Removel of malachite green on a bio-adsorbent derived from Walnut shells: characterization, Kinetic and isotherm study

Mahfoudi Leila
Science and Technology Laboratory of Water and Environment, Department of Material Sciences, Faculty of Sciences and Technology, Mohammed Cherif Messaadia University, Souk Ahras, 41000, Algeria.
Laboratory of Water Treatment and Valorization of Industrial Wastes, Department of Chemistry, Faculty of Sciences, Badji-Mokhtar University, B.P.12, Annaba 23000, Algeria.

Ali Ahmed Atef
Science and Technology Laboratory of Water and Environment, Faculty of Science and Technology, Mohammed Cherif Messadia University, Souk Ahras 41000, Algeria.

Tobbi Ouafa
Department of Science and Technology, Faculty of Technology, University Mostapha Benboulaid, Batna 2, 05000 Batna Algeria.

Hamoudi Souaad
Technology Laboratory of Materials and Process Engineering (LTMGP), Faculty of Exact Sciences, University of Bejaia, 06000 Bejaia, Algeria.
Department of Chemistry, Faculty of Sciences, Badji-Mokhtar University, B.P.12, Annaba 23000, Algeria.

Gheid Abdelhak
Science and Technology Laboratory of Water and Environment, Department of Material Sciences, Faculty of Sciences and Technology, Mohammed Cherif Messaadia University, Souk Ahras, 41000, Algeria

Hattab Zhour
Laboratory of Water Treatment and Valorization of Industrial Wastes, Department of Chemistry, Faculty of Sciences, Badji-Mokhtar University, B.P.12, Annaba 23000, Algeria.

***Corresponding Author:** Hattab Zhour
*Laboratory of Water Treatment and Valorization of Industrial Wastes, Department of Chemistry, Faculty of Sciences, Badji-Mokhtar University, B.P.12, Annaba 23000, Algeria.

Abstract
The sorption of malachite green (MG) in aqueous solution using Walnut shells was carried out in batch mode. Powder of Walnut shells was prepared within a size between 100 and 250 µm. The Walnut shells was characterized by Fourier Transform infrared spectra (FTIR), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and pH_{pzc}. Batch experiments were conducted to study the effect of different operating parameters such as contact time, pH, stirring speed, temperature, adsorbent dose and initial MG concentration on the adsorption of MG by Walnut shells. The results showed that the maximum adsorption capacity was 3.06 mg g^{-1} at pH 6,8, adsorbent dose of 3 g L^{-1} and initial MG concentration of 10 mg L^{-1}. The equilibrium data were analyzed using two isotherm models such as Langmuir and Freundlich by linear method. A satisfactory correlation coefficient value of the Langmuir isotherm demonstrates that the MG adsorption by Walnut shells is monolayer physical adsorption. The kinetic studies showed that the experimental data were best describing by pseudo- second-order model.

Keywords: *treatment, water, malachite green, walnut shell, adsorption, biosorbent, Kinetics.*

Introduction:

Dyes are substances widely used in various industries, including the textile, food, and chemical industries, to add color to different products. However, some dyes can be toxic to the environment and human health [1-4]. One of these dyes is malachite green [5], which is used in many applications, including dyeing textiles and coloring food products. Malachite green, also known as Schweinfurt green, is a copper-based pigment widely used since the 19th century. It has strong lightfastness and a vibrant color, making it a popular choice for many applications. However, it is important to note that malachite green is considered toxic [6-8]. It can cause skin, eye, and respiratory irritations, as well as adverse effects on aquatic organisms. In the face of these toxicity issues, research has been conducted to find alternative and sustainable treatment solutions. Biomaterials, such as walnut shells, have proven to be promising options. Walnut shells are residues from the food industry and can be used to adsorbend remove toxic dyes from water and other environments. Walnut shells are rich in compounds such as lignin and tannins [9-11], which have the ability to bind with

dyes and effectively remove them. These biomaterials [12-16] are not only abundant and inexpensive, but they are also environmentally friendly, providing a more sustainable alternative to treatment methods.

