

Experimental study of methylene blue adsorption from aqueous solutions onto natural Algerian goethite

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ABSTRACT

The objective of this work is to study and model the methylene blue (MB) sorption, from aqueous solutions by goethite. The equilibrium time was reached during 10 min of agitation with 26.21 % efficiency. MB removal efficiency is improved with an increased absorbent dose (0.5–08 g/L) for an initial 10 mg/L concentration. Treatment efficiency decreases with the increase of initial MB concentration (2–100 mg/L). The best adsorption yields were obtained in basic media. MB sorption kinetics via goethite leads to several results as to mechanisms that govern kinetics and isotherms equilibrium: Blanchard's model provides a better fit of the experimental results compared to Lagergren's model. Thus, the MB sorption kinetics is described by the pseudo-second order. Particle diffusion is involved in the MB removal mechanism, but it is not the only limiting step and the Boyd model application confirms that diffusion in the pores is the limiting step of the MB sorption process. The Elovich model is well verified and translated probably the existence of chemical-type interactions between MB and goethite. The study of MB adsorption isotherms showed that Freundlich, Temkin, and Elovich models are the best adapted than the Langmuir model. Finally, we can assess that goethite can be an interesting natural adsorbent for MB elimination from polluted waters in basic environments.

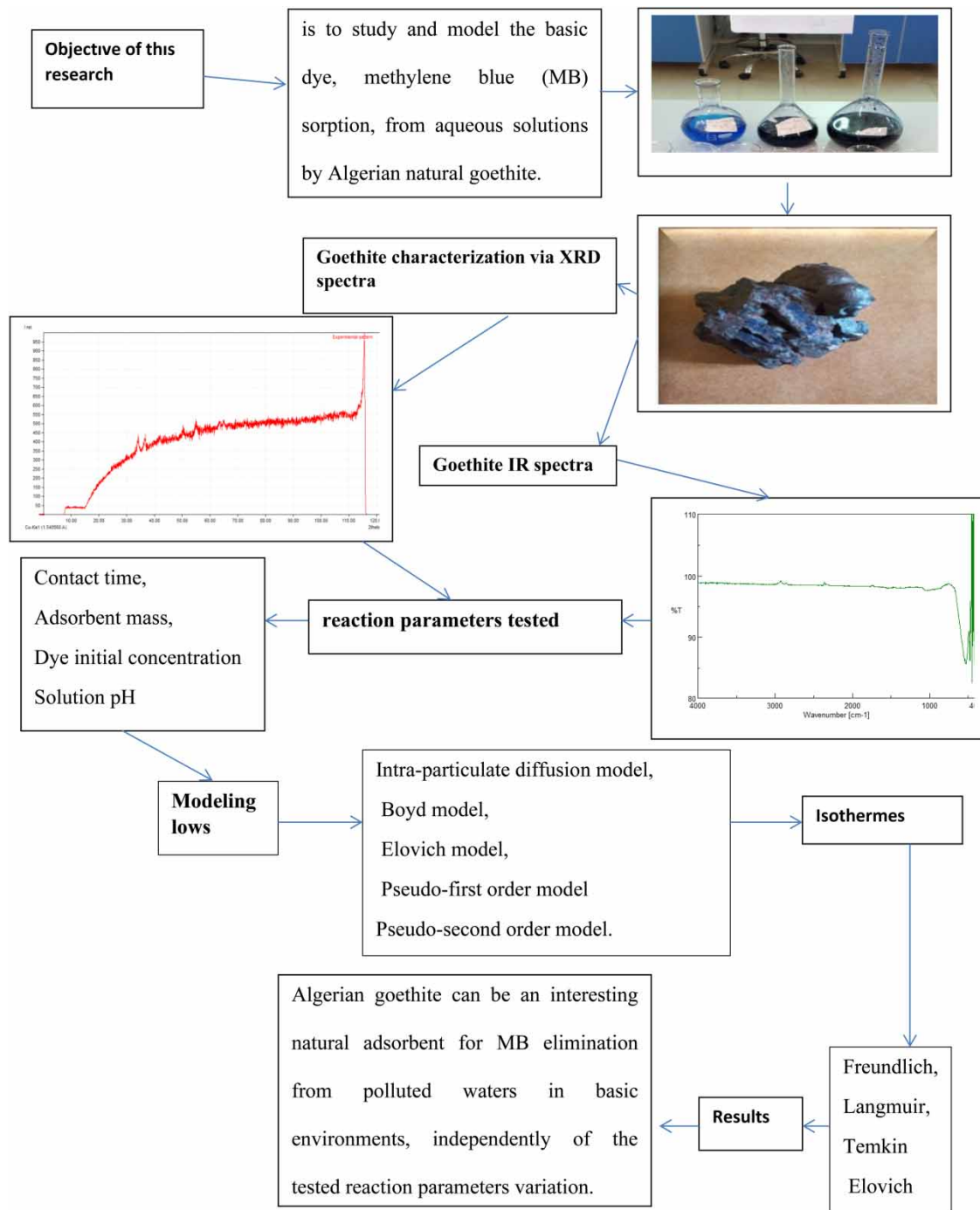
Key words: adsorbents, basic dye, kinetics and isotherms, modeling, wastewater treatment, water pollution

HIGHLIGHTS

- Using goethite as an adsorbent for removing MB offers a potentially effective, economical, and environmentally friendly solution for treating contaminated water.
- The influence of operating parameters can also be integrated into the reflections on the use of the adsorption technique.
- MB sorption kinetics via goethite leads to several results regarding mechanisms that govern kinetics and isotherms equilibrium.

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GRAPHICAL ABSTRACT



1. INTRODUCTION

Environmental protection is a major problem for humanity. An essential and vital aspect involves water resource preservation; they are threatened by diffuse and multifaceted pollution aggravated by progress in human well-being, uncontrolled industrialization and galloping demography (Benaissa 2011). Water and soil pollution, accidentally or deliberately caused by some chemical products of industrial (dyes, hydrocarbons, phenols, etc.) or agricultural (pesticides, fertilizers, etc.) origin has now become a crucial problem and of great concern since it constitutes a source of environmental degradation and currently arouses particular interest at an international level (Boumelik 2017).

The presence of dyes in water, even in meager quantities, is highly visible and undesirable, color interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota, and interferes with gas solubility in water bodies (Garg *et al.* 2004; Wang *et al.* 2005; Hamdaoui 2006; Özer & Dursun 2007).

In this study, we have considered the methylene blue (MB) dye (methylthionium chloride) case, an organic molecule belonging to the Xanthenes family. It is chosen as a representative model of medium-sized organic pollutants and is used to test the solid's adsorbent powers and determine its specific surface area. MB toxicity is the measure of a substance's ability to cause adverse effects on any form of life (Messemeche 2014).

As per Sebrou & Sebgag (2001), the toxicological data relating to the use of MB in humans for many years have so far indicated the absence of danger linked to the use of this product as a drug. The total dose administered must not exceed 7 mg/kg.

According to Kheda & Maziri (2019), at high doses, it can cause chest pain, dyspnea, anxiety, tremors, hypertension, and even skin discoloration. MB is not highly hazardous but has harmful effects on living organisms and water; prolonged exposure to this product will cause:

- *Via external exposure*: skin irritation and permanent eye damage (Saidi 2013; Chemlal & Erriri 2019).
- *Via inhalation*: rapid or difficult breathing and increased heart rate (it may cause short periods of rapid or difficult breathing) (Rezaiguia 2017; Kheda & Maziri 2019).
- *Via ingestion*: irritation of the gastrointestinal tract, vomiting, nausea, profuse sweating, mental confusion, cyanosis, and necrosis of human tissues (Rezaiguia 2017; Belazizia 2018).

