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A comparative study of the adsorption of a cationic dye on three substrates

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ABSTRACT

In many countries, water pollution from industrial wastewater is a serious problem. This type of pollutant can have a harmful impact on the environment. To reduce these pollutants, several physicochemical methods are implemented, including adsorption on bioadsorbents, which is a common process to remove trace pollutants from water. The aim of our work is to perform a comparative experimental study of isotherms, kinetics, and thermodynamics of the adsorption of methylene blue on three substrates: sugarcane bagasse (SCB), almond shell (AS), and walnut shell (WS), as well as examine the effects of the parameters of contact time, initial concentration of the adsorbent dose, pH, and temperature. The equilibrium kinetics results show that walnut shell (WS) binds better to methylene blue than other substrates. The results of the optimization study showed an adsorption amount equal to 49.2610 mg/g for sugarcane bagasse, 106.83 mg/g for walnut shell, and 107.527 mg/g for walnut shell, with optimum conditions of 127 rpm, 25°C, 60 min, 100 mg/L and 0.1 g for stirring speed, temperature, contact time, initial methylene blue concentration, and adsorbent dosage, respectively. The results also show that the adsorption kinetics are described by the pseudo-second-order model expression with R^2 = 0.99. The adsorption isotherms of methylene blue by sugarcane bagasse (SCB), almond shell (AS), and walnut shell (WS) are perfectly described by the Langmuir model with R^2 = 0.98 for sugarcane bagasse and almond shell and 0.99 for walnut shell, and walnut shell (WS) adsorbs methylene blue better than the other substrates; moreover, the thermodynamic parameters of the methylene blue system on the three substrates indicate that the exothermic adsorption process is spontaneous.

Keywords: Wastewater; Adsorption; Methylene blue; Sugarcane bagasse; Almond shell; Walnut shell

1. Introduction

Water is life, the basic need for all livings in the ecosystem, yet the rapid growth of technological, technical, and industrial technologies, have brought catastrophic environmental issues which significantly affected the quality of water [1]. Among the industrial sectors which affect water's purity is the textile industry, which is one of the major polluters as they use and discharge various types of dyes in water which has a significant threat to the environment and the ecosystem [2] one of those overused dyes are synthetic dyes which are considered as the most important environmental pollutants that negatively affect human and aquatic life, bearing in mind that more than 7 × 10^5 metric tons of dyes are produced annually in the world and 5%–10% of them are discharged into water [3]. The classification of textile dyes have been classified according to their chemical structure or industrial application and can be classified into two categories: cationic and anionic according to the charge they carry, the cationic dyes have a positive charge on the molecule and are also called basic dyes; they are usually associated with a complex $ZnCl_2$ or HCl [4].

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This study investigates a type of cationic dyes, which is the methylene blue (MB), an organic and water soluble dye that has many uses, for instance, it is used for dyeing cotton, wood and leather, it is used for medicinal purposes, yet methylene blue can have harmful effects on human beings as it can cause many health complications like acceleration of the heart rate, nausea and vomiting in case it was inhaled; eye/skin irritation and systemic effects in case of accidental use, including cyanosis [5,6]. In this regard, a wide variety of physical, chemical and biological techniques have been developed and tested for the treatment of these dye-laden effluents.

Adsorption is an interesting technology for the separation and removal of salts and other ions from water, as it can be developed at relatively low costs and it is quite simple in its process design, as well as its operations and maintenance [7]. Activated carbon is recognized worldwide as the oldest adsorbent, the most widely used adsorbent for water and wastewater treatment industries [8] but the search for low-cost alternatives is the drive of this study including others around the world as they put their efforts in this direction, including the use of a wide range of materials such as lignite, coffee charcoal, bagasse, bones, pulp mill waste, palm cobs, coconut, kelp and algae [9]. Therefore, the present study aims at making a comparative study of methylene blue (MB) dye removal for its efficiency and practicality between three durable and low-cost adsorbent materials: sugarcane bagasse (SCB), almond shell (AS) and walnut shell (WS) using the closed loop batching control process under various physicochemical conditions that can be applied in a large-scale range of industries. It is worth mentioning that sugarcane bagasse, almond shell and walnut shell are low-cost lignocellulosic wastes are marked by their high selectivity and sensitivity traits as well as their low-cost and their abundance in large quantities in the country, Morocco.

2. Materials and methods

2.1. Materials

Methylene blue ($C_{16}H_{18}ClN_3S$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and sodium chloride (NaCl) are obtained from Sigma-Aldrich and used without any prior purification.

2.2. Adsorbent

The three selected adsorbents: sugarcane bagasse, almond shell, and walnut shell are low-cost lignocellulosic wastes widely available in Morocco. Sugarcane bagasse is a fibrous residue from sugar cane grinding after juice extraction and is collected in the Gharb region of Morocco. For walnut and almond shells, they were collected in the region of Guir, in the province of Midelt. The preparation of these three substrates has undergone these preparation phases: First, it is washed several times to remove impurities. Second, it is dried in the oven at a temperature of 105°C for 24 h before grinding and sieving it to obtain a particle size equal to 250 μm.

