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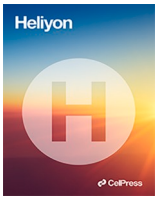

Research article

Removal of textile pollutants from aqueous medium using biosynthesized CuO nanoparticles: Theoretical comparative investigation via analytical model

Afrah Atri [a], Fatma Dhaouadi [b,*], Nesrine Mechi [b], Lotfi Sellaoui [b,c], Mosaab Echabaane [c], Rafik Ben Chaabane [a], Alessandro Erto [d], Michael Badawi [e], Abdelmottaleb Ben Lamine [b]

[a] *Laboratory of Advanced Materials and Interfaces (LIMA), Faculty of Sciences of Monastir, University of Monastir, Avenue of the Environment, 5000 Monastir, Tunisia*
[b] *Laboratory of Quantum and Statistical Physics, LR18ES18, Faculty of Sciences of Monastir, Monastir University, Monastir, Tunisia*
[c] *CRMN, Centre for Research on Microelectronics and Nanotechnology of Sousse, NANOMISENE, LR16CRMN01, Code Postal 4054, Sousse, Tunisia*
[d] *Dipartimento di Ingegneria Chimica, deiMaterialie della Produzione Industriale, Universitàdi Napoli Federico II, P.LeTecchio 80, 80125 Napoli, Italy*
[e] *Université de Lorraine, CNRS, L2CM, F-57000 Metz, France*

A R T I C L E I N F O

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A B S T R A C T

The work deals with the removal of two dyes, namely methylene blue (MB) and methyl orange (MO), from polluted water by adsorption onto CuO nanoparticles synthesized with a green synthesis procedure, starting from plant resources. Adsorption isotherms are determined at different temperatures aiming at investigating the adsorption mechanisms of the two dyes. The experimental results indicate that, for both MB and MO, the adsorption capacity increases with increasing temperature, with slight differences in the case of MO. Comparatively, the CuO nanoparticles show a higher MB adsorption capacity with respect to MO.

A modelling analysis is carried out with a multilayer model derived from statistical physics, selected among a group of models, each hypothesizing a different number of adsorbed molecules layers. The analysis of model parameters allows determining that the adsorbate molecules exhibit a non-parallel orientation on the surface of biosynthesized CuO nanoparticles and each functional group of the adsorbent binds multiple molecules, simultaneously.The model also allows determining the number of dye molecule layers formed on adsorbent surface, in all the cases resulting higher than three, also confirming the effect of temperature on the maximum adsorption capacity. Specifically, the total number of dye layers formed on biosynthesized CuO nanoparticles surface exhibited a range of 4.17–4.55 for MB dye and of 3.01–3.51 for MO dye.Finally, the adsorption energies reveal that adsorption likely involves physical forces (all resulting all below 22 kJ/mol), i.e. hydrogen bonding and van der Waals forces. The adsorption energies for the interactions between dye molecules are lower than those calculated for the interactions between the dye molecules and the adsorbent surface.

* Corresponding author.
E-mail address: dhaouadifatma2018@gmail.com (F. Dhaouadi).

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1. Introduction

Nowadays, environmental pollution is a significant and impacting issue for humanity and has a negative effect on human health and living beings [1].One of the most worrying concerns is related to the contamination of aquatic ecosystems by numerous organic compounds, including chlorinated, pesticides, dyes, and polychlorinated biphenyls. Each of these classes of pollutants is formed by a wide variety of different compounds; for instance, synthetic dyes may be divided into different categories, including azo, basic, acid, reactive, and direct dyes [2]. Azo dyes are among the most popular and commonly used food colors due to their affordability and durability. Methyl orange (MO), one of the well-known anionic azo dyes, has been widely used in the pharmaceutical and textileindustries, research laboratories, paper production, andin printing applications too. Methylene blue (MB) is one of the most popular cationic azo dyes used for the dyeing of silk, cotton, and wood [3,4]. Due to the extensive utilization of these colorants by industries, there has been a consequential rise in the annual production of dyes (800,000 tons/year), leading to an increase in environmental pollution caused by their usage [5]. On the other hand, azo dyes are toxic, carcinogenic, and they induce genetic changes when they come into contact with humans and other living beings, for example due to incorrect disposal or treatment of the related waste effluents [4]. They also do not degrade quickly, and their persistence significantly contributes to their spreading and to the diffusion in different environmental phases. In addition, methylene blue and methyl orange dyes have been linked to adverse effects in humans, including diarrhea, eye irritation, vomiting, and nausea [6,7].