Several pollution control methods and techniques have been developed in recent years. Among these techniques, membrane filtration, coagulation/flocculation (Yahia Cherif 2013), heterogeneous photocatalysis (Fodil Cherif *et al.* 2014), and adsorption on different materials such as clays (Daouadi & Hamdi 2012; Lakhache 2017; Batana *et al.* 2019; Bengaid 2021). Coals (Messemeche 2014; Medekhel 2018), hydroxides (Kaidari 2017; Chedik & Belmiloud 2019; Harizi 2020; Wang *et al.* 2021), while recently several studies have been focused on organic waste recovery (Kifuani *et al.* 2018; Mortad & Hachemi 2019; Zemouri & Zougagh 2019; Hamadouch 2020).

However, there are challenges associated with the removal of MB through adsorption:

- *Adsorbent selection*: The selection of an appropriate adsorbent depends on factors such as cost, availability, adsorption capacity, and regeneration potential (Crini 2006).
- *Optimization of conditions*: The efficiency of MB adsorption is influenced by various factors such as pH, temperature, initial dye concentration, contact time, and agitation speed. Finding the optimal conditions for adsorption can be challenging and may require extensive experimentation (Kumer 2007).
- *Competing ions and compounds*: The presence of other ions and compounds in the water matrix can interfere with MB adsorption by competing for adsorption sites or altering the surface chemistry of the adsorbent material (Robinson *et al.* 2001).
- *Regeneration and disposal of spent adsorbent*: While some adsorbents can be regenerated and reused, the regeneration process may require additional resources and can be technically challenging. Moreover, the disposal of spent adsorbents, particularly if they contain high concentrations of adsorbed MB, must be appropriately managed to prevent environmental contamination (Wang & Li 2007).
- *Environmental impact and safety*: Some adsorbents may pose environmental risks in their production, use, or disposal. It is essential to use adsorbents that do not introduce secondary pollutants (Mittal *et al.* 2009).

This study's purpose is to study the disposal of MB via adsorption using Algerian natural goethite. Many reaction parameters were tested to optimize the process: contact time, adsorbent dose effect, initial MB concentration effect, and process pH.

Several kinetic and non-kinetic relations were used to model and validate the results obtained experimentally, such as the intra-particle diffusion model, Boyd's model, Lagergren's model (pseudo-first-order), Blanchard's model (pseudo-second-order), and the isotherms of Freundlich, Langmuir, Temkin, and Elovich.

2. MATERIALS AND METHODS

2.1. MB solutions

We used distilled water with a pH varying from 5.5 to 6.8 and a conductivity ranging from 3 to 5 $\mu\text{S}/\text{cm}$. The MB stock solution at 1,000 mg/L was prepared by dissolving $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ with a molar mass of 319.85 g/mol in

distilled water. Successive dilutions of the stock solution prepared the treated MB solutions until the desired concentration was obtained.

2.2. Tested adsorbent

Goethite originates from the deposits of El-Ouenza, Tebessa, situated in eastern Algeria. Samples were taken from the iron mine at the main quarry level, operated by the ArcelorMittal Tébessa group. The geological reserves amount to 87 million tons with 48% Fe, and the annual production is 2 million tons. This goethite has a brown color in its raw condition, with a chemical formula of FeHO_2 and a diameter of $d \leq 250$ nm (see Figure 1).



Figure 1 | Tested goethite (laboratory photo).

2.2.1. Goethite characterization via X-ray diffraction (XRD) spectra

Synthesized goethite XRD models were checked as shown in Figure 2. According to code 98-041-5251, this goethite contains hematite. Peaks at 2θ angle are 33.20, 35.70, 40.93, 49.54, 54.15, and 62.55°.

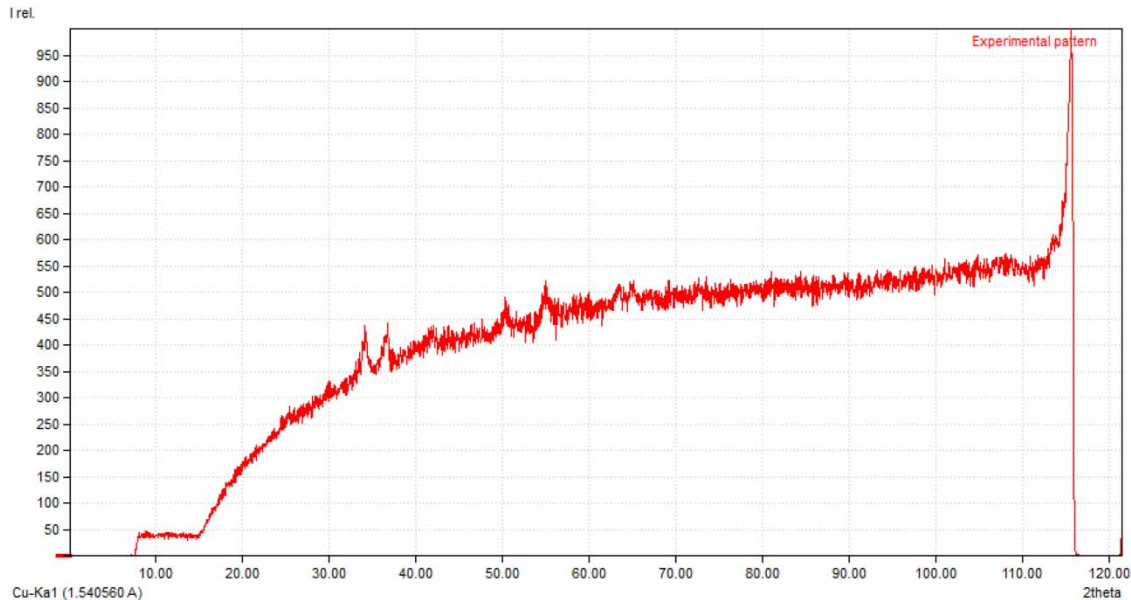


Figure 2 | XRD spectra of the tested goethite.

According to Wang *et al.* (2021) study, peaks are clearly observed at 2θ values of 22.17°, 24.85°, 32.38°, 38.6°, 43.07°, and 53.06°, which confirms that pure goethite was obtained via comparison with standard XRD pictures (29-0713).

According to Heng *et al.* (2016), who have studied the electro-enhanced activation of peroxydisulfate goethite for orange II discoloration at neutral pH; peaks at 2θ angle that are 21.223°, 33.241°, 34.700°, 36.649°, 39.984°, 41.186°, 50.613°, 53.237°, and 59.023° are specific of α -FeOOH.

2.2.2. Goethite infrared (IR) spectra

Infrared analyses were performed on a Fourier transform spectrophotometer (FT/IR-4700typeA) with a range between 399 and 4,000 cm^{-1} . The spectra of goethite are shown in Figure 3.

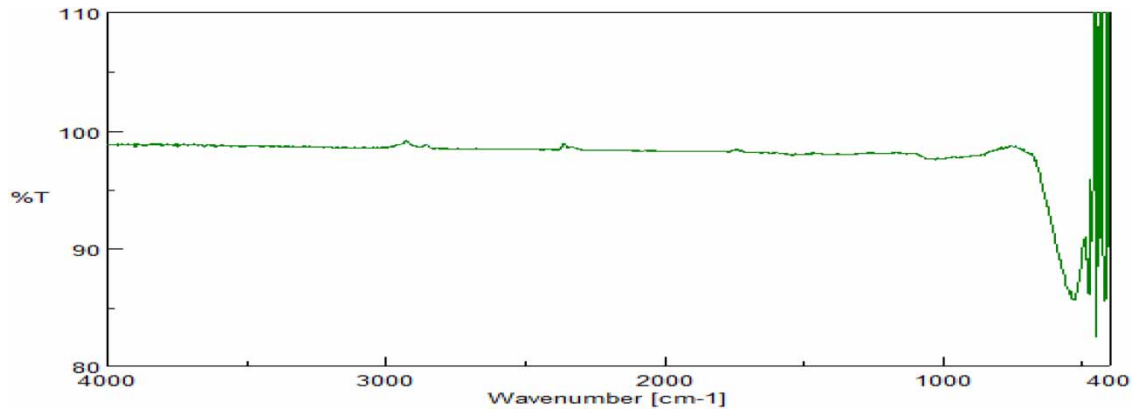


Figure 3 | IR spectra of goethite.