2.3. Adsorbate

The cationic dye methylene blue (MB) is used as an adsorbate to determine the efficiency of the biosorbents prepared in this study. MB is a cationic thiazine dye with a molecular formula of $C_{16}H_{18}ClN_3S$, a molar mass of 319.85 g/mol and a maximum absorbance peak at a wavelength of 665 nm. The chemical structure of MB is shown in Fig. 1.

To prepare the MB solution for each experiment, we dilute a stock solution of 1 g/L in the desired initial concentration. Distilled water is used to prepare all solutions, in addition, the initial pH of the working solutions is left without adjustment equal to 6.8.

2.4. Adsorption process

The study of MB adsorption by sugarcane bagasse (SCB), almond shell (AS), and walnut shell (WS) was carried out in Batch and does not require any complicated experimental protocol. The adsorption experiments were carried out in a set of 250 mL Erlenmeyer flasks containing 50 mL of the MB solution with different masses of biosorbents (particle size = 250 μm) and contacted in a shaker-type stirrer at 127 rpm. The effects of the initial concentration of methylene blue (25–200 mg/L), contact time (5–120 min), temperature (15°C–65°C), and pH (2–12) were studied; the pH adjustment was performed by adding hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M). After adsorption, the adsorbate–adsorbent separation was carried out using a Whitman-type filtration system with a diameter of 0.45 μm. The supernatant was analysed using a UV-Visible spectrophotometer (Shimadzu 1601) at a maximum wavelength of MB, which corresponds to 665 nm. The concentration of residual dye is then determined using a calibration curve and the Beer–Lambert law. The retention percentage of the studied dye is calculated by the ratio of the dye concentration after adsorption and the initial dye concentration before adsorption according to Eq. (1):

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0: equilibrium dye concentration expressed in (mg/L); C_t: dye concentration in the solution at time t (mg/L)

The adsorption capacity of the dye at equilibrium q_e (mg/g) and q_t is calculated using the Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

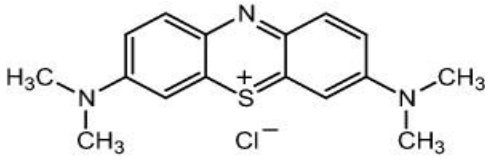

Fig. 1. Chemical structure of methylene blue.

where C_e: equilibrium dye concentration expressed in mg/L; C_0: initial concentration of the dye in mg/L, m: mass of the adsorbent (g); V: volume of the solution (L).

3. Results and discussion

3.1. Effect of the mass

The influence of the mass of the three biosorbents was determined, the masses' values were between 0.05 to 0.5 g, as well as keeping the other parameters constant, that is to say: the initial MB concentration of 100 mg/L, the stirring speed of 127 rpm, a room temperature, and a solution pH of 6.8. The results obtained are presented in Fig. 2.

Fig. 2 shows the variation of MB removal rate with adsorbent amount. The figure shows that the adsorption rate increases (linearly) with the increase of the adsorbent amount from 0.05 to 0.1 g until it reaches a maximum of 98.48%, 96.37% for 0.1 g of WS and AS, and 94.273% for a mass of 0.3 g for SCB. This phenomenon could be explained by the fact that the increase in dose leads to an increase in the exchange surface, thereby increasing the availability of the adsorption sites [10]. It is worth mentioning that beyond 0.1 g, we observe a slowing down of the adsorption of MB, which tends towards a quasi-stable state for WS and AS and beyond 0.3 g for SCB. The mass of 0.1 g was seen to be the optimal mass for further studies.

3.2. Contact time effect

To study the effect of contact time on the adsorption of MB on the three materials (SCB, AS, and WS), the experiments were conducted under the same operating conditions. A mass of 0.1 g of each of the supports was mixed with 50 mL of a 100 mg/L dye solution under vigorous stirring at 127 rpm and the normal pH of the solution (without correction) at room temperature. The samples were collected and analysed at regular intervals to determine the residual concentration of the dye. The results obtained are shown in Fig. 3.

Sugarcane bagasse, almond shell, and walnut shell had contact times ranging from 0 to 120 min. Fig. 3 shows that the curves for the three substrates present two almost perpendicular slopes, the first is vertical, indicating a very rapid fixation of large amounts of dye during the first 20 min of the reaction due to the availability of a large surface area for biosorption and binding sites and decreasing as time progresses [11]; the second is horizontal, presenting a stable equilibrium from the 30th min on. After this time, the residual MB concentration remains constant. For the following studies, a contact time of 60 min was chosen.

3.3. Initial concentration effect

The experiments on the effect of MB concentration on its adsorption as well as on the surfaces of SCB, AS, and WS were carried out in an initial concentration that ranges between 15 and 200 mg/L, while keeping the other parameters constant, in other words, a mass of 0.1 g of the substrates is brought into contact with 50 mL of the MB solution (pH = 6.8) at a stirring speed of 127 rpm for 60 min at room temperature. The results obtained are illustrated in Fig. 4.

