfactory due to the composition and nature of these discharges, which were difficult to biodegrade [8, 9]. Indeed, some of these methods had revealed their limits, linked on the one hand to the production of toxic by-products and on the other hand, to the sometimes very high financial cost of their implementation. To overcome these difficulties, research is increasingly moving towards less expensive, flexible and efficient adsorption methods [10, 11]. These alternative methods showed a remarkable elimination of methylene blue. However, parameters such as particle size, adsorbent mass, pH, contact time, initial methylene blue concentration, agitator speed and temperature showed that the adsorption capacity of MB on biosorbents was influenced by these quantities. Similarly, the positive and negative enthalpy values (ΔH°) indicated that adsorption process could be endothermic or exothermic. Other thermodynamic parameters, such as the negative value of Gibbs free energy (ΔG°) and the positive value of entropy (ΔS°), also showed that the adsorption process was feasible and spontaneous.

**Keywords:** Adsorption, Methylene blue, Biosorbents, Thermodynamic, Physico-chemical
The environment, the surface of the deactivated lichen is charged with positive ions (H\(^+\)), making it more difficult to adsorb the positively charged MB. For this reason, several studies have reported the effect of pH on MB adsorption rates over a wide range of values from pH = 1 to pH = 12 [39].

Effect of contact time
The contact time corresponds to the adsorption/desorption equilibrium, or equilibrium state in which the substrate saturates the support. Analysis of the results showed that the amounts of adsorbed dyes increased with contact time [24–26], then subsequently, the curves described a plateau, reflecting the biosorption chemical equilibrium. This balance could be explained by the occupation of the majority of sites by coloring molecules. The results also showed that the elimination rate increased rapidly, reaching 50% in the first minutes of the experiment, after which the increase was slow until equilibrium was reached. The increase in removal rate in the first part might be due to the availability of more vacant adsorption sites on the adsorbent surface at the initial stage of adsorption. Additionally, the MB molecules were relatively medium in size and could be easily diffused into the internal pores of the adsorbent until saturation, which would reduce the mass transfer between the liquid and solid phases over time. This would result in a reduction in the adsorption rate, and a plateau corresponding to the stationary state would be observed, that is to say a saturation of the sites available on the adsorbent.

Effect of initial dye concentration
The study of the effects of MB concentration on adsorption capacity was carried out with known initial MB concentrations while keeping all other conditions constant. The reported data showed that the increase in initial MB concentration was proportional to the adsorption capacity of the biosorbent [27, 28]. These results could be explained by the accelerated diffusion of MB ions on the adsorbent due to the increased driving force of the concentration gradient between the dye ions and the adsorbent. This would lead to increased mass transfer of MB ions onto the adsorbent surface. The increase in adsorption capacity could be attributed to the ratio of available active adsorption sites to the initial number of MB molecules. These results were in agreement with those observed in other works [29, 30]. However, at higher MB concentrations, lower adsorption efficiencies were observed due to saturation of the adsorption sites [31, 32].

Effect of adsorbent dose
The dose of biosorbent is also one of the parameters that can have a major impact on the adsorption process. Indeed, results reported in various studies showed that the removal rate gradually increased with increasing biosorbent dose while the adsorption capacity decreased [33, 34]. The increase in MB removal rate could be attributed to greater availability of adsorption active sites and functional groups on the biosorbent surface at the beginning of the experiment. However, the continuous increase in the adsorbent dose could represent a limit to the adsorption phenomenon due to the possible formation of an agglomerate which would disrupt the binding of the MB.

Effect of stirring speed
The reported results showed an increase in the amount of biosorbed MB as a function of shaking speed at relatively moderate values. However, at very high stirring speeds, a decrease in dye adsorption was observed [35]. This could be explained by the fact that an increase in the stirring speed would make the suspension inhomogeneous and, therefore, the binding of the dye ions to the surface of the biosorbent would be disrupted.