According to Figure 3, three prominent IR bands at 423, 450, and 527 cm^{-1} have been observed. These bands are due to the bending vibration Fe–O–H (Gotić & Musić 2007).

In the IR spectra of Wang *et al.* (2021) study, the band at 3,123 cm^{-1} can be assigned to the OH stretch mode in the goethite structure, while the band around 1,642 cm^{-1} is close to the position of H₂O bending vibrations. Two prominent IR bands at 889 and 794 cm^{-1} are due to Fe–O–H bending vibration. The band around 634 cm^{-1} could be due to Fe–O stretch vibrations (Gotić & Musić 2007).

2.3. pH measurement

To measure the pH of water samples, a pH meter (Hanna pH 210) was used with a combined electrode (Bioblock Scientific). The pH meter is calibrated before any measurement series using two buffer solutions of pH 4.01 and 9.18.

2.4. Adsorption test description

Using an analytical scale and spatula, we weigh precise quantities of adsorbents, which we put in Erlenmeyer flasks. We add MB solutions of given concentrations according to the desired experience. The mixtures are then stirred on a multi-position stirring plate using magnetic bars. After equilibrium time, each sample is filtered via vacuum using a membrane of 0.45 μm porosity.

To determine the MB content of the sample to be analyzed, we proceed in the same way as for the standards. We note the corresponding reading at a wavelength $\lambda = 663 \text{ nm}$, and then, using the calibration curve equation, we calculate the unknown concentration of MB. To measure adsorbance, a type spectrophotometer was used UV min1240.

Various reaction parameters, including contact time (0–5 h), adsorbent quantity (0.5–8 g/L), initial dye concentration (2–100 mg/l), and solution acidity (4–10), were investigated.

The removal efficiency R (%) is defined as: $R = ((C_0 - C)/C_0) \times 100$, where C_0 is the initial concentration of MB. C is the residual concentration of MB in solution.

2.5. Modeling lows

Several kinetic models describe the transport mechanism of adsorbate inside the adsorbent particles and determine certain kinetic parameters, such as the velocity constant and maximum quantity equilibrated.

These models depend on the nature and complexity of the adsorbent material. Three cases may occur (Errais 2011):

The adsorbent solid material is non-porous, and rapid adsorption will occur on surfaces that are directly accessible.

The adsorbent material is porous, and not all adsorbent surfaces are accessible. The adsorption rate depends on the adsorption itself and the diffusion rate in porous spaces.

The porous material is complex with pores of different sizes (micro-mesomacropores); the rate of adsorption will depend on several phenomena, including diffusion in micropores and convection-dispersion in meso and macropores.

Among the best-known in the literature, we will mention four kinetic models during our work: the intraparticle diffusion model, the Boyd model, the Elovich model, the pseudo-first-order model, and the PSO model.

2.5.1. Intra-particle diffusion model

It was proposed by [Weber & Morris \(1963\)](#) and represented by the following equation:

$$q = k_d \cdot t^{1/2} + C_d \quad (1)$$

where K_d is the diffusion rate constant in the pores ($\text{mg/g min}^{1/2}$), and C_d is the order at the origin (mg/g). If $q = f(t^{1/2})$ is a line, the slope of this line will be equal to K_d .

Weber and Morris reported that if intraparticle diffusion is involved in the sorption process, by carrying the sorbed amount as a function of the square root of time, we must get a straight line. This step is the limiting step if the right goes through the origin.

2.5.2. Boyd's model

[Boyd et al. \(1947\)](#) proposed a model based on the assumption that intra-particle diffusion is the only limiting step controlling the process.

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (2)$$

With

$$Bt = -0.4977 - \ln(1 - F) \text{ or } F = q/q_e \quad (3)$$

where q is the amount adsorbed at time t (mg/g), q_e is the amount adsorbed at equilibrium (mg/g), Bt is the mathematical function of F , K_d is the constant diffusion rate in the pores ($\text{mg/g min}^{1/2}$), C_d is the originally ordered (mg/g). If $q = f(t^{1/2})$ is a straight line, the slope of this line will be equal to K_d .

If the Bt plot as a function of time is a line that passes through the origin, sorption is controlled by diffusion into the pores; otherwise, it is limited by extra particulate transport.

2.5.3. Lagergren's model (pseudo-first-order)

It was proposed by the Lagergren equation in the form ([Lagergren 1898](#)):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (4)$$

where k_1 (mn^{-1}) is the velocity constant of the first-order adsorption reaction; q_e (mg/g) is the amount adsorbed at equilibrium; q_t (mg/g) is the amount adsorbed at time t ; t (mn) is the contact time.

After integration with the initial conditions $q_t = 0$ to $t = 0$, the equation becomes:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

$$\text{The linearization of the previous equation gives: } \ln(q_e - q_t) = \ln q_e - k_1 t. \quad (6)$$

The amount adsorbed q_e (mg/g), and the adsorption rate can be found in two different ways:

By plotting $q_t = f(t)$ from the original equation.

By plotting $\ln(q_e - q_t) = f(t)$ from the linear transform of the original equation.

The graph of $\ln(q_e - q_t)$ versus t should give a line where k_1 and q_e can be determined from the slope and the intercept, respectively.

2.5.4. Blanchard's model (pseudo-second-order)

This model allows us to define the PSO of the reaction in a sorption process (Ho & McKay 1998):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

This model is verified when the plot of t/q_t as a function of t gives a linear relation, with a slope equal to $1/q_e$ and an ordinate originally equal to $1/k_2q_e^2$.

2.5.5. Elovich model

The Elovich model is often used to describe chemisorption. The linearized form of this model (Low 1960) is expressed as:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (8)$$

where α is the initial adsorption rate (mg/g/min), β is the desorption constant (g/mg) related to the extent of surface and surface coverage activation energy for chemisorption.

This equation was used to simulate the experimental data by drawing the curve $q_t = f(\ln t)$.

2.5.6. Isotherms

The specific relation obtained between the concentration of a solute in solution and its degree of elimination by constant temperature sorbent is defined as a sorption isotherm. The sorption isotherm provides physicochemical data to assess the applicability of the sorption process as a unitary (Giles *et al.* 1960).

Exploiting results as per Freundlich, Langmuir, Temkin, and Elovich laws is achieved by considering a fixed adsorbent dose (1 g/L) and varying the initial variable MB concentrations from 1 to 100 mg/L.

a. Freundlich and Langmuir isotherms

Linearized forms of these models are expressed by Weber *et al.* (1991):

$$\text{Freundlich isotherm equation: } \log \frac{x}{m} = \log k + \frac{1}{n} \log C_e \quad (9)$$

$$\text{Langmuir isotherm equation: } \frac{m}{x} = \frac{1}{q_m} + \frac{1}{q_m \times b} \times \frac{1}{C_e} \quad (10)$$

C_e is the MB concentration at equilibrium (mg/l), $x = (C_0 - C_e)$ is the fixed MB quantity (mg/l), m is the adsorbent mass (g), q_m is the ultimate adsorption capacity (mg/g), k , n , and b are the adsorption constants. For Freundlich model, if the variation of $\log x/m$ as a function of $\log C_e$ is linear, we must obtain a line of slope equal to $1/n$ and ordinate to the origin equal to $\log k$.

For Langmuir, $1/q_e$ is plotted as a function of $1/C_e$, and a slope line of $1/b q_m$ is obtained.

b. Temkin isotherm

This model is applied to describe chemical adsorption. It is given by the equation (Temkin & Pyzhev 1940a, 1940b):

$$q_e/q_m = \theta = R.T/\Delta Q. \ln K_T + R.T/\Delta Q. \ln C_e \quad (11)$$

where ΔQ is the variation in adsorption energy (kJ/mol and K_T : Temkin constant (L/mg)).