Fig. 4 shows the effect of initial concentration on the removal efficiency of MB by the three substrates. The observation shows that the removal efficiency of MB has reached 97.36% for SCB, 99.37% for WS, and 99.92% for AS at a low concentration of 15 mg/L and then decreases to 40.91% for SCB, 77.18% for AS, and 83.85% for WS at a higher concentration of 200 mg/L. It is worth mentioning that dye removal efficiency was higher at the low initial concentrations due to the availability of unoccupied sites on the adsorbents and decreased with increasing dye concentrations due to the almost complete coverage of binding sites at high dye concentrations [12].

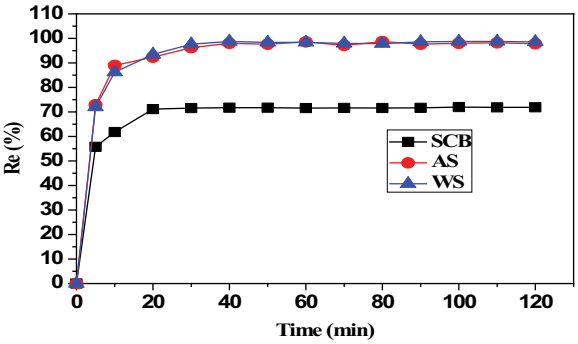

Fig. 3. Effect of contact time on methylene blue removal efficiency.

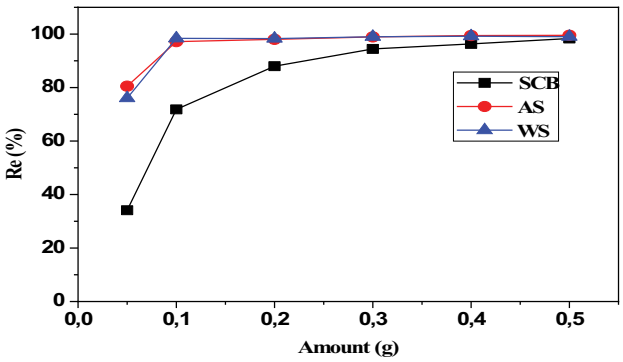

Fig. 2. Effect of adsorbent amount on methylene blue removal efficiency.

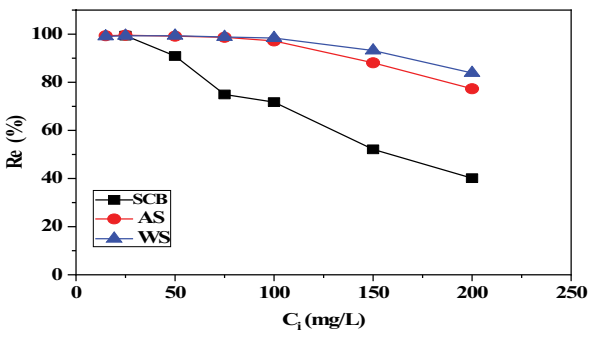

Fig. 4. Effect of initial methylene blue concentration on methylene blue removal efficiency.

3.4. Effect of pH

The pH of the solution is one of the essential factors in adsorption studies. It influences the surface charge of the adsorbent and the solubility of the dyes and it controls the adsorption efficiency [13]. Thus, the influence of pH on the rate of removal of MB was studied under the same conditions for the three selected biosorbents, by contacting a mass of 0.1 g of each of the biosorbents with 50 mL of the dye at a concentration of 100 mg/L and varying the pH between 2 and 12 by the addition of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M) using a pH-meter. The variations in the removal rate according to the pH are presented in Fig. 5.

Fig. 5 depicts a linear relationship between pH and MB removal rate; the zero charge point of SCB is 4.61, 5.35 for AS, and 5.67 for WS. Moreover, it is clear that the adsorption of MB by the three substrates occurred when the solution pH > PCN; this means that the surface of the substrates is negatively charged at this point, which favors the adsorption of methylene blue on the three substrates, resulting in an increase in the percentage of removal of MB with the increase of pH. On the other hand, when pH values go below PCN, the surface of the substrates is positively charged, which leads to a repulsion between the cations of the dye and the surface of the substrates [14].

3.5. Effect of NaCl

Wastewater contains alkalis and inorganic ion salts. Generally, cations such as Na^+, K^+, Ca^{2+}, Cu^{2+}, Mg^{2+}, and Cr^{3+} are the most common metal ions present in wastewater containing dyes. Adsorption can be influenced by varying the ionic strength of the solution [15]. The effect of ionic strength on adsorption was studied by adding a concentration of NaCl ranging from 0.1 to 0.6 while keeping the other parameters constant, that is to say leaving the same initial dye concentration at the level of 100 mg/L, the mass of the substrates at 0.1 g, the same room temperature, and the pH of the solution without any changes. Fig. 6 shows the rate of removal of MB for the three substrates studied as a function of ionic strength.