Effect of pH
pH is an important factor in studying the adsorption process because it could influence both the structure of the adsorbent and adsorbate, as well as the adsorption mechanism. Indeed, pH could affect both the surface charge of the material as well as the distribution and speciation of cations [36–38]. For this reason, several studies have reported the effect of pH on MB adsorption rates over a wide range of values from pH = 1 to pH = 12 [39]. In these studies, the pH of the solution was adjusted to the desired values by adding solutions (0.1 N) of hydrochloric acid (HCl), nitric acid (HNO\(_3\)) or sodium hydroxide (NaOH). The mixtures were stirred at constant speed for homogenization for one hour then filtered. Then, to elucidate the role of the net charge carried by the adsorbent surface in the binding of dye ions, the pH of zero charge point (pH\(_{PZC}\)) was determined. This point corresponds to the pH value of the medium for which the resultant of the positive and negative charges on the surface is zero. In the example of the net charge carried by the adsorbent surface in the binding of dye ions, the pH of zero charge point (pH\(_{PZC}\)) was determined. This point corresponds to the pH value of the medium for which the resultant of the positive and negative charges on the surface is zero. In the example of the study on the adsorbent obtained from the deactivated Parmotrema didlatatum lichen, the pH\(_{PZC}\) was 6.5. Consequently, in a strongly acidic pH environment, the surface of the deactivated lichen is charged with positive ions (H\(^+\)), making it more difficult to adsorb the positively charged MB cationic dye in aqueous solution. As pH approaches the pH\(_{PZC}\) value, the number of positively charged sites decreases while the number of negatively charged sites increases. This favors MB adsorption by electrostatic attraction between hydroxide ions (OH\(^-\)) and cationic dye ions. However, an opposite trend was observed for a strongly acidic pH medium in the case of an anionic dye such as orange II. Indeed, the surface of the deactivated lichen is charged with positive ions (H\(^+\)), which promotes the adsorption of the anionic dye by electrostatic attraction between the cationic and anionic ions [40, 41]. In most studies, in the pH range above 5, it was noted that the adsorbed amount could exceed 50% [42, 43]. This could be explained by the fact that at low pH (acidic environment), the surface of the adsorbent would be surrounded by H\(^+\) ions, thus reducing the interaction of MB ions (cationic dye) with the adsorbent sites due to electrostatic repulsion and competition between H\(^+\) ions and cationic dye for adsorption sites. On the other hand, at higher pH values (basic medium), the concentration of H\(^+\) ions decrease, resulting in good interaction between the dye ions and the adsorbent surface. A similar observation was reported for the adsorption of MB onto wheat bran [44]. In the case of anionic dyes, as the pH increases, the number of negatively charged sites increases and there is competition between the negatively charged hydroxide ions and the anionic dye for sorption sites, and the adsorption rate decreases [45].
Effects of temperature and thermodynamic parameters

Temperature is also a factor that can affect the adsorption process. Thus, in order to determine the optimal temperature to obtain optimal adsorption capacity, several studies were carried out at different temperatures ranging from 0 to 60 °C. According to the reported results, the adsorption capacity of MB increased with temperature, reaching a maximum at a temperature of 25 °C. However, above this temperature value, a gradual decrease in dye removal efficiency was observed, revealing that the adsorption of MB onto the adsorbent was exothermic in nature. Thus, overheating would negatively affect the adsorption process in accordance with Le Chatelier's principle, which could lead to an increase in desorption kinetics [46, 47]. Thus, according to these results, increasing temperature is detrimental to the adsorption phenomenon and consequently, the best results were obtained in the room temperature range. However, other results also revealed that the amount of dye adsorbed was proportional to the increase in temperature, indicating that the adsorption phenomenon could also be endothermic in nature [48]. This increase in adsorption with increasing temperature could be explained by adsorbent-adsorbate chemical interactions leading to the creation of new adsorption sites depending on the matrices studied. This effect of temperature on MB adsorption capacity was determined in these studies depending on the matrices studied. This effect of temperature on MB adsorption capacity is consistent with the results obtained by Khelifi et al [49]. In addition, thermodynamic parameters such as enthalpy variation (\(\Delta H^\circ\)), entropy variation (\(\Delta S^\circ\)) and Gibbs free energy (\(\Delta G^\circ\)) were determined in the various works to assess the feasibility and nature of the adsorption process. Indeed, a negative value of \(\Delta H^\circ\) indicates an exothermic process and a positive value indicates an endothermic process. On the other hand, the parameters \(\Delta S^\circ\) and \(\Delta G^\circ\) were used to identify the feasibility and spontaneity of the sorption process. The Gibbs free energy (\(\Delta G^\circ\)) of the adsorption reaction was determined in these studies from the following equation:

\[
\Delta G^\circ = -RT\ln K_c
\]

Where \(K_c\) is the thermodynamic equilibrium constant, \(T\) is the temperature, \(R\) is the perfect gas constant (8.32 J mol\(^{-1}\)K\(^{-1}\)).

Similarly, the relationship between \(\Delta G^\circ\), \(\Delta H^\circ\) and \(\Delta S^\circ\) was expressed by the following equations:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

\[
\ln K_c = -\frac{\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

The results reported in these studies showed a negative value for the enthalpy variation (\(\Delta H^\circ\), kJ mol\(^{-1}\)), confirming the exothermic nature of MB ion adsorption to the adsorbent surface. In addition, the negative value of the Gibbs free energy (\(\Delta G^\circ\), en kJ mol\(^{-1}\)) and the positive value of the entropy (\(\Delta S^\circ\), J mol\(^{-1}\) K\(^{-1}\)) revealed that the adsorption process was feasible and spontaneous [50, 51]. Similar results were obtained by Srivastava and al. [52]. The evolution of the \(\Delta G^\circ\) value towards increasingly negative values with increasing temperature confirmed that MB adsorption was favored with increasing temperature [53]. Other works have also reported a positive value of \(\Delta H^\circ\) during the methylene blue adsorption process, indicating the endothermic nature of the methylene blue adsorption process. This same trend towards the endothermic nature of the methylene blue adsorption process has also been reported in other works [54, 55].

CONCLUSION

According to the results reported in these various works, physicochemical and thermodynamic parameters had a strong influence on the adsorption process of methylene blue by biosorbents. Consequently, their values should be monitored when studying the adsorption process in order to obtain the best results.

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CONFLICT OF INTERESTS

The authors declare that they have no conflict of interest.

REFERENCES