The plot of q_e according to \ln allows us to determine the slope of the line a ($a = q_m R.T/\Delta Q$) and calculate the adsorption energy variation ΔQ and the constant K_T . The value of the introduced q_m is calculated by the Langmuir equation.

c. Elovich isotherm

The Elovich model describes the multi-layer adsorption; it is given in the form (Elovich & Larinov 1962):

$$\ln q_e/C_e = \ln(K_E \cdot q_m) - q_e/q_m \quad (12)$$

where q_m (mg/g) is the maximum adsorbed capacity per unit adsorbent mass, K_E (L/mg) is the Elovich adsorption constant related to surface site affinity with adsorbate. The curve plot: $\ln q_e/C_e = f(q_e)$, gives us a slope line $a = -1/q_m$.

3. RESULTS AND DISCUSSION

3.1. Kinetics of adsorption

3.1.1. Experimental kinetics results

We studied this parameter by considering the MB content during a stirring period ranging from 0 min to 5 h. The introduced mass of the adsorbent was 1 g/L. The initial MB content in the treated solutions was set at 10 mg/L.

We can distinguish three steps during the MB adsorption kinetics. In the first stage, there is a rapid increase in yield up to the equilibrium time. This time corresponds to the maximum efficiency of the MB adsorption and, therefore, the minimum residual MB contents. A fast removal rate is attributed to rapid sorption on the external surface of the solid and the disparity between the solute concentration in the solution and at the solid surface: the driving force. The sorption rate is slowed as the solute is adsorbed due to decreased sorption sites and the driving force.

An equilibrium stage, where there are no more free or accessible sorption sites. The onset of this phase is indicated by a time called equilibrium time. Beyond this time, there is a decrease in the MB elimination yield.

The results presented in Figure 4 show that the equilibrium time corresponds to 10 min. The maximal removal value is 26.21% and 2.62 mg/g for the adsorption capacity.

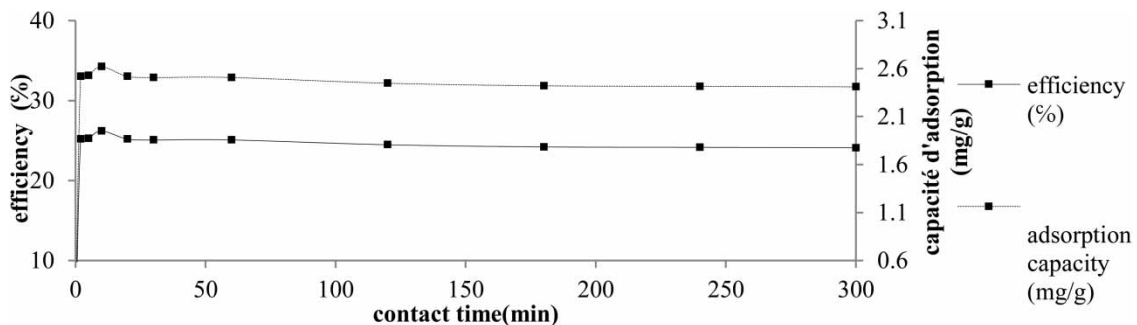


Figure 4 | Evolution of MB adsorption kinetics at 10 mg/l on goethite 1 g/L (pH varies from 6.5 to 7.5) (T varies between 17 and 19 °C) (particle size of ≤ 250 nm).

Abdellah (2006) tested the removal of MB in aqueous media via adsorption on treated and untreated pyrophyllite (aluminum silicate hydroxide). This study showed that 5 min of agitation is enough to achieve balance, which shows that the MB adsorption kinetics on pyrophyllite are very fast. Maximum adsorption is achieved with an adsorption percentage of 78.45, 66.58, and 54.71%, respectively, for initial concentrations of MB 75, 225, and 374 ppm.

Lakhache (2017) tested adsorption of blue methylene (50 mg/L) on clays (raw and sodated) whose iron is in their compositions; this study showed that 60 min of agitation is sufficient to achieve balance for the raw and sodated clay.

3.1.2. Kinetics modeling

a. Intra-particle diffusion

The experimental data modeling through the Weber and Morris model is shown in Figure 5.

The Y-axis provides information on the effect of the boundary layer; if this value is high, the contribution of external diffusion in limiting sorption velocity is significant (Djelloul 2014; Djelloul & Ghodbane 2022).

Data in Table 1 and Figure 5 show that the line of linear regression before equilibrium time has good correlation coefficients but does not pass through the origin ($C_d \neq 0$). This means that intra-particle diffusion is

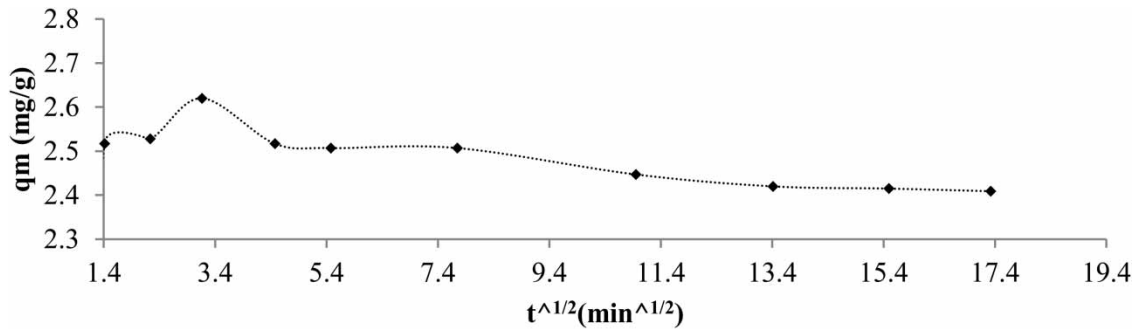


Figure 5 | Evolution of the amount sorbed as a function of the square root of time for various masses of sorbent (pH varies between 6.5 and 8.5) (T varies between 17 and 19 °C).

Table 1 | Weber and Morris model parameters and correlation coefficients for different initial concentrations

	$k_d (\text{mg/g min}^{1/2})$	$c_d (\text{mg/g})$	R
1 g goethite	0.0598	2.4293	0.8542

involved in the elimination mechanism but is not the only limiting step. Plots are not linear for the entire time interval, indicating that sorption is affected by several processes (Zamouche *et al.* 2014).

According to the results of Harizi (2020), who made synthesis and characterization of materials based on zeolite and double lamellar hydroxides for the elimination of (MB); graphics show that not all initial concentrations represent straight lines over the entire time range. This multilinearity indicates that the adsorption process involves more than one mechanism in addition to intra-particle diffusion. Also, the lines do not pass through the origin.

Feddal (2016) tested the adsorption of MB on raw, sodated, and calcined clay; the results show that the MB adsorption follows the intraparticle diffusion model ($R^2 > 0.9$). The R^2 regression coefficients are highest for the second-order kinetics for all clay types. The adsorbed quantities' experimental values are close to those calculated from the kinetic equations of the second order for the different types of clays.

Ben Houit & Khenblouchi (2018) tested the elimination of a cationic dye (MB) by aqueous biosorption using plant biomass (date pedicels); the study shows that the graphs of the biomaterials examined do not pass through the origin. This indicates that intra-particle diffusion is involved in the adsorption process. Still, it is not the only step controlling the diffusion speed and reveals the existence of three distinct regions: the first region is fast. It is attributed to external surface adsorption (the layer diffusion limit). The second region represents the progressive adsorption step (the flow-limiting step). The third region is considered the final stage of equilibrium (saturation of the biosorbent surface). The values of the R^2 correlation coefficients obtained from this model are in the range of $0.72 < R^2 < 0.99$, which reveals that intra-particle diffusion is not the speed limitation step for this material (Daoud *et al.* 2017).

b. Boyd's model

The evolution of Bt as a function of time is shown in Figure 6 where we notice that the experimental results of the sorption kinetics represent lines that pass through the origin. Therefore, we can confirm that diffusion in the pores is the limiting step of the sorption process of MB by goethite.