Fig. 6 shows that an increase in ionic strength from 0 to 0.6 M resulted in a decrease in the rate of MB removal by the three substrates studied. This goes from 72.24% without adding NaCl to 39.41% for a concentration of 0.1 M NaCl in sugarcane bagasse; for almond shell, it goes from 96.26% without adding NaCl to 82.05% if we add 0.1 M; and it goes from 98.34% without adding NaCl to 85.67% if we add 0.2 M in walnut shell. Fig. 6 shows as well that beyond 0.1 M NaCl for sugarcane bagasse and almond shell and 0.2 for walnut shell, a slight decrease is noticed due to the decrease of electrostatic attractive forces between the dye molecules and the biosorbents with the increase of NaCl ionic strength in the solution, as well as the dissolved NaCl reducing the negative sites available on the surface of the adsorbents as a consequence of the decrease of the dye adsorption [16].

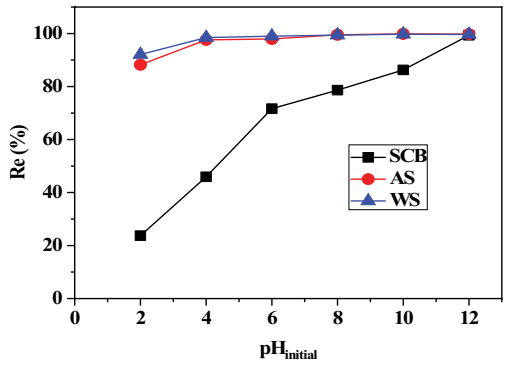

Fig. 5. Effect of solution pH on methylene blue removal rate.

3.6. Temperature effect

It is important to mention that the temperature of the solution plays a key role in the adsorption process as well as a significant indicator of the nature of adsorption, whether it is exothermic or endothermic; that is to say, if the adsorption capacity increases with temperature, adsorption is an endothermic process; on the other hand, if the adsorption capacity decreases with increasing temperature, adsorption is an exothermic process [17]. In order to study the effect of temperature on the adsorption of MB on the three prepared biosorbents (SCB, AS, and WS), the experiments were carried out by mixing 0.1g of each biosorbent with a mixture series of the dye (concentration 100 mg/L, pH = 6.8) in a water bath maintained at constant temperature: 15°C, 25°C, 35°C, 45°C, 55°C, and 65°C under agitation of 127 t/min during 1 h. The results are presented in Fig. 7.

The adsorption efficiency of MB with the three substrates (SCB, AS, and WS) at different temperature degrees (15°C, 25°C, 35°C, 45°C, 55°C, and 65°C) were studied to collect more data on the thermodynamic characteristics of adsorption. The results obtained are presented in Fig. 7 in which the results show a decrease in the removal rate of MB by SCB, AS, and WS with the increase of the solution temperature, which means that the adsorption of MB by the three biosorbents is exothermic. The removal rate of MB by the three biosorbents decreases from 75.08% at 15°C to 66.29% at 65°C for SCB, from 98.08% at 15°C to 83.34% at 65°C for AS, and from 98.08% at 15°C to 96.79% at 65°C for WS. This observation is related to the weakening of the physical bond between the dye molecules and the sorption sites of three substrates at higher temperatures on the one hand,

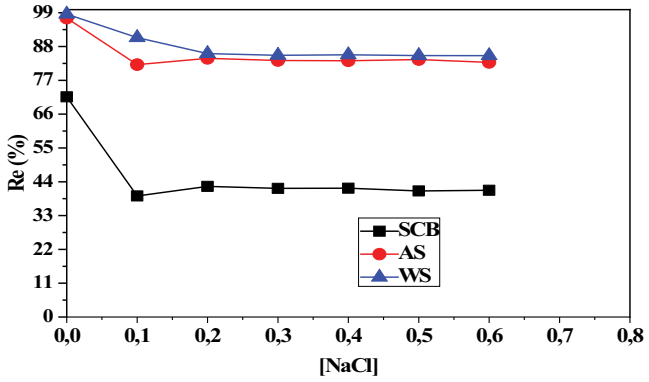

Fig. 6. Effect of ionic strength on the removal rate of methylene blue.

and on the other hand, the solubility of the dye increases at high temperatures, which leads to stronger interactions between the dye molecules and the solvent [2].

3.7. Adsorption kinetics

The thermodynamic equilibrium between the adsorbate in the liquid phase and the adsorbate fixed on the solid is reached at a speed that depends not only on the speed with which the constituents diffuse in the adsorbent and in the fluid but also on the adsorbent–adsorbate interaction. The time-dependent study of the adsorption of a compound on an adsorbent allows us to examine the influence of the contact time on its retention. In order to examine the adsorption mechanism, the kinetic models of pseudo-first-order, pseudo-second-order, and intraparticle diffusion have been used to test the dynamic experimental data [18]. The equations are described more precisely in the following section.