For these reasons, effluent and wastewater treatmentsare urgently needed to address the demandsfor an effective water depuration and for a correct management of aquatic media. Several physical, chemical, and biological techniques, such as electrolysis, oxidation processes, adsorption, coagulation, precipitation, photodegradation, and filtration have been proposed for the treatment of waters contaminated by dyes [1,8,9].These techniques offer both benefits and drawbacks for the removing of dyes from water. For many reasons, adsorption is one of the most attractive techniques for removing color molecules from aqueous solutions. Indeed, this technology consists in a generally biocompatible system that does not give rise to secondary contamination. It is simultaneously characterized by a notable cost-effectiveness, especially if coupled with effective and reliable regeneration steps, a significant simplicity in design, an enhanced efficiency and high removal performances for a large variety of different pollutants, and an appreciable versatility in terms of potential adsorbents useable [2,9–11].

In this regard, a large variety of adsorbents have been suggested for the removal of dyes from industrial effluents, including zeolites, silica gel, alumina, agricultural waste, organic composites, and ion exchange resins [12]. Currently, metal nanoparticles have become attractive among researchers, due to their unique physical, chemical, and biological characteristics. In particular, CuO is a very good candidate because of its simplicity and low-cost in production, non-toxicity, and widespread availability, as well as for its similar qualities and uses to other nanoparticles (NPs) made with noble metals, like silver and gold, but having far larger costs [1,6,10,13]. In the past, CuO-NPs were produced using a variety of chemical, and physical techniques, but these processes have several drawbacks, including high cost, the need for costly and hazardous reagents and organic solvents, and the possible production of toxic by-products.

Therefore, thanks to recent dedicated scientific studies, new non-toxic, environmentally acceptable, and economically advantageous approaches can be adopted, utilizing plant extracts as natural reducing agents, as well as a reservoir of alkaloids and flavonoids to facilitate NP synthesis. This procedure, known as "green synthesis," stands out as an accessible, low-cost, simple, environmentally friendly, and biologically safe approach, alternative to classic ones [10,14]. Depending on the specific source of the reagents, various approaches have been recentlyreported for the biosynthesis of CuO-NPs by the green chemistry method, using aqueous extracts deriving from plants like Carica papaya [15], Citrus limon [16], aloevera [17], Ruelliatuberosa [17], Gloriosasuperba [18], Sida acuta [19], and Malvasylvestris [20].The same adsorbents have been successfully proposed for applications in the adsorption field for the removal of different pollutants, and almost all the studies have followed the classic approach by coupling an experimental study with a canonical modelling analysis, mainly based on the use of models derived from the Langmuir theory.

In details, many scientists have studied the adsorption of CuO nanoparticles using several isotherm approaches, including Langmuir, Freundlich, and Temkin. These models have been adopted to have an easy and quickly retrievable instrument for the analysis of the adsorption of dyes onto CuO nanoparticles, in terms of maximum adsorption capacity and equilibrium constant of the adsorption process [13,21]. However, these models do not allow the determination of the specific adsorption mechanism occurring, for the absence of well-defined parameters. So, to properly comprehend the adsorption phenomena utilizing statistical physics theory, a new modelling approach has been employed to offer a physical knowledge with deeper insight into the adsorption mechanism by considering steric and energetic physico-chemical factors, retrievable from experimental data fitting by dedicate models.

In this study, MB and MO dyes were adsorbed at various temperatures onto biosynthesized CuO-NPs. Physical models were used to interpret the experimental adsorption isotherms and to analyze and better comprehend the adsorption data, by determining the occurring adsorption mechanism. To this aim theoretical studies of the model parameters were carried out, supported by a dedicated experimental campaign, so to retrieve new understandings at molecular level about the removal of various dyes on the studied adsorbent.

This study contributes with innovative theoretical insights into the adsorption mechanism of Methylene Blue and Methyl Orange using biosynthesized Copper Oxide Nanoparticles (CuO-NPs), potentially applicable to different adsorption systems.