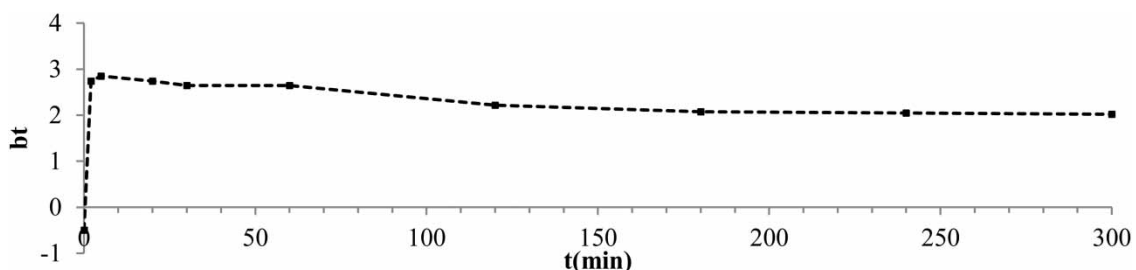


Figure 6 | Evolution of Bt as a function of time (pH varies from 6.5 and 8.5) (T varies from 17 to 19 °C).

The same result was found by [Batana et al. \(2019\)](#), who tested the adsorption kinetics of MB on raw and treated bentonite. Using Boyd's law application results, the slope is defined as a velocity parameter that characterizes the adsorption kinetics in the region where diffusion in the pores is the limiting step.

[Kifuani et al. \(2018\)](#) tested the adsorption of a basic dye, MB, in an aqueous solution to a bio adsorbent from agricultural waste from *Cucumeropsis mannii* Naudin. They concluded that the increase in adsorption percentage or adsorption capacity with contact time is due to the availability of free adsorption sites on the adsorbent surface from the first contact. These sites are becoming progressively saturated. The rapid increase in adsorption is due to the extra particulate diffusion (or external diffusion) of the adsorbent particles, characterized by the transfer of the solute through the film located on the geometric surface of the adsorbent.

An opposite result was found by [Djelloul \(2014\)](#) who studied and modeled the MB adsorption on milk thistle seeds (MTS; grain de chardon de lait (GCL)), and after applying Boyd's law, he found that the experimental results of the sorption kinetics do not represent straight lines that pass through the origin. As a result, he confirmed that extra particulate diffusion is the rate-limiting step in the MB sorption process by GCL.

c. Lagergren model (pseudo-first order)

The Lagergren model parameters and correlation coefficients recorded in [Table 2](#) and [Figure 7](#) are not good, while the theoretical sorption capacities values show a considerable deviation from the experimental values. This confirms that the Lagergren model is not adequate for describing the sorption kinetics of goethite.

Table 2 | Pseudo-first order sorption rate constant values and correlation coefficients

	<i>R</i>	<i>K</i> (1/min)	<i>Q_e</i> theo (mg/g)	<i>Q_e</i> exp (mg/g)
1 g goethite	0.6729	0.6199	1.23924212	2.62

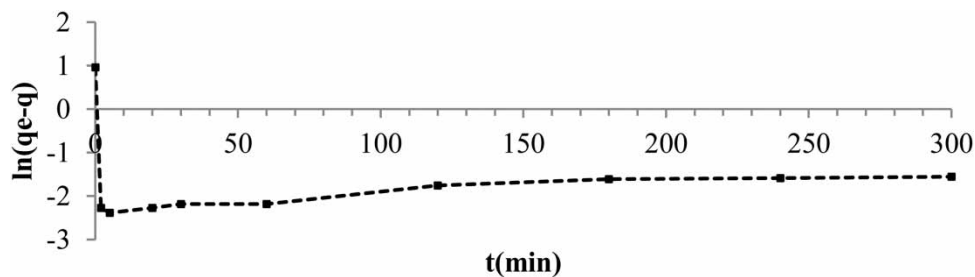


Figure 7 | Determination of the sorption rate constant via the Lagergren model (pH varies between 6.5 and 8.5) (*T* varies between 17 and 19 °C).

([Harizi 2020](#)) confirmed that the theoretical and experimental results are not consistent. These results show that the dye adsorption on the zeolite and double lamellar hydroxides did not follow a first-order reaction.

The study of [Ben Houit & Khenblouchi \(2018\)](#) shows that; on the one hand, the pseudo-first-order models provide low coefficients of correlation R^2 , far from 1; on the other hand, the adsorbed quantity values calculated from this model $Q_{e \text{ theo}}$, are much lower than those obtained experimentally ($Q_{e \text{ exp}}$), which confirms that the application of this model is not adequate.

d. Blanchard model (pseudo-second order)

The experimental results of the modeling of goethite sorption kinetics are shown in [Figure 8](#). Blanchard model parameters are represented in [Table 3](#), and the results indicate that the correlation coefficients are excellent. The k_2 values increase as the equilibrium time increases. The adsorbed quantity values obtained at equilibrium are very close to the experimental values. Thus, the results are adequately presented by PSO kinetics.

[Harizi \(2020\)](#) concluded that the highest R^2 was obtained using the PSO model, where the R^2 is very close to 1. The linear plot of t/q_t as a function of t represents the regression of the adsorption kinetics second model. The PSO plots have straight lines with very good accordance between the theoretical and experimental values.

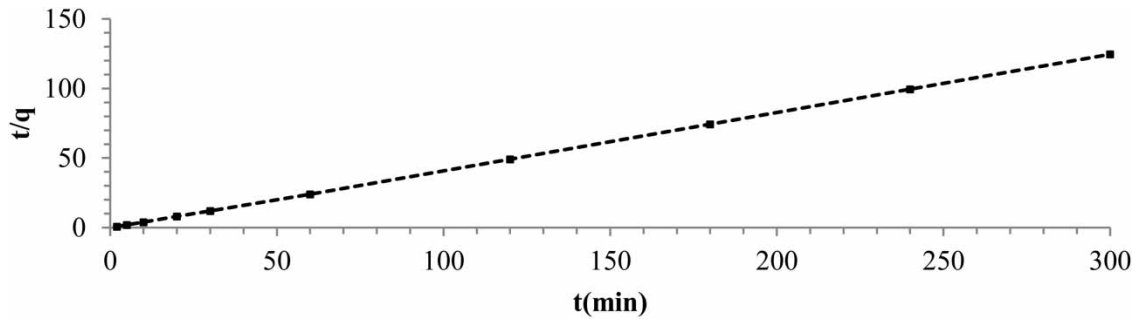


Figure 8 | Determination of the pseudo-second-order sorption rate constant via the Blanchard model pH varies between 6.5 and 8.5 (T varies between 17 and 19 °C).

Table 3 | Values of PSO sorption rate constants and correlation coefficients

	R	h (mg/g min)	K_2 (g/mg min)	q_e (mg/g) théorique	q_e (mg/g) (exp.)
1 g goethite	0.998	2.4061	0.4156	2.4061	2.62

Even though the results were found by Ben Houit & Khenblouchi (2018) and Feddal (2016), the values of the equilibrium adsorbed quantities (Q_e cal) calculated from this model are very close to the values obtained experimentally (Q_e exp) for all MB/biosorbant matrices. Moreover, the values of the correlation coefficients (R^2) are very close to the unit $R^2 > 0.99$.

Kaidari (2017) developed double-layered hydroxide materials based on Ni^{2+} , Fe^{2+} , and Ti^{3+} with a molar ratio system $R = (Ni^{2+} + Fe^{2+})/Ti^{3+} = 2$, using the constant pH co-precipitation method in aqueous solution. They tested MB adsorption on these hydroxides. The best model representing the experimental results of adsorption kinetics is the PSO model.

If we compare our modeling results according to the Lagergren and Blanchard law (Figure 9), as well as the difference found in the correlation coefficient between the models, and even the difference between Q_{theo} and Q_{exp} (Tables 2 and 3), this confirms that adsorption follows the pseudo-second-order model. The pseudo-first-order model is generally appropriate for systems where adsorption follows a diffusion process through a boundary layer (extra particulate transport) (Lagergren 1898), which is not our case (Figure 6). The PSO model is generally more suitable for processes where chemisorption is the determining mechanism (Ho & McKay 1999), which has been confirmed below by the results of the Elovich model (Figure 10).