3.8. Modeling experimental data of MB adsorption kinetics

3.8.1. Pseudo-first-order model: Lagergren model

The pseudo-first-order kinetic model of Lagergren has been used; the following is a representation of its equation:

$$\ln\left(q_e - q_t\right) = \ln q_e - K_1 t \tag{3}$$

where q_e and q_t are the amounts of adsorbate (mg/g) at equilibrium and time t (min), respectively, K_1 is the pseudo-first-order adsorption rate constant (min^{-1}). The validity of the model can be verified by linearizing ln ($q_e - q_t$) as a function of t as well as the amount of solute adsorbed per gram of adsorbent at equilibrium (q_e) and the first-order sorption rate constant (K_1) can be evaluated from the slope of the intercept. The results obtained from the kinetic experiments were treated by the pseudo-first-order model is represented in Fig. 8; concerning the numerical results of the rate constant (K_1) and the quantities adsorbed at equilibrium (q_e), they are grouped in Table 1.

3.8.2. Pseudo-second-order model

The pseudo-second-order model based on the equilibrium adsorption capacity can be expressed by the study of Batana et al. [19]:

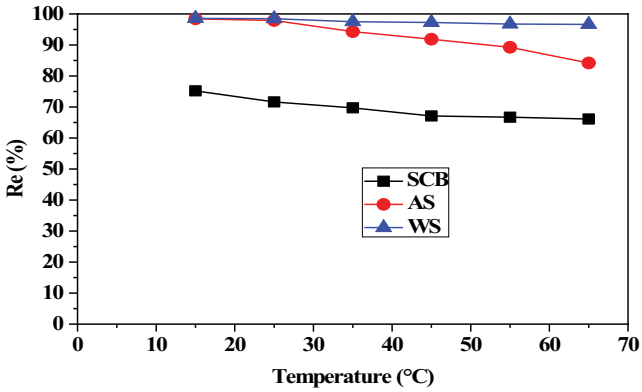

Fig. 7. Effect of solution temperature on methylene blue removal rate.

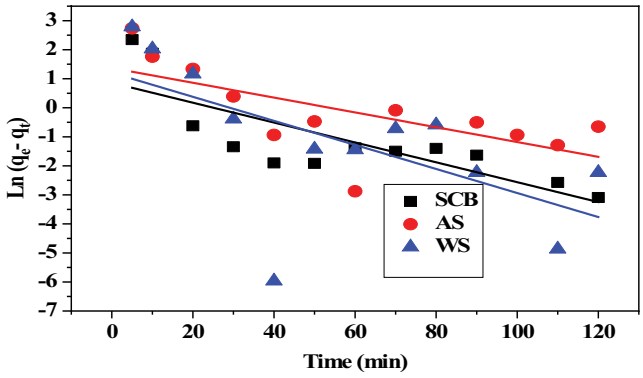

Fig. 8. Modelling of methylene blue adsorption kinetics by the pseudo-first-order model.

Table 1
Kinetic parameters of methylene blue adsorption

	Biosorbents	Sugarcane bagasse (SCB)	Almond shell (AS)	Walnut shell (WS)
	$q_{e,exp}$ (mg/g)	46.39	59.078	59.816
Pseudo-first-order model	K_1 (min^{-1})	0.0342	0.0261	0.0505
	$q_{e,cal}$ (mg/g)	2.362	3.9904	4.66
	R^2	0.6413	0.4492	0.4209
Pseudo-second-order model	K_2 (g/mg·min)	0.000458	0.0002822	0.000272
	$q_{e,cal}$ (mg/g)	46.73	59.524	60.60
	R^2	0.9999	0.998	0.9999
Intraparticle diffusion model	$k_{i,1}$ (g/mg·$min^{1/2}$)	4.2042	10.36	9.3194
	I	26.544	20.497	22.761
	R^2	0.9994	0.8223	0.914
	$k_{i,2}$ (g/mg·$min^{1/2}$)	0.0524	0.342	0.2863
	I	45.772	55.477	56.98
	R^2	0.76	0.69	0.99

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q} \quad (4)$$

The pseudo-second-order constant K_2 (g/mg·min) can be expressed experimentally from the slope and intercept of the line $t/(q_t)$ as a function of t.

The adsorption kinetics of MB on biosorbents can also be studied according to a pseudo-second-order equation, whose plot is shown in Fig. 9. The pseudo-second-order equation used is based on the sorption capacity of the solid phase. The graphical representation of t/q_t vs. t (Fig. 9) gives a straight line, allowing the calculation of the constant K_2. Table 1 summarizes the pseudo-second-order rate constants K_2 and the correlation coefficients.