Objectives:
Our study aims to assess the effectiveness of raw walnut shells as an adsorbent material for the biosorption of malachite green dye. By utilizing this natural waste, we explore an environmentally friendly and cost-effective alternative for treating effluents containing toxic dyes. Parameters such as initial dye concentration, contact time, pH, and the mass of walnut shells will be analyzed to determine the feasibility of this approach in the environmentally friendly treatment of water contaminated with industrial dyes.

2. Materials and methods

2.1. Chemicals

The Malachite green (MG) Fig.1 was dissolved in distilled water to prepare a stock solution of 1000 $mg.L^{-1}$, and then a series of diluted solutions were prepared with concentrations from 10 to 100 $mg.L^{-1}$. The residual concentration of MG was measured using a UV–Vis spectrophotometer (JENWAL 7315) at a wavelength 617 nm. The adjustment of the pH of solution was achieved with 0.1 M HCl and 0.1 M NaOH and monitored by a pH meter (HANNA HI9812-5). The chemicals of analytical grade were purchased from Sigma–Aldrich-Fluka (Saint-Quentin, Fallavier, France).The used Walnut shells were collected from northeastern corner of Algeria (Annaba region).

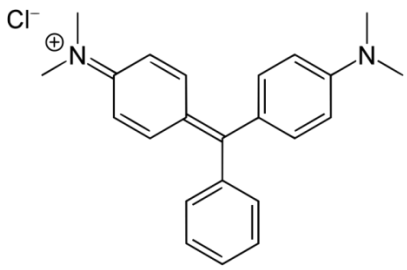

Fig. 1. Chemical Structure of Malachite Green

2.2. Preparation of adsorbent

Walnut shells were washed with distilled water to remove impurities, dried in open air then in an oven at 105 °C for 24 hours to remove residual moisture. The as-obtained sample was ground in an electric grinder and then sieved using a sieve (Afnor). Only particles with diameters between 100 and 250µm were used for further studies.

2.3. Characterization of adsorbent

The sample of Walnut shells was characterized by Fourier transform infrared (FTIR) analysis to determine the surface functional groups of the material using IR^{-1} affinity in combination with a single ATR reflection. The infrared spectra were registered in the range of 400-4000 cm^{-1} with a resolution of 2 cm^{-1}. The structure and purity were checked by X-ray diffraction (XRD) using Rigaku Ultima IV diffractometer equipped with copper Kα (λ = 1.5460 Å) radiation source, operating at 40 kV and 40 mA, with a scanning rate of 0.01° min^{-1} and 2θ range 0-70º. The morphology of the adsorbent was described using a scanning electron microscopy (JEOL 6400F).

The solid addition method determined the pH at the point of zero charge pH_{ZPC} [17]. This is done by the addition of a defined quantity of adsorbent 0.1g of Walnut shells to a series of 100 mL Erlenmeyer flasks containing 20 mL of KNO_3solution under shaking for 24 h. Before adding the adsorbent, the pH of each solution was adjusted to be in the range of (1.0–10.0) by the addition of either 0.1 M HCl or 0.1 M NaOH. And pH values were measured at the end of the test (pH_f).The pH_{PZC} was determined from the point of intersection of the resulting curve, at which $\Delta pH = 0$.

2.4. Kinetic and equilibrium studies

Adsorption experiments in batch mode were performed in order to study the influence of the Walnut shells dose, contact time, stirring speed, temperature, pH and dye initial concentration. During the study of adsorption of MG on Walnut shells, batch tests were conducted in room temperature 25±0.2°C. The adsorption experiments were conducted by mixing 20 mL of MG and 0.06 g of Walnut shells in glass container tubes. Afterwards, these tubes were posed in rotatory shaker on initial concentration of 10 mg L^{-1} at 50 rpm during 60 min at free pH. The Samples for analysis were taken at different time intervals. The suspension was then centrifuged for 5 min at 3000 rpm and the left-out concentration in the supernatant solution was analyzed using UV-Vis spectrophotometer.
The efficiency of MG removal rate R was calculated using Eq. (1).