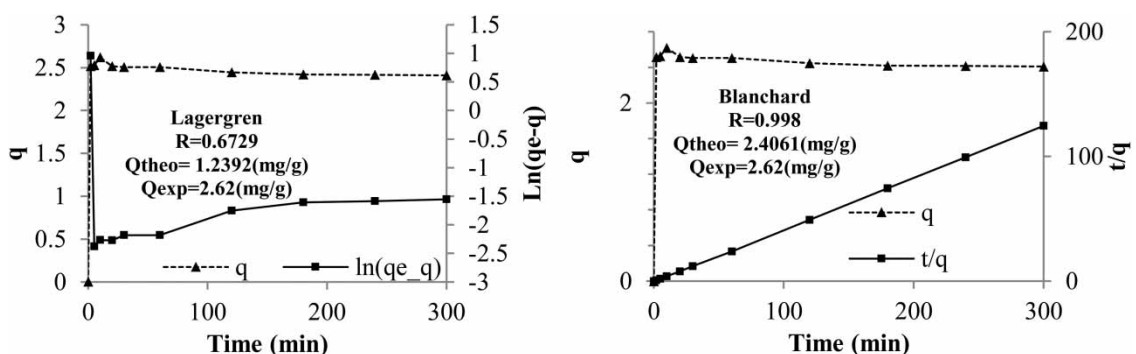


Figure 9 | Comparison between the measured and linearly modeled time profiles of pseudo-first and -second order.

e. Elovich model

The experimental results of the modeling of goethite sorption kinetics are shown in Figure 10. Elovich model parameters are represented in Table 4. Looking at the linear regression results, we can see good linearity between

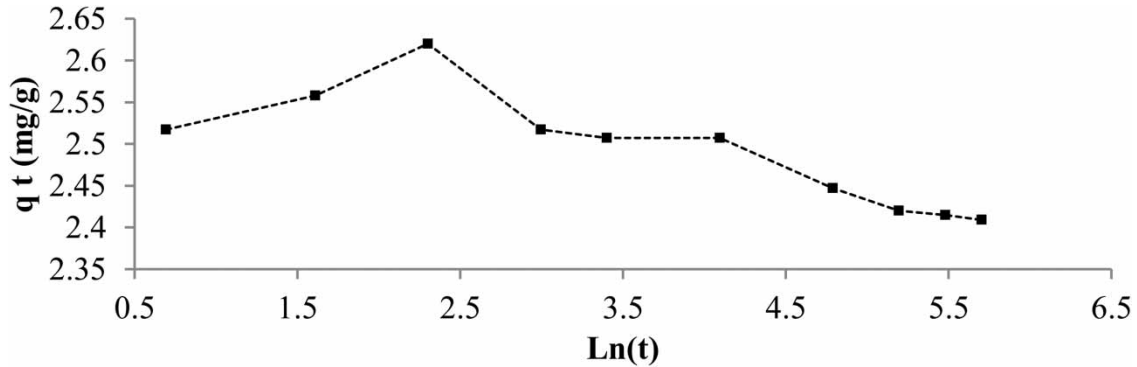


Figure 10 | Presentation of the Elovich model of MB sur on goethite ($[MB]_0 = 10 \text{ mg/l}$, goethite = 1 g/L).

Table 4 | Parametres of the Elovich model of MB sur on goethite ($[MB]_0 = 10 \text{ mg/L}$, goethite = 1 g/L)

	β (g/mg)	α (mg/g/min)	R^2
1 g goethite	15.8730	$6.47859 \cdot 10^{15}$	0.9617

q_t and $\ln(t)$. This indicates that the Elovich model is well verified and translated, probably indicating the existence of chemical-type interactions between MB and goethite.

The results of Feddal (2016) confirm that the Elovich model can also well represent the study of MB adsorption kinetics with coefficients of correlation reaching 0.993 for the gross clay.

3.2. Effect of adsorbent dose

We followed the evolution of the elimination yield of the MB concentration of 10 mg/L by adding variable doses of the adsorbent (0.5, 2, 3, 4, 5, and 8 g/L).

The tests were carried out by setting the stirring time at 10 min. The obtained results are shown in Figure 11. It is clear that MB elimination is improved by increasing the adsorbent dose, while at 8 mg/L of goethite, efficiency reaches 48.87%. Increasing the adsorbent dose means an additional adsorption surface for MB particles.

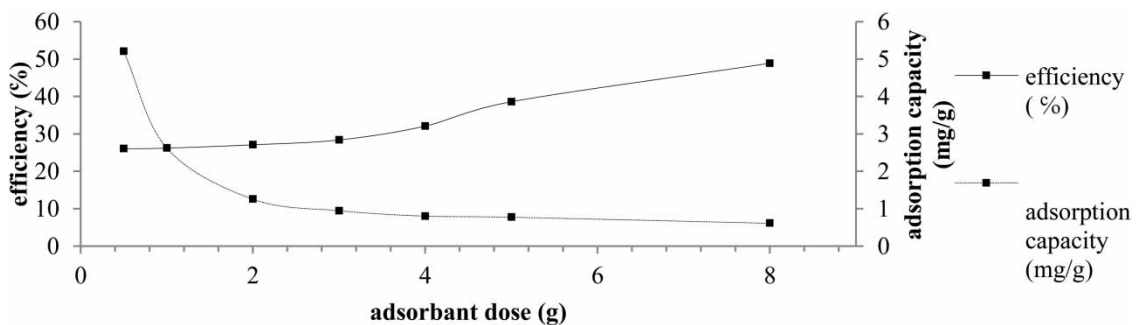


Figure 11 | Evolution of the MB removal yield ($C_0 = 10 \text{ mg/l}$) as a function of the adsorbent (goethite) dose (pH varies between 6.5 and 7.5) (T varies between 17 and 19 °C) (particle size of $\leq 250 \text{ nm}$).

Kaidari (2017) noticed that MB elimination percentage increases as mass increases from 0.01 to 0.1 g regarding each introduced layered double hydroxide (LDH) $[NiFe_2Ti]$, $[NiFe_5Ti]$, $[NiFe_7Ti]$. Results from Lakhache (2017) showed that the amount of adsorbed MB increases with the increase in the mass of the two introduced clays. The same results were found by Zemouri & Zougagh (2019).

The increase in the percentage of elimination can be explained by the fact that when the mass of the adsorbent increases, the specific area and the number of sites adsorption, and thus, the removal of dye (Lva *et al.* 2006). This behavior can be explained by:

- As long as the amount of adsorbent added to the dye solution is low, cations can easily access the adsorption sites. The addition of adsorbent increases the number of adsorption sites, but dye cations have more difficulty in approaching these sites due to congestion;
- A large amount of adsorbent creates clusters of particles, reducing the total adsorption area and decreasing the amount of adsorbate per unit of adsorbent mass.

3.3. MB initial concentration effect

3.3.1. Results of the test

We performed this testing with a constant dose of goethite (1 g/L) by varying the initial MB contents from: (2, 5, 10, 20, and 50 to 100 mg/L). Agitation was maintained during the balance time (10 min). As per the results shown in Figure 12, we can notice that adsorption yields decrease as the initial MB content increases in the solution. This leads to the assumption that goethite adsorption sites become saturated by increasing the initial MB content.

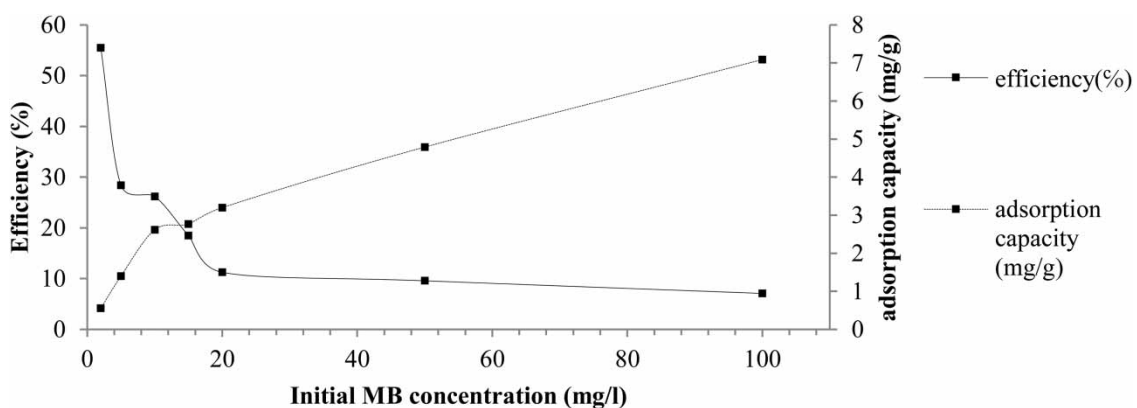


Figure 12 | Variation in the adsorption yield of goethite according to the initial MB content (dose of the adsorbent 1 g/L; stirring time: 10 min) (pH varies between 6.5 and 7.5) (T varies between 17 and 19 °C).