3.8.3. Intraparticle diffusion model

The transfer of solute from the aqueous phase (dye in our case) to the solid phase generally follows four steps, where the phases can be independent of each other or simultaneous. The first represents the migration of the solute to the aqueous phase at the solid surface. The second represents the diffusion through the space between the particles (external diffusion). The third concerns the intraparticle diffusion, and finally, the surface chemical reaction between the surface function of the adsorbent and the active dye group. It is worth mentioning that the first step can be controlled by good agitation, while the last one is quite fast, which suggests that the diffusion process is most likely to be the limiting step that controls adsorption [20]. So, the intraparticle diffusion model, where the model of Weber and Morris [21] assumes that the diffusion process is the only limiting step that controls adsorption. The mathematical expression of this model is as follows:

$$q_t = K_{int} t^{1/2} + I \quad (5)$$

where K_{int}: intraparticle diffusion rate constant (mg/g·min$^{1/2}$); I: Weber and Morris parameter represents the value of the boundary layer thickness; q_t: quantity adsorbed at the moment (mg/g).

The values of the constants K_i and I are deduced from the slopes and intercepts of the linear parts of the model curves, respectively (Fig. 10), Table 1 summarizes the constants K_i and I as well as the correlation coefficients R^2.

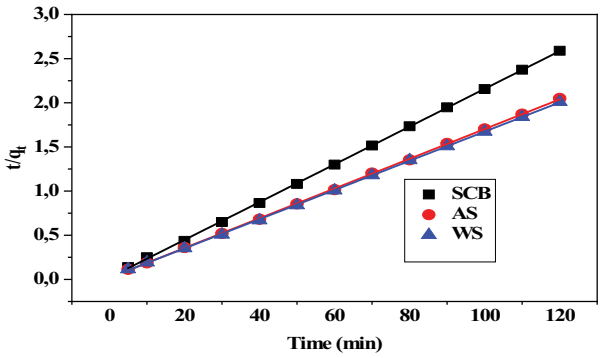

Fig. 9. Modelling of methylene blue adsorption kinetics by the pseudo-second-order model.

3.9. Comparison of kinetic models

Table 1 groups the pseudo-first-order K_1, pseudo-second-order K_2 velocity constants adsorbed quantities ($q_{e,cal}$) and experimental equilibrium adsorbed quantities ($q_{e,exp}$), as well as the intraparticle diffusion model velocity constants K_i and the constant I for the three biosorbents.

To determine the adsorption rate constants, the kinetic data are analysed using the kinetic models, namely the pseudo-first-order model proposed by Lagergren and the pseudo-second-order model, as well as the intraparticle diffusion model. The most representative model of the data is discussed based on the value of the correlation coefficient R^2. The parameters of Lagergren's model and the correlation coefficients are not satisfactory for the three materials, which confirm that Lagergren's model does not apply in this case. While the adsorption of MB on the three substrates does not correspond to the pseudo-first-order kinetics. And we notice that the pseudo-second-order model is adequate to describe the adsorption kinetics of MB dye by the three substrates studied since the correlation coefficient is high (R^2 = 0.99), and also that the values calculated by the pseudo-second-order model are very close to those determined experimentally, which confirms this result. Fig. 10 presents the plots of the intraparticle diffusion model. For the three substrates SCB, AS, and WS, the graphical representations reveal the existence of a double linearity, which means the presence of two kinetic mechanisms dominating the adsorption: the first linearity represents the instantaneous adsorption stage or adsorption on the external surface. The second portion represents the progressive adsorption stage or intraparticle diffusion, which represents the limiting stage of the adsorption mechanism [22].

3.10. Adsorption isotherm

The adsorption isotherm is a characteristic representative of the thermodynamic equilibrium between an adsorbate and an adsorbent. It characterizes the adsorption process and expresses the quantity of adsorbate present on the adsorbent q_e (expressed in mg per g of adsorbent).

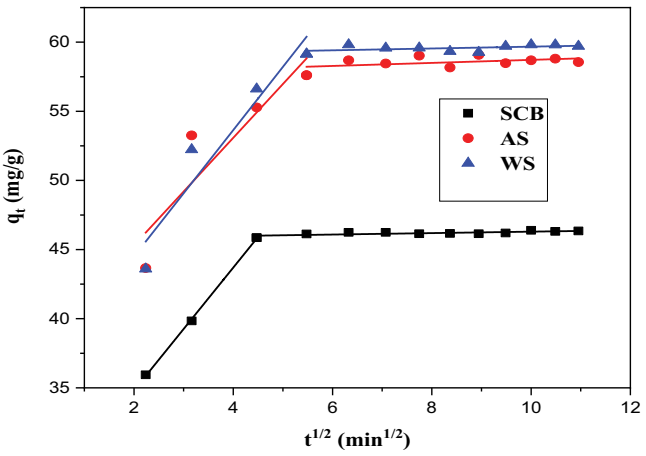

Fig. 10. Modelling of methylene blue adsorption kinetics by the intraparticle diffusion model.

3.10.1. Study of adsorption isotherm (modelling)

There are different theoretical models that describe the relationship between the mass of adsorbate fixed at equilibrium and the concentration. These are non-kinetic relationships that are called isotherms. These models can illustrate adsorptions in static or dynamic mode. In the following, we will present the experimental results of the adsorption of methylene blue by the three prepared substrates, which can be simulated by the two most commonly used isotherm models: the Langmuir model and the Freundlich model.