2. Materials and methods

In this work, the analytical-grade chemicals copper sulfate pentahydrate ($CuSO_4 \bullet 5H_2O$), methylene blue ($C_{16}H_{18}ClN_3S$, 319.9 g/mol) dye, and methyl orange ($C_{14}H_{14}N_3NaO_3S$, 327.34 g/mol) were purchased from Sigma-Aldrich. Double-distilled (DDW) and deionized (DI) water were used to prepare all the aqueous solutions. *E. Alata* plants, also locally referred to as Alenda, were gathered in

Mednine (Tunisia), and identified by the Institute of Arid Lands in Mednine(Tunisia). An amount of 120 ml of DDW was added to 45 g of *E. Alata* powder and placed onto Whatman filter sheets. To synthesize CuO nanoparticles, 10 ml of DI water was combined with 1 g of copper sulfate pentahydrate ($CuSO_4 \bullet 5H_2O$) and stirred at room temperature for 15 min. The copper oxide solution was added to 30 ml of *E. Alata* extract when the extract temperature reached 90 °C. The solution was stirred for 2 h at 90 °C. Finally, the paste was centrifuged, dried in an oven at 40 °C for 24 h, and calcined for 4 h at 400 °C [22].

Adsorption tests were carried out in batch mode. The experiments aimed to explore the impact of dye concentration and temperature on the adsorption of Methylene Blue (MB) and Methyl Orange (MO). The adsorption investigations were conducted in beakers containing 25 ml of the dye solution, with continuous stirring at a speed of 300 rpm for 24 h. The study delved into the influence of three temperature levels ranging from 25 to 50°Con MB and MO adsorption, varying adsorbent dosages from 0.01 to 0.04 g and initial dye concentrations from 5 to 20 mg/l, at constant pH 7.

The relationships between the quantity of dye molecules (MB and MO) adsorbed per unit mass of biosynthesized CuO nanoparticles and their equilibrium concentration at varying temperatures (adsorption isotherms) is illustrated in Fig. 1.

In general, it can be observed that the adsorbed quantities of these dyes gradually increased as the equilibrium concentration increases, for all the tested temperatures, and almost approached the saturation point of the adsorbent.This saturation plateau allows hypothesizing that the functional groups on the surface of the biosynthesized CuO nanoparticles became fully occupied, likely indicating the formation of multiple layers of adsorbed dyes. Moreover, the experimental findings clearly indicate that the adsorption temperature positively influences the removal of MB and MO dyes, slightly for the latter. In fact, as the solution temperature increases, there is an observable rise in the quantity of dye adsorbed on the nanoparticle surface. In order to gain a deeper understanding of the mechanisms of the adsorption of these dyes from aqueous solutions using biosynthesized CuO nanoparticles and to provide reliable explanations for the temperature's impact on the adsorbed quantities, three analytical models derived from statistical physics were set up and then applied to the experimental data set. These models incorporated physicochemical parameters that represent the operative instruments for interpreting the steric and energetic factors influencing dye adsorption. Below, a description of thesemodelsisprovided.

- **Monolayer model**

In this model, it is assumed that the adsorption of the dye occurs through the formation of a monolayer on the surface of the adsorbent, with all the active sites having the same adsorption energy. The equation Eq. (1) used to determine the equilibrium adsorbed quantity (Q_e) in this model is expressed as follows [23,24]:

$$Q_e = \frac{n_{dm} D_{fg}}{1 + \left(\frac{C_{1/2}}{C_e}\right)^{n_{dm}}} \tag{1}$$

- **Double layer model**

The second model hypothesizes the formation of a double-layer, i.e. the adsorption of the dye molecules occurs through the formation of two adsorbate layers on the surface of the biosynthesized CuO nanoparticles. The interactions between the dye molecules and the functional groups located on adsorbent surface are characterized by a first energy ($-\varepsilon_1$), while the interactions between the adsorbate molecules corresponding to the second layer are characterized by a second energy ($-\varepsilon_2$). The relationship describing the equilibrium adsorbed quantity of the dye as a function of the adsorbate equilibrium concentration on solid can be expressed as Eq. (2) [23]:

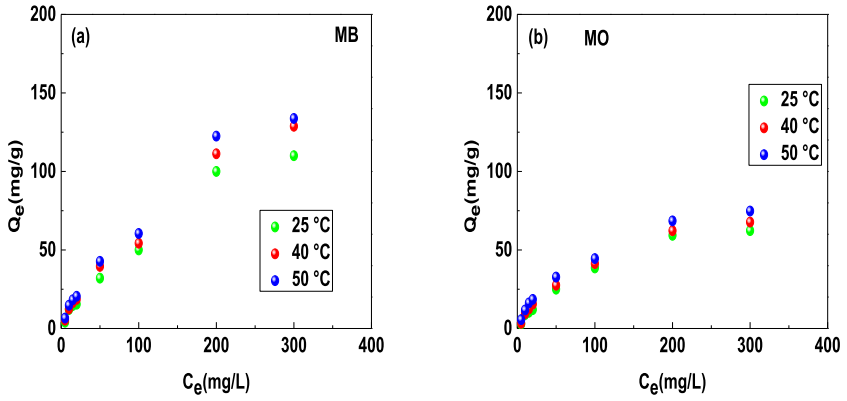

Fig. 1. Adsorption isotherms of MB (a) and MO (b) on biosynthesized CuO nanoparticles at different temperatures (20, 30 and 50 °C) and pH = 7.

$$Q_e = n_{dm} D_{fg} \frac{\left(\frac{C_e}{C_1}\right)^{n_{dm}} + 2\left(\frac{C_e}{C_2}\right)^{2n_{dm}}}{1 + \left(\frac{C_e}{C_1}\right)^{n_{dm}} + \left(\frac{C_e}{C_2}\right)^{2n_{dm}}} \quad (2)$$

- **Multilayer model**

In the case of multilayer adsorption, the model suggests that the adsorption of the dye involves the formation of a variable number of adsorbate layers ($N_T = 1 + N_2$). The model takes into account two adsorption energies ($-\varepsilon_1$ and $-\varepsilon_2$) that represent the interactions between the adsorbate and the adsorbent (first layer), as well as the interactions between adsorbate molecules of all the subsequent layers. The expression of the corresponding adsorption capacity of this model is determined by equation Eq. (3) [23, 25]:

$$Q_e = n_{dm} D_{fg} \frac{\frac{-2\left(\frac{C_e}{C_1}\right)^{2n_{dm}}}{1-\left(\frac{C_e}{C_1}\right)^{n_{dm}}} + \frac{\left(\frac{C_e}{C_1}\right)^{n_{dm}}\left(1-\left(\frac{C_e}{C_1}\right)^{2n_{dm}}\right)}{\left(1-\left(\frac{C_e}{C_1}\right)^{n_{dm}}\right)^2} + \frac{2\left(\frac{C_e}{C_1}\right)^{n_{dm}}\left(\frac{C_e}{C_2}\right)^{n_{dm}}\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}N_2}\right)}{\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}}\right)} - \frac{N_2\left(\frac{C_e}{C_1}\right)^{n_{dm}}\left(\frac{C_e}{C_2}\right)^{n_{dm}}\left(\frac{C_e}{C_2}\right)^{n_{dm}N_2}}{\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}}\right)} + \frac{\left(\frac{C_e}{C_1}\right)^{n_{dm}}\left(\frac{C_e}{C_2}\right)^{2n_{dm}}\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}N_2}\right)}{\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}}\right)^2}}{\frac{\left(1-\left(\frac{C_e}{C_1}\right)^{2n_{dm}}\right)}{\left(1-\left(\frac{C_e}{C_1}\right)^{n_{dm}}\right)} + \frac{\left(\frac{C_e}{C_1}\right)^{n_{dm}}\left(\frac{C_e}{C_2}\right)^{n_{dm}}\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}N_2}\right)}{\left(1-\left(\frac{C_e}{C_2}\right)^{n_{dm}}\right)}} \quad (3)$$

In each of these models, the n_{dm}parameter represents the number of dye molecules adsorbed by the single functional group of the adsorbent surface. C_1 denotes the concentration at which the first layer formed on the surface of the biosynthesized CuO nanoparticles reaches half-saturation. Similarly, C_2 represents the concentration at which the formation of N_2 layers with the second interaction energy reaches half-saturation. The parameter D_{fg} corresponds to the density of the functional groups on the nanoparticles. Additionally, the total number of layers, denoted as 'N_T,' is defined as ($1+ N_2$), where N_T equals 1 and 2 in monolayer and double layer models, respectively.