Zemouri & Zougagh (2019) tested the effect of the initial MB dye concentration on the efficacy of the treatment on coconut shells. The process was carried out with an initial MB concentration between 10 and 20 mg/L while keeping the other parameters constant. $m = 0.2$ g, $w = 200$ tr/min, $d = 0.2$ mm, pH = 6, and $t = 120$ min. The adsorption yield showed a downward trend when the initial MB concentration was increased. At lower concentrations, all methylene bleu (MB) present in the adsorption medium may interact with the binding sites on the adsorbent surface, so higher adsorption yields have been obtained. At higher concentrations, lower adsorption yields were observed due to the saturation of adsorption sites. The same results were found by Daouadi & Hamdi 2012; Kaidari (2017).

Contrary results were found by Abdellah (2006), who varied the initial concentrations of MB from 10^{-5} to $1,6 \cdot 10^{-3}$ M for pH = 5.5. The results show that the adsorption capacity increases with an increase in the initial pollutant contents.

3.3.2. MB adsorption isotherm

a. Langmuir equation

The experimental results modeling of the MB sorption isotherms by goethite is presented in Figure 13 and the parameters obtained are grouped in Table 5.

From the results collected in Table 5, we observe that the correlation coefficients obtained via the Langmuir equation are very bad. It appears that Langmuir's model does not adequately describe the experimental results of goethite sorption isotherms.

Saoudi & Hamouma (2013) tested the adsorption of MB on acidified clay. Modeling of dye adsorption isotherms by the Langmuir model was carried out with the linearized form $C_e/q_e = f(C_e)$. The values of the isotherm models show that the Langmuir model has a good correlation coefficient ($R = 0.915$), but the error is very high (45.72%).

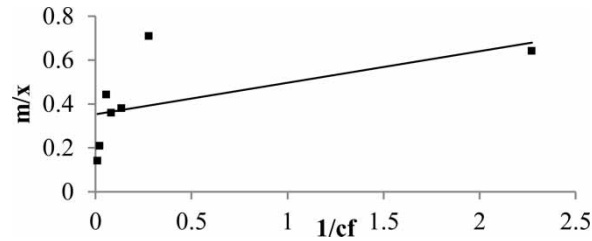


Figure 13 | Langmuir line for the adsorption of MB on goethite.

Table 5 | Langmuir model parameters

	b (L/mg)	R^2	RL	q_m (mg/g)
1 g goethite	2.4565	0.3255	0.03911598	2.8328

The study's modeling of the isotherms (Kaidari 2017) shows that the Langmuir model is better suited to describe MB adsorption.

b. Freundlich equation

The experimental results of the modeling of the goethite MB sorption isotherms are shown in Figure 14 and Freundlich parameters and correlation coefficients are recorded in Table 6.

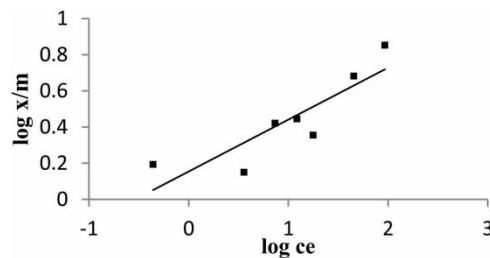


Figure 14 | Freundlich line for the MB adsorption on goethite.

Table 6 | Freundlich model parameters

	n	R	K
1 g goethite	3.4843	0.7555	1.3324

The obtained correlation coefficient is acceptable. The value of n is greater than 1 ($n \geq 1.84$), which means that the MB sorption by goethite is favorable. This confirms that the Freundlich model provides a better fit the experimental data compared to the Langmuir equation.

The study of the isotherms of Zemouri & Zougagh (2019) revealed that the adsorption of the two dyes (blue methylene and methyl orange) on the shell of the coconuts follows the isotherm of Langmuir and Freundlich. The values obtained from R^2 and RI lead to the conclusion that MB adsorption on the surface of the biosorbant is multi-layer adsorption.

The results of the Freundlich model isotherm in the study of Saoudi & Hamouma (2013) confirmed that the adsorption of MB on clay is favorable, depending on the numerical value of n obtained (between 1 and 10).

According to the study by Kaidari (2017), this model's R^2 correlation coefficients are lower than those of Langmuir.

c. Temkin equation

The results of the linearization of experimental points by the Temkin model are presented in Figure 15, and the calculated parameters are summarized in Table 7.

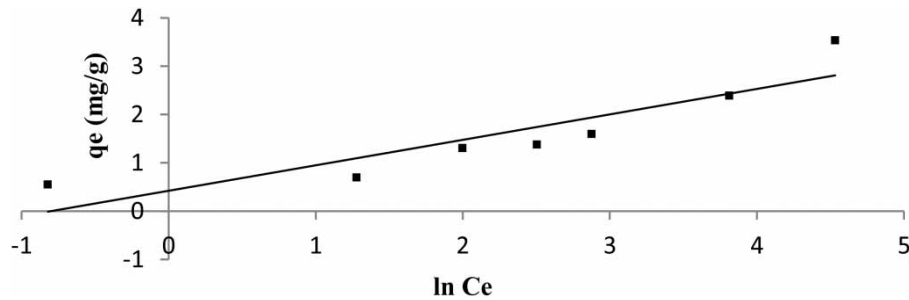


Figure 15 | Temkin line for the MB adsorption on goethite ($C_0 = 10$ mg/L MB, $T = 293 \pm 1$ K).

Table 7 | Temkin model parameters

	ΔQ (kJ/mol)	K_T (L/mg)	R^2
1 g goethite	13.09	2.23	0.80

The results obtained show that the Temkin isotherm can describe MB adsorption on the goethite as a result of obtaining a good correlation (0.80). We also noted that the variation in adsorption energy is positive (endothermic adsorption).

Based on the results observed in the Djelloul (2014) study, the correlation coefficients obtained by the Temkin equation are good (R 0.97), confirming that the Temkin equation acceptably describes sorption isotherms.

However, Rabehi & Mezhoud's (2022) application of this model shows that the curve does not have linearity. Therefore, MB-zeolite adsorption does not follow the Temkin model.

d. Elovich equation

The curve plot: $\ln q_e/C_e = f(q_e)$, gives us a slope line $a = -1/q_m$ (Figure 16), and the model's calculated parameters are shown in Table 8.

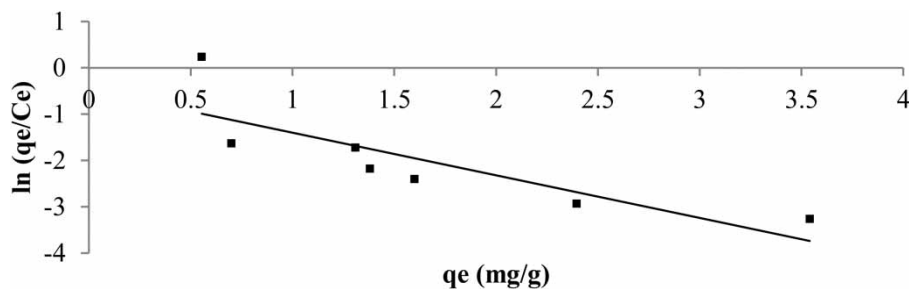


Figure 16 | Elovich line for the MB adsorption on goethite ($C_0 = 10$ mg/L MB, $T = 293 \pm 1$ K).