3.10.1.1. Langmuir isotherm

Langmuir's model quantitatively describes the formation of a monolayer of adsorbate on the outer surface of the adsorbent, so that Langmuir's isotherm is valid for a monolayer adsorption on a surface containing a finite number of identical sites. The model assumes uniform adsorption energies on the surface and no transmigration of the adsorbate in the plane of the surface. On the basis of these assumptions, Langmuir represented the Eq. (6) [23]:

$$q_e = \frac{q_0 C_e K_L}{1 + K_L C_e} \tag{6}$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation into linear form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m C_e K_L} \tag{7}$$

where C_e = concentration of the adsorbate at equilibrium (mg/L); q_e = amount of MB adsorbed per gram of adsorbent at equilibrium (mg/g); q_m = the theoretical maximum adsorption capacity expressed in (mg/g); K_L = constant of the Langmuir isotherm (L/mg).

The values of q_{max} and K_L were calculated from the slope and intercept of the Langmuir plot of C_e/q_e vs. C_e (Fig. 12).

3.10.1.2. Freundlich isotherm

This method is commonly used to describe the adsorption characteristics for a heterogeneous surface. These data often correspond to the empirical equation proposed by Freundlich [23]:

$$q_e = K_f \cdot C_e^{1/n} \tag{8}$$

where K_f = Freundlich isotherm constant; n = adsorption intensity; C_e = equilibrium concentration of the adsorbate; q_e = amount of adsorbed dye per gram of adsorption at equilibrium in (mg/g). The linear form of the Freundlich isotherm is given by the Eq. (9):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{9}$$

where K_f and n are determined from plotting $\ln q_e$ vs. $\ln C_e$ (Fig. 13).

3.11. Comparison of isotherm models

Table 2 shows the values of the Langmuir and Freundlich constants extrapolated from the equations of these two models.

From Table 2 it is noticed that the Langmuir correlation coefficients are equal to 0.9848, 0.9886, and 0.9978 for SCB,

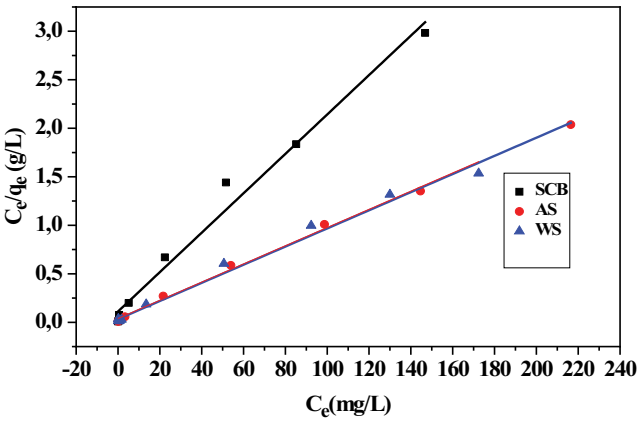

Fig. 12. Modelling of the adsorption isotherms of methylene blue by the Langmuir model.

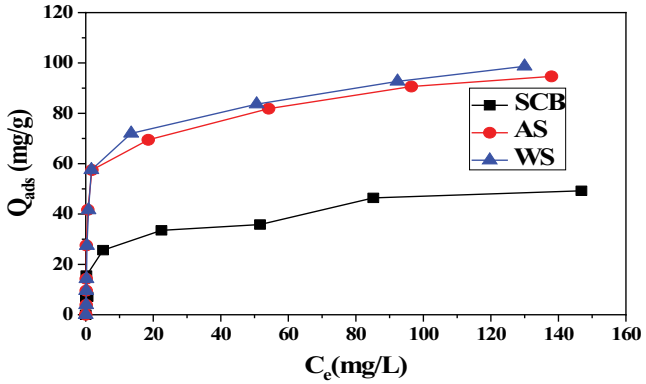

Fig. 11. Adsorption isotherm of methylene blue by SCB, AS and WS biosorbents.

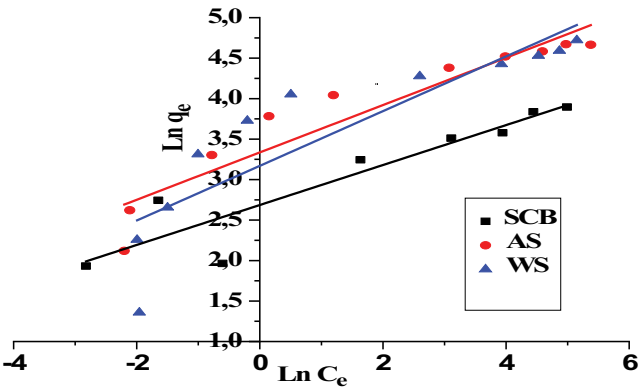

Fig. 13. Modelling of the adsorption isotherms of methylene blue by the Freundlich model.