$$R(\%) = \left(\frac{C_0 - C_e}{C_0}\right) 100 \qquad (1)$$

Where, R is the yield (%); C_0 and C_e are, respectively, the initial and equilibrium concentrations ($mg.L^{-1}$)
The quantity of the absorbed MG qe was calculated using Eq. (2).

$$q_e = \frac{(c_0 - c_e)V}{m} \qquad (2)$$

Where q_e ($mg.g^{-1}$) is the capacity of adsorption of equilibrium; represent the initial and the equilibrated concentrations of adsorbate respectively ($mg.L^{-1}$); V (L) is the volume of the solution (L); m (g) is the adsorbent mass (g).

3. Results and discussion

3.1. Characterizations of Materials

3.1.1. Structure analysis by FTIR

The FTIR spectra of Walnut shells are shown in Fig.2. The bands at 3380 and 2350 $cm^{-1}$are attributed to –OH and C–H, respectively (groups present in the lignin). The bond C=O of hemicellulose and C=C are observed at 1740 and 1613 cm^{-1} whereas C=O of the aromatic ring of lignin appears at 1512 cm^{-1}. The bands detected at 1368 cm–1 corresponds to the CO of lignin and xylene. The band at 1012 cm^{-1} is assigned to C–OH of hemicellulose and cellulose [18].

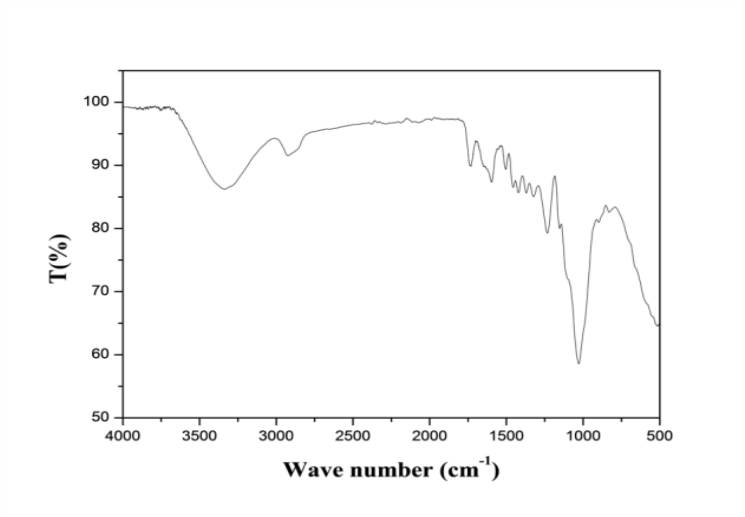

Fig. 2. FTIR spectra of Walnut shells.

3.1.2. Structure analysis by XRD

The X-ray diffraction pattern shown in Fig.3 reveals a typical spectrum of cellulosic material. Two peaks are observed; a main peak at 2θ = 29° associated with the presence of highly organized crystalline cellulose, and a secondary peak at 2θ = 21° which is often associated with a less organized polysaccharide structure. This result is confirmed by the FT-IR analysis where cellulosic peaks have been identified, it can therefore be concluded that Walnut shells used is semi amorphous, which is in good agreement with the literature [19, 20].

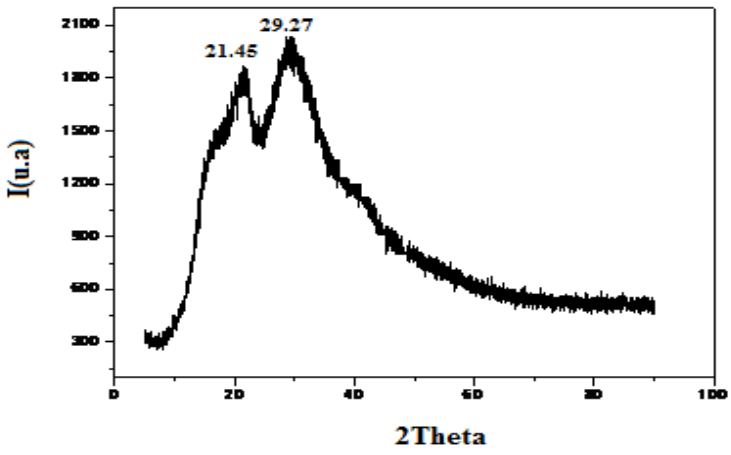

Fig. 3. XRD analysis results for the Walnut shells.