To analyze the experimental isotherms and provide more accurate predictions, these advanced adsorption models were adjusted on the experimental data set. They aimed estimating several key parameters, such as the number of dye layers formed on the surface of the biosynthesized CuO nanoparticles during the adsorption process, the number of dye molecules adsorbed per functional group, the density of functional groups, the saturation adsorption capacities, and the corresponding adsorption energies. The Levenberg-Marquardt algorithm was utilized to mathematically adjust the experimental data using a multivariate nonlinear regression procedure. Table 1 presents the determination coefficients R^2 for the three models used and separately for the data related to each tested dyes. These coefficients provide a measure of how well the models fit the experimental data and allowed a selection among the tested models.

For both the adsorbates and all the tested temperature, the multilayer model demonstrated the best coefficients of determination ($R^2 = 0.991–0.998$) and significantly surpassed the other tested models. Additionally, it provided interpretable variations in steric and energetic parameters with respect to solution temperature, enabling us to analyze the adsorption mechanism of the dye molecules. Therefore, this model was utilized to elucidate the adsorption equilibrium of these dye molecules (MB and MO) under the tested operating conditions. Fig. 2 illustrates the fitting of the experimental adsorption isotherms using the multilayer model. These curves exhibit an excellent fitting of the experimental data, indicating a high level of agreement between the model predictions and the experimental observations. The corresponding steric and energetic parameters, included in the model as adjustable parameters, are presented in Table 2.

Table 1
Determination coefficient deriving from the fitting of dye adsorption isotherm with statistical physical models.

Temperature, °C	Determination coefficients R^2		
	Monolayer model	Double layer model	Multilayer model
MB- biosynthesized CuO nanoparticles			
25	0.979	0.976	0.995
40	0.983	0.980	0.994
50	0.977	0.973	0.991
MO- biosynthesizedCuOnanoparticles			
25	0.991	0.989	0.993
40	0.994	0.993	0.998
50	0.992	0.991	0.996

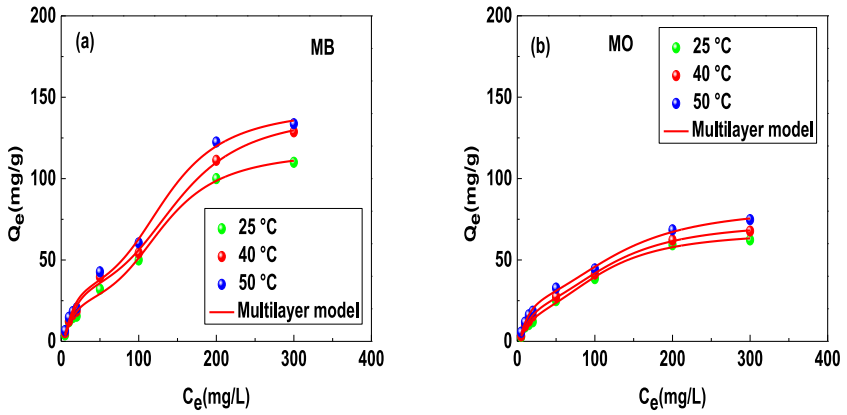

Fig. 2. Modeling results obtained from fitting the MB (a) and MO (b) experimental isotherms on biosynthesized CuO nanoparticles using the multilayer model.

3. Results and discussion

3.1. Examination of the adsorption mechanism of MB and MO molecules via model parameters

In the following sections, the influence of temperature on the parameters of the multilayer model (Table 2) was investigated and analyzed. This insight aimed to provide specific indications about the occurring adsorption mechanisms of the tested dyes onto the biosynthesized CuO nanoparticles.

3.1.1. Insights into adsorbed molecules aggregation and orientation on the surface of biosynthesized CuO nanoparticles

The stoichiometric coefficient n_{dm}, a steric parameter, offers valuable insights into both the adsorption orientation of MB and MO molecules on the surface of biosynthesized CuO nanoparticles and the aggregation behavior of these dye molecules upon adsorption. Typically, the binding of MB and MO molecules to functional groups on the surface of biosynthesized CuO nanoparticles can occur in different ways, influenced by the conformational structure of the dye molecules and the surface chemistry of the nanoparticles. If the stoichiometric coefficient $n_{dm} < 0.5$, this indicates a parallel anchoring, witha specific orientation of the dye molecules on the surface. On the other hand, if $0.5 < n_{dm} < 1$, it suggests a mixed anchoring, i.e. indicating that dye molecules may exhibit multiple orientations on the surface. Finally, if$n_{dm} > 1$, it testifies a non-parallel anchoring, suggesting that the adsorption site can bind simultaneously several dye molecules. Fig. 3 illustrates the relationship between the number of adsorbed molecules per functional group and temperature for the two systems formed by single dye + biosynthesized CuO nanoparticles.