Table 2
Langmuir and Freundlich constant models of methylene blue adsorption isotherms by SCB, AS and WS

	Biosorbents	Sugarcane bagasse (SCB)	Almond shell (AS)	Walnut shell (WS)
Langmuir model	K_L (L/g)	0.1824	0.237	0.2844
	q_{max} (mg/g)	49.2610	106.383	107.526
	R_L	0.0519	0.0404	0.034
	R^2	0.9848	0.9886	0.9978
Freundlich model	K_f	14.678	23.807	28.0987
	$1/n$	1/0.2467	1/3.317	1/0.2923
	R^2	0.8666	0.7812	0.8967

Table 3
Thermodynamic parameters of methylene blue adsorption

Parameters / Biosorbents	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol)	$\Delta G°$ (kJ/mol)						R^2
			288 K	298 K	308 K	318 K	328 K	338 K	
Sugarcane bagasse (SCB)	–0.0091	–0.084	–7.428	–7.685	–7.943	–8.201	–8.458	–8.716	0.901
Almond shell (AS)	–27,571.75	–72.584	–6,667	–5,941	–5,215	–4,490	–3,764	–3,038	0.982
Walnut shell (WS)	–14,716.17	–22.0987	–8,351	–8,130	–7,909	–7,688	–7,467	–7,246	0.937

AS, and WS, respectively, so the correlation coefficient values are higher compared to the Freundlich isotherm correlation coefficients, which means that the Langmuir isotherm better describes the adsorption process. This suggests that the adsorption of methylene blue on the biosorbent surface is a monolayer adsorption.

3.12. Thermodynamic study

The determination of thermodynamic parameters is very important to fully understand the effect of temperature on adsorption. It primarily allows us to predict the strength of the bonds between the adsorbent and the adsorbate. In general, the adsorption phenomenon is always accompanied by a thermal process, either exothermic or endothermic. These parameters can be calculated by the association of the thermodynamic equation and the Van't Hoff equation [24]:

$$\Delta G° = -RT\ln K \quad (10)$$

$$\Delta G° = \Delta H° - T\Delta S° \quad (11)$$

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (12)$$

where K: equilibrium constant K; $\Delta G°$: free enthalpy (kJ/mol); $\Delta H°$: variation of the enthalpy (kJ/mol); $\Delta S°$: entropy variation (J/mol·K); T: temperature (K); R: perfect gas constant.

Plotting $\ln K_d$ as a function of $1/T$ (Fig. 14) yields a straight line with slope $-\Delta H°/R$ and intercept $\Delta S°/R$ the results obtained are grouped together in Table 3.

The results obtained show that the negative values gathered reflect that the process of MB on SCB, AS and WS is exothermic in nature and can be qualified as physical adsorption since the value of $\Delta H°$ is negative and higher than

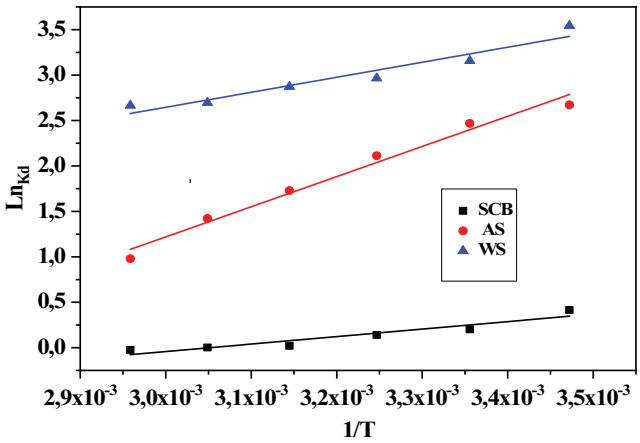

Fig. 14. Variation of the logarithm of the distribution coefficient K_d as a function of the inverse of temperature for SCB, AS and WS.

–40 kJ/mol, the negative values of $\Delta S°$ indicate a decrease in disorder at the solid/liquid interface, which means that the dye molecules are more organised at the interface than in the solution, thus an increase in the order of the molecules, the negative values of $\Delta G°$ indicate that the feasibility decreases at high temperatures and the spontaneity of adsorption of MB by the three biosorbents [25].

4. Conclusion

The aim of this study is to evaluate the purification performance of three biosorbents based on three substrates: sugarcane bagasse, almond shell, and walnut shell, for the treatment of wastewater that is contaminated with organic dyes. The adsorption experiments were carried out in order

to understand the effect of each parameter on the adsorption capacities as well as the individual materials. The parameters studied were contact time, adsorbent mass, dye concentration, pH, ionic strength, and temperature. The results show that the rate of adsorption of the MB increases with the increase of the adsorbent mass when passing from 0.05 to 0.5 g due to the increase of the specific surface, as well as the rate of adsorption increases for pH higher than the pH_{pzc} of the biosorbents and reaches a maximum at pH 12, with adsorption being very fast after 5 min and the equilibrium being reached at the end of 20 min. In a nutshell, the selected materials present good biosorbents for the removal of MB, which makes them excellent alternatives for wastewater treatment and dyeing effluents, especially in underdeveloped countries because of their low cost, high selectivity qualities; abundance, and efficiency.

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