Table 8 | Elovich model parameters

	q_m (mg/g)	K_E (L/mg)	R^2
1 g goethite	1.0866	0.5697	0.70

According to the Elovich equation, the linear regression shows that the correlation coefficients obtained are slightly lower than those obtained by the other isotherms (Freundlich and Temkin) (Figure 17). Fitting to the Elovich model suggests multi-layer adsorption consistent with the observations from the Freundlich model.

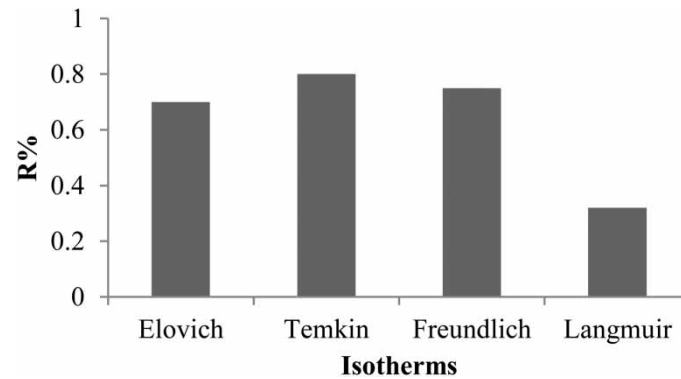


Figure 17 | Comparison between the correlation coefficients obtained from the four laws.

3.4. Effect of pH

In our study, we tracked the effect of pH on adsorption for an initial concentration of 10 mg/L of MB dye at different pH values (4, 5, 6, 7, 8, 9, and 10) with 1 g of adsorbent.

We can notice an improvement in MB adsorption whenever the pH increases (Figure 18), while the best one is at pH 10, with removal rates at 39.25%. In basic solutions, the goethite surface is negatively charged ($\text{pH} > \text{pHPZC}$), which promotes the electrostatic attraction between the MB cations and the adsorbent surface. On the other hand, under acidic pH conditions, the goethite surface is positively charged, causing electrostatic repulsions between the MB cations and the surface of the sorbent. Therefore, sorption at a basic pH is better (Sehil *et al.* 2022).

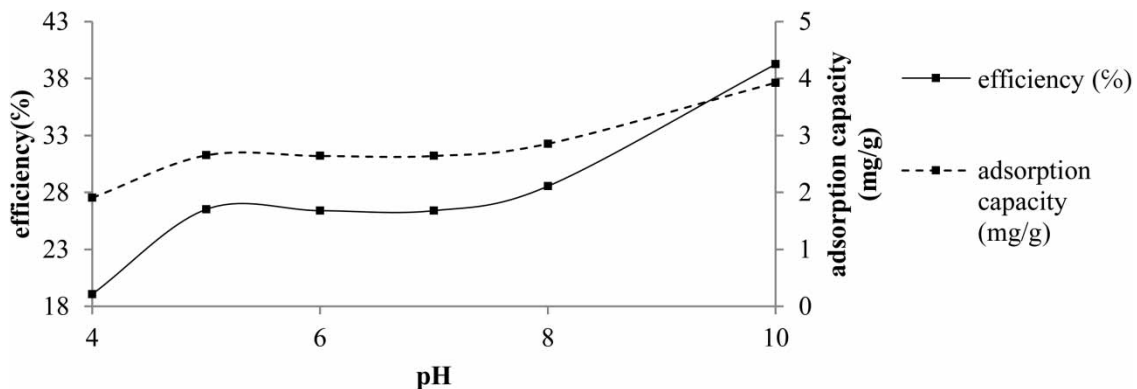


Figure 18 | Variation in adsorption yield as a function of pH.

Abdellah (2006) tested the influence of pH on the adsorption of MB on pyrophyllite; he used solutions of MB (225 ppm) in contact with the adsorbent at a content of 2 g/L and for pH varying between 2 and 10 values. Analysis of these results shows that the amount of MB adsorbed on pyrophyllite increases with pH increasing.

Khoualdi & Medjani (2016) tested the effect of pH on the adsorption of MB by activated carbon and clay, they varied the pH of (3, 5, 7, 10–2) in an acid medium ($\text{pH} < 7$): the adsorption capacity of the dye MB on both coal-active adsorbents and clay increases significantly with the decrease in pH. On the other hand, at a strongly acidic pH, there is a noticeably high electrostatic attraction between the surface of two positively charged adsorbents and the acid (anionic) form of the negatively charged dye. In basic medium ($\text{pH} > 7$): the adsorption capacity of the MB dye decreases with increasing pH.

3.5. Results of some previous studies on MB adsorption

For years, several researchers have been trying to find a mineral or organic sorbent with high adsorption capacities without any treatment. In Table 9, we will present the main sorption characteristics of MB by several adsorbents (hydroxides and clays) described by the kinetic model of PSO.

Table 9 | Main sorption characteristics of MB by various adsorbents

References	Adsorbant	Kinetic model	Isotherm model
Zou <i>et al.</i> (2015)	Calcined layered double hydroxides	PSO	Langmuir
Li <i>et al.</i> (2013)	Goethite	PSO	Langmuir
Shafaei <i>et al.</i> (2020)	Goethite	PSO	Langmuir
Wu <i>et al.</i> (2013)	Montmorillonite	PSO	–
Li <i>et al.</i> (2016)	Bentonite/chitosan composite	PSO	Freundlich

4. CONCLUSIONS

This study was part of the overall process of optimizing the adsorption process to remove undesirable contaminants from aqueous solutions. By studying the effect of different reaction parameters on the adsorption mechanism. The pollutant and the adsorbent we used are MB dye and a natural iron hydroxide being goethite, respectively. The adsorption tests were carried out on synthetic solutions of distilled water.

We also studied the influence of some parameters on adsorption, such as agitation time, media pH, and ratio adsorbent/adsorbent. Kinetic models and adsorption isotherms were applied to simulate experimental data and describe the mechanisms involved.

The experimental study we carried out allowed us to notice that:

- The equilibrium time is reached after 10 min of agitation for goethite with 26.21 % efficiencies and 2.62 mg/g adsorption capacity.
- The MB elimination efficiency improves as the adsorbent dose increases (0.5–8 g/L). Sorption capacity decreases from 5.20 to 0.61 mg/g, but the elimination percentage increases from 26.03 to 48.87%. This can be attributed to the increase in available surface area and the increase in the number of active sites on the surface of the material used.
- An increase in concentration from 2 to 100 mg/L results in an increase in sorption capacity from 0.55 to 7.09 mg/g and a decrease in elimination percentage from 55.49 to 7.10%, respectively, and this is due to the saturation of adsorption sites.
- The amount of sorbed MB increases from 1.90 to 3.92 mg/g, and the elimination percentage increases from 19.06 to 39.25% when the pH increases from 4 to 10, respectively. These results can be explained by the loading of the surface of the goethite, which is negatively charged at the basic pH and promotes electrostatic attraction between the MB's cations and the goethite's surface.
- The comparison of the theoretical sorption capacities obtained via the linear transforms of the Lagergren and Blanchard models with those of the experimental data reveals that the Blanchard model gives a better fit of the experimental results. Thus, the MB sorption kinetics are of the pseudo-second order.
- Intra-particle diffusion is involved in the MB elimination mechanism but is not the only limiting step.
- The application of the Boyd model confirms that diffusion in the pores is the limiting step of the sorption process of MB by goethite.
- The application of the Elovich model indicates that it is well verified and probably translated into the existence of chemical-type interactions between MB and goethite.
- The adjustment of the experimental results of the MB sorption isotherms obtained by Freundlich, Temkin, and Elovich equations are more adequate than the Langmuir equation.

Our results showed that natural goethite, without any activation, can be an interesting adsorbent of MB in basic media, independently of the tested reaction parameters' variation. The use of goethite offers a potentially effective, economical, and environmentally friendly solution for treating contaminated water.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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