3.1.3. SEM observations

The textural morphology was observed by Walnut shells analysis and the obtained images are shown in Fig.4. Walnut shells powder exhibits porous architectures with hollow cavities which can boost the fixation of the highamount of dyes molecules [21].

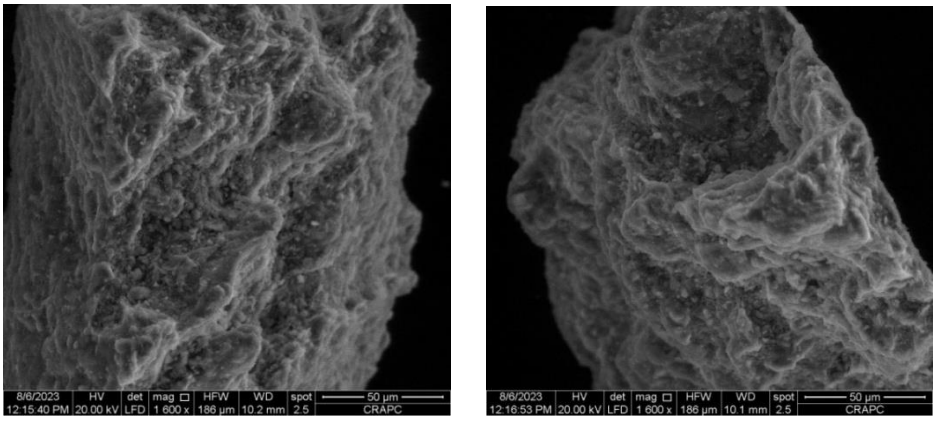

Fig. 4. SEM images of the Walnut shells sample

3.1.4. Determination of pH_{PZC}

Point of zero charge (PZC) The pH_{PZC} of an adsorbent is a very important characteristic that determines the value at which acid or basic functional groups no longer contribute to the pH of the solution [22]. Fig.5 shows that pH_{PZC} of CN is 5 .87, which implies that its surface is positively charged at pH < 5 .87 and negatively charged at This pH > 5.87.

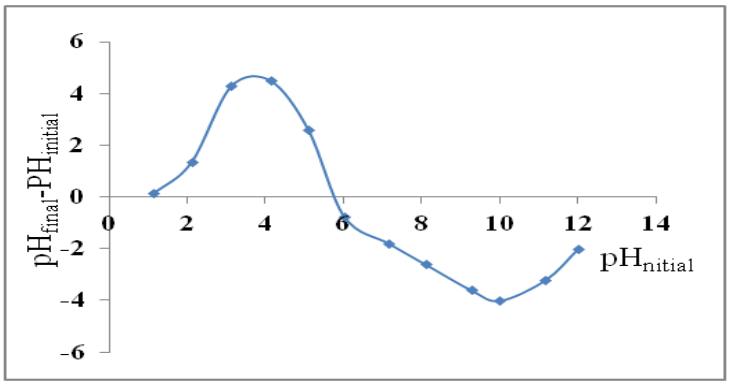

Fig. 5. Point of zero charge of Walnut shells.

3.2. Adsorption testes

3.2.1. Effect of adsorbent mass

To determine the optimal amount of walnut shells required for effective elimination of MG, we conducted an experiment using Pyrex tubes. We prepared a series of suspensions, each consisting of 20 ml of an aqueous solution containing 20ppm MG. The suspensions were varied with different amounts of walnut shells, ranging from 0.01 g to 0.1 g.