Fig. 3 allows visualizing the effect of temperature on n_{dm} values, which exceeded the value1, for both the dyes and for all the tested adsorption temperatures. This result indicates that the adsorbate molecules exhibited a non-parallel orientationon the biosynthesized CuO nanoparticle's surface. These findings suggested that each functional group of the adsorbent had the capability to bind multiple molecules, simultaneously. Furthermore, this parameter also revealed the aggregation of dye molecules. The influence of adsorption temperature on the uptake of molecules by the biosynthesized CuO nanoparticles adsorbent was observed to be positive, as evidenced by an increase in the value of n_{dm} with temperature. Therefore, it can be inferred that temperature facilitated the aggregation process of the textile pollutants under study, leading to the formation of a dimer on the adsorbent surface.

3.1.2. Evaluation of the density of functional groups (d_{fg}) and numberof adsorbed dye layers (N_2+ 1)

Fig. 4 depicts the relationship between adsorption temperature and the estimated functional group density of biosynthesized CuO nanoparticles at the saturation stage of the adsorbent.

The relationship between adsorption temperature and the density of functional groups resulted to positive, as evidenced by the

Table 2
Physicochemical parameters predicted by the multilayer model for MB and MO adsorption onto CuO nanoparticles at different temperature.

T(°C)	n_{dm}	D_{fg}(mg/g)	N_T	C_1(mg/L)	C_2(mg/L)	Q_s(mg/g)
MB						
25	1.78	14.62	4.55	13.38	134.33	118.40
40	1.89	18.35	4.10	15.86	153.65	142.19
50	1.92	18.07	4.17	13.72	137.68	144.67
MO						
25	1.55	12.54	3.51	14.52	113.80	68.22
40	1.68	13.93	3.16	14.23	124.71	73.95
50	1.69	16.44	3.01	12.76	135.75	83.62

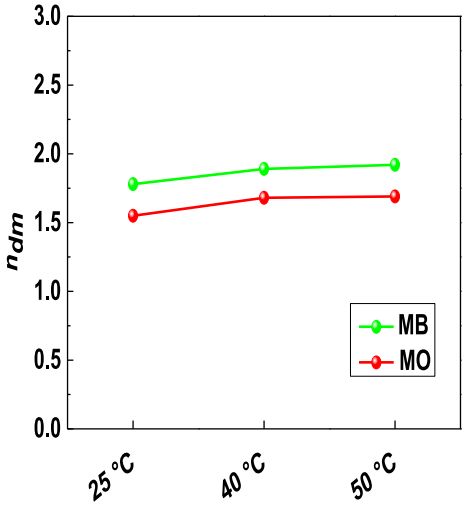

Fig. 3. Trend of n_{dm}parameter as a function of temperature for the adsorption of cationic (MB) and anionic (MO) dyes on biosynthesized CuO nanoparticles at pH 7.

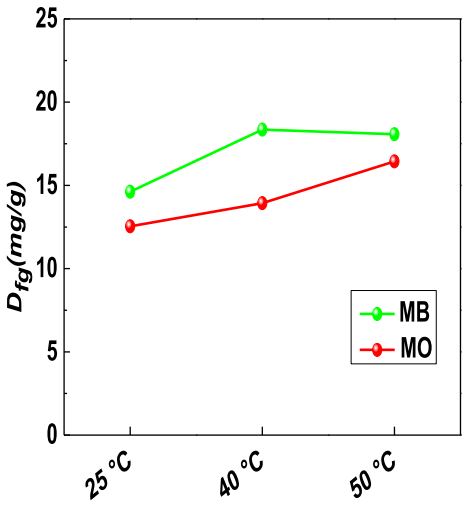

Fig. 4. Impact of temperature on the density of functional groups of biosynthesized CuO nanoparticles for the adsorption of cationic (MB) and anionic (MO) dyes at pH 7.

increase in functional group density along with an increase in temperature for both the tested dyes. These findings suggest that the temperature causes the generation of additional sites on the surface of nanoparticles, likely related to the decrease in competitive adsorption of water, facilitating the binding of molecules and ultimately resulting in an augmented functional group density.