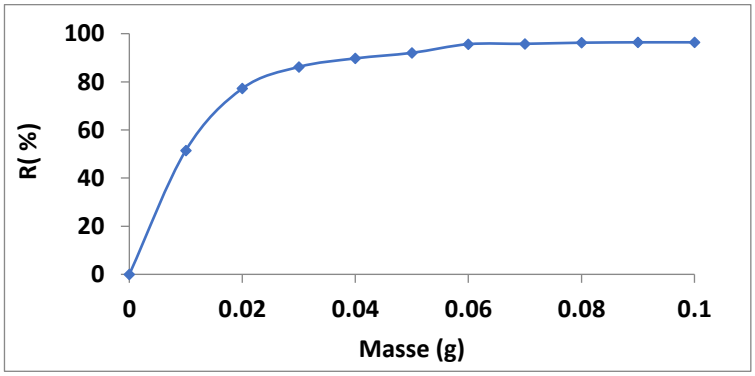

Fig. 6. Effect of adsorbent dose on MG removal by walnut shells ($[MG]_0$ = 10 mg L^{-1} ; stirring speed = 50 rpm; T = 25°C; pH = 6,8).

According to Fig.6, it can be observed that increasing the quantity of the support has a positive influence on the walnut shells retention yield. This is attributed to the increase in available surface area and therefore active sites on the surface [23,24]. Beyond a mass of 0.06 g of walnut shells (as shown

in the figure), the adsorption rate tends to stabilize, reaching a saturation plateau.

3.2.2. Effect of agitation speed

The effect of stirring speed on the removal rate was investigated at different stirring speeds such as 50, 100and 200 rpm at initial MG concentration of 10 mg L^{-1} and room temperature. According to the Fig.7 above, it can be observed that the curves are superimposed, indicating that the agitation speed does not have a significant effect on retention capacity. However, for energy reasons, we have chosen to work at an agitation speed of 50 rpm.Similar phenomena were observed in the kinetic experiments of MB on activated carbon and on Perlite [25, 26].

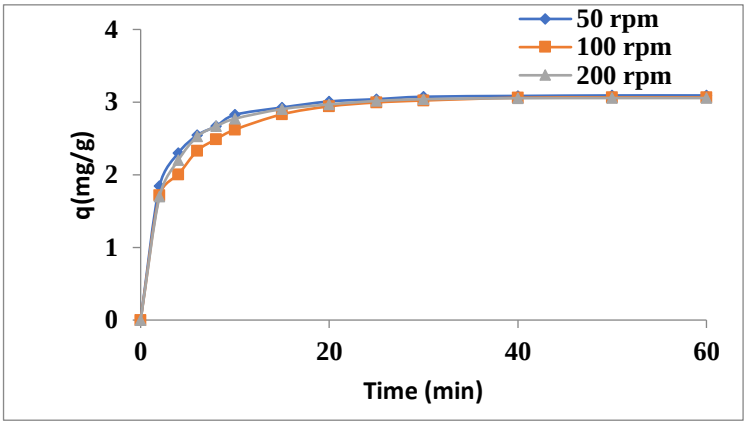

Fig. 7. Effect of agitation speed on MG removal by walnut shells (m = 3 g L^{-1} ; $[MG]_0$ = 10 mg L^{-1} ; T = 25°C; pH = 6,8).

3.2.1. Effect of initial MG concentration

Experiments were conducted to examine how the concentration of the adsorbent material affects the fixation of MG. Three different concentrations of 10, 20, and 30 mg/l were used, while the other parameters remained constant.

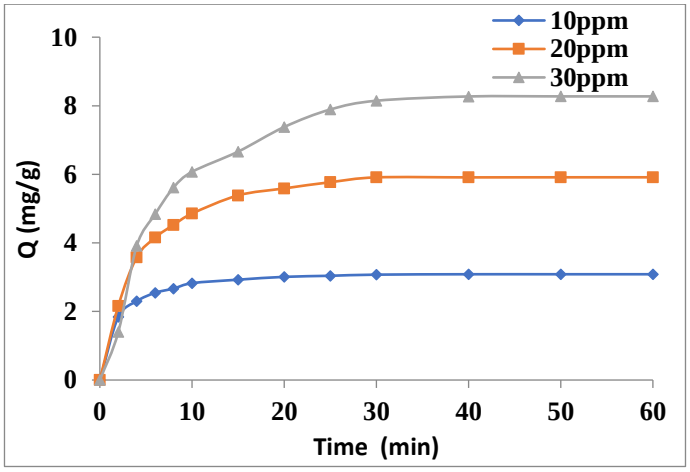

Fig. 8. Effect of initial concentration on the adsorption of MG onto walnut shells (m = 3 g L^{-1} ; agitation speed = 50 rpm; T = 25 °C; pH = 6,8).

The fig.8 demonstrates an increase in the adsorbed quantity of MG as a function of the initial concentration. This trend can be explained by the presence of a significant concentration gradient of MG between the solution and the surface of the adsorbent [27].

3.2.3. Effect of temperature

In order to study the effect of temperature on MG retention by walnut shells, we selected three different temperatures: 25, 35 and 45°C.

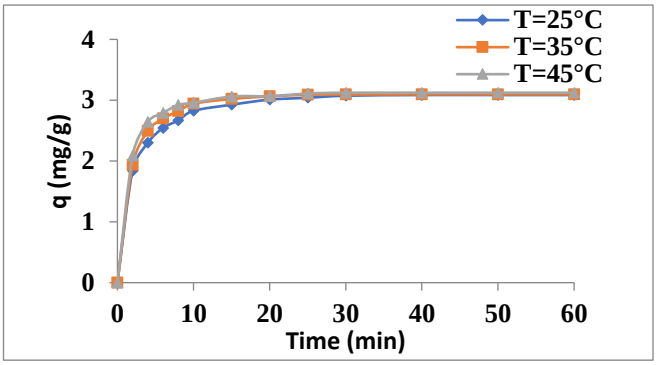

Fig. 9. Effect of temperature on MG removal by walnut shells
(m = 3 g L^{-1} ; agitation speed = 50 rpm; $[MG]_0$ = 10 mg L^{-1}; T = 25°C; pH = 6,8).

The fig.9 demonstrates that the increase in temperature has no impact on the adsorption capacity. This compartment can be due to the partial deactivation of the walnut shells surface or it can be explained by the destruction of some active sites by destroying their surface bonding. A similar result was found by other researchers [28, 29].

3.2.4. Effect of pH

pH plays a significant role in the adsorption process of pollutants, as it directly affects the surface charge of adsorbents and the nature of ionic species of adsorbates.

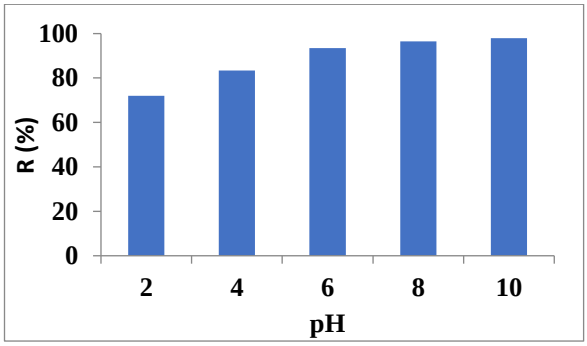

Fig.10: Effect of pH on the adsorption capacity of walnut shells for the removal of MG
(m = 20 g L^{-1} ; agitation speed = 50 rpm; $[MG]_0$ = 10 mg L^{-1} ; T = 25°C).