The multilayer statistical physics model yielded supplementary insights into the changes in the total number of adsorbed layers on the surface of biosynthesized CuO nanoparticles, denoted as $N_T = 1 + N_2$, as depicted in Fig. 5.

The total number of dye layers formed on biosynthesized CuO nanoparticles surface exhibited a range of 4.17–4.55 for MBdye and of 3.01–3.51 for MO dye. These results demonstrated the classical influence of thermal agitation on this parameter, as higher adsorption temperatures led to a decrease in the number of adsorbed dye layers.As an example, let us considering MB dye at 25 °C, where $N_T = 4.55$. This means that part of the molecules is adsorbed by five layers and part by four; the relative amount can be determined by applying the simple equation $z \times 4 + (1\text{-}z) \times 5 = 4.55$, in which z represents the percentage of MB molecules forming four layers and (1-z) the share of adsorbed molecules corresponding to five layers. Thus, based on the calculations, it was determined that approximately 44% of the dye molecules formed four layers, while the remaining 56% formed five layers. This result indicates that the formation of adsorbate layers on the surface of biosynthesized CuO nanoparticles is heterogeneous.

3.1.3. Investigation of the dye adsorption capacities at saturation (Q_s)

The multilayer model suggests that the adsorbed quantity of adsorbate at saturation is influenced by the parameters n_{dm}, D_{fg}, and

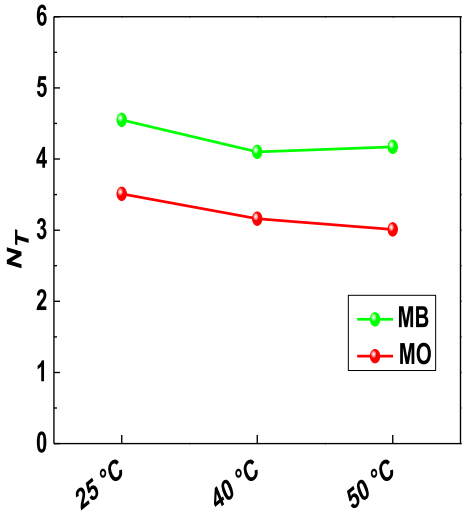

Fig. 5. Influence of temperature on the total number of formed layers of dyes molecules on the biosynthesized CuO nanoparticles surface at pH 7.

N_T, as expressed by the relationship Eq. (4):

$$Q_s = n_{dm} \times D_{fg} \times N_T \tag{4}$$

The relationship betweentemperature and saturation adsorption capacity for the two testeddyes is plotted in Fig. 6.

Based on Fig. 6, it can be observed that the increase in temperature has a positive effect on the adsorbed amounts of both the dyes, namely MB and MO, thus confirming the experimental evidences. This finding provides an evidence supporting the endothermic nature of the adsorption process, which could be ascribed to a reduced competitive effect of water by raising the temperature. It is important to note that the adsorption capacities were primarily influenced by the changes in n_{dm} and D_{fg} as a function of the solution temperature.

Comparatively, it can be concluded that the biosynthesized CuO nanoparticles exhibit a higher capacity for capturing MB molecules as compared to MO molecules. This implies that, in the given experimental setup, the CuO nanoparticles have a stronger affinity or ability to adsorb MB molecules when compared to MO molecules. In addition, the specific factors influencing the differential adsorption capacity between MB and MO molecules could include the chemical composition and morphology of the CuO nanoparticles, and the size and polarity of the dye molecules.

3.1.4. Evaluation of adsorption energies

Using the results obtained from the multilayer model, an examination of the interaction energies in these adsorption systems was conducted. Consequently, the adsorption energies were computed utilizing the two equations Eq. (5) and Eq. (6):

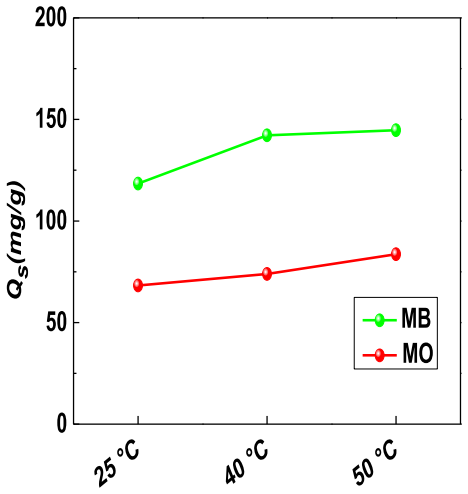

Fig. 6. Effect of temperature on the MB/MO dye adsorption capacities at saturation on biosynthesized CuO nanoparticles at pH 7.