The fig.10 demonstrates an increase in the adsorption percentage, going from 72% to 97%, when the pH of the solution increases from 1 to 10. It is therefore obvious that an increase in pH favors the formation of groups such as: $R-NH^-$, $R-CO-NH^-$, $R-O^-$, $R-COO^-$, which leads to an increase in negative electric charges on the surface of walnut shells. This leads to an electrostatic attraction of the MG (R^-, Cl^-)due to its positive charge in solution, as shown by the following reactions:

$$R-NH_2 + OH^- \rightarrow R-NH^- + H_2O$$
$$R-CO-NH_2 + OH^- \rightarrow R-CO-NH^- + H_2O$$
$$R-OH + OH^- \rightarrow R-O^- + H_2O$$
$$R-COOH + OH^- \rightarrow R-COO^- + H_2O$$

However, in an acidic environment, functional groups such as amines, carboxyls, hydroxyls, etc. are protonated, resulting in a positive charge on the surface of the material [30, 31]. Therefore, electrostatic repulsion occurs with the VM, which inhibits adsorption. This can be expressed by the following reactions:

$$R-NH_2 + H^+ \rightarrow R-NH_3^+$$
$$R-CO-NH_2 + H^+ \rightarrow R-CO-NH_3^+$$
$$R-OH + H^+ \rightarrow R-OH_2^+$$
$$R-COOH + H^+ \rightarrow R-COOH_2^+$$

3.2.5. Effect of contact time

The study of the adsorption of MG on walnut shells in solution involves: the determination of the contact time which corresponds to the adsorption/desorption equilibrium or to an equilibrium state of saturation of the support by the substrate. The adsorption experiments to evaluate the effect of contact time on the adsorption of MG on the chosen adsorbent were carried out on MG solutions with an initial concentration of 10 mg/L and at a temperature of 25°C for a duration which varies from 2 to 60 minutes. The determination of the contact time, corresponding to the adsorption

equilibrium, allowed the establishment of adsorption isotherms for the adsorbent. Knowledge of this time is essential for calculating the maximum adsorption capacity and for identifying the type of adsorption that can occur in mono or multilayers.
The results presented in Fig.11 show a strong fixation from the beginning of the contact process, and equilibrium is reached after 30 minutes of contact. The rapidity of adsorption can be explained by the fact that at the beginning of adsorption, the number of available active sites on the surface of the adsorbent material is much higher than the number remaining after a certain time [32]. At this point, there is a pseudo-equilibrium between the adsorption and desorption rates, and adsorption becomes relatively slower, giving the impression of an equilibrium. In all adsorption experiments, we chose a time of 60 minutes to check the establishment of equilibrium between the different phases.

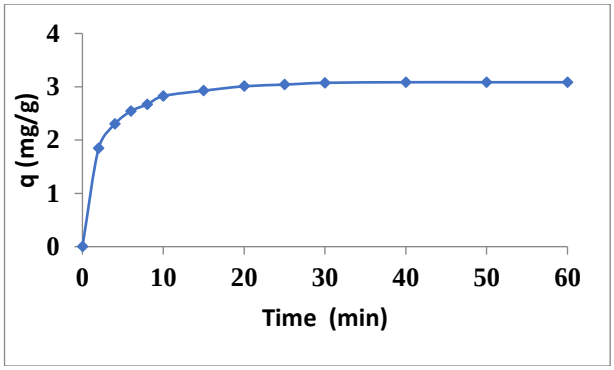

Fig.11: Effect of contact time on MG removal by walnut shells
(m = 3g L^{-1} ; $[MG]_0$ = 10 mg L^{-1} ; agitation speed = 50 rpm; T = 25 °C; pH = 6,8).

3.3. Kinetic modeling

Several kinetic models are developed to highlight the essential parameters of adsorption kinetics. Two models were used to model the adsorption of MG on walnut shells: the pseudo-first order model and the pseudo-second order model.

3.3.1. Pseudo-first-order kinetic model (PFO)

The pseudo-first order model is the oldest of the kinetic models, and was proposed by Lagergren (1898) [33]. This model makes it possible to describe the phenomena taking place during the first minutes of the adsorption process and it is more compatible with low solute concentrations.

The linear form of this model is represented by the following equation:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (3)$$

Where, t contact time; K_1: constant of adsorption speed of the kinetics of pseudo-first order; $q_t$and q_e: adsorption capacities respectively at the moment t and at equilibrium.
Fig.12 illustrates the pseudo-first-order kinetics.