Table 3
Calculated energies corresponding to the adsorption of MB and MO molecules on CuO nanoparticles at different temperatures and pH 7.

T (°C)	ΔE_1 (kJ/mol)	ΔE_2 (kJ/mol)
MB		
25	19.76	14.06
40	20.36	14.46
50	21.38	15.20
MO		
25	14.42	9.34
40	15.24	9.59
50	16.00	9.66

$$\Delta E_1 = RT \ln \frac{C_s}{C_1} \tag{5}$$

$$\Delta E_2 = RT \ln \frac{C_s}{C_2} \tag{6}$$

The solubility of the tested molecules in water, denoted as C_s, and the ideal gas constant R = 8.314 J/mol·K were utilized in determining the interaction energies, which are listed in Table 3.

Table 3 reveals that the adsorption of MB and MO molecules on the CuO nanoparticles adsorbent primarily consists of physical interactions, as indicated by the estimatedadsorption energies values, all below 22 kJ/mol. Hence, it can be inferred that the adsorption mechanism of the dye molecules potentially involves hydrogen bonding and van der Waals forces. Importantly, it should be noted that the adsorption energies for the interactions between dye molecules (from second layer) were found to be lower than those calculated for the interactions between the dye molecules and the adsorbent surface (first layer). It is also evident that the interactions between MB molecules and nanoparticles are stronger than those associated to the adsorption of MO molecules. In other words, the interactions between MB molecules and nanoparticles are more favorable and more powerful than the interactions between MO molecules and nanoparticles. This suggests that the process of adsorption of MB molecules onto nanoparticles is more efficient and predominant than the adsorption of MO molecules.

4. Conclusions

In this work, the adsorption mechanism of methylene blue (MB) and methyl orange (MO), two of the most used dyes in industrial sector, onto CuO nanoparticles was investigated. To this aim, adsorption isotherms were determined at different temperature and a detailed modelling analysis based on statistical physics was carried out. The experimental results indicated that, for both MO and MB, adsorption increases along with temperature, with slight differences in the case of MO. Comparatively, the CuO nanoparticles showed a higher MB adsorption capacity with respect to MO.

For a deeper insight into adsorption mechanism, three models derived from statistical physics and hypothesizing single, double, or multilayer of dye adsorbed molecules were set up. The experimental data set was fitted with all the models and the higher coefficients of determination of the multilayer model indicated it as the best fitting one. The analysis of model parameters allowed to retrieve interesting information about the dynamics mechanism of dye adsorption onto the investigated adsorbent. A first important result indicated that the adsorbate molecules exhibited a non-parallel orientation on the biosynthesized CuO nanoparticle's surface. These findings suggested that each functional group of the adsorbent had the capability to bind multiple molecules, simultaneously. Furthermore, this parameter also revealed the occurrence of dye molecules aggregation upon adsorption. The increase in temperature determined the generation of additional sites on the surface of nanoparticles, likely related to the decrease of competitive adsorption of water, facilitating the binding of molecules and ultimately resulting in an augmented functional group density. The model also allowed determining the number of dye molecule layers formed on adsorbent surface, in all the cases resulting higher than three, confirming the effect of temperature on the maximum adsorption capacity.

Finally, the calculated adsorption energies revealed that a physisorption occurred, and adsorption likely involved hydrogen bonding and van der Waals forces. The adsorption energies for the interactions between dye molecules were found to be lower than those calculated for the interactions between the dye molecules and the adsorbent surface.

Ethical approval

Not applicable.

Consent to participate

Not applicable.

Consent to publish

All authors consent to this publication.

Availability of data and materials

Data and materials are contained within the article.

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CRediT authorship contribution statement

Afrah Atri: Writing – original draft. **Fatma Dhaouadi:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Nesrine Mechi:** Software. **Lotfi Sellaoui:** Writing – review & editing, Visualization, Validation, Supervision, Software, Project administration. **Mosaab Echabaane:** Investigation, Data curation. **Rafik Ben Chaabane:** Supervision, Conceptualization. **Alessandro Erto:** Writing – review & editing, Resources, Project administration, Funding acquisition. **Michael Badawi:** Supervision, Resources, Funding acquisition. **Abdelmottaleb Ben Lamine:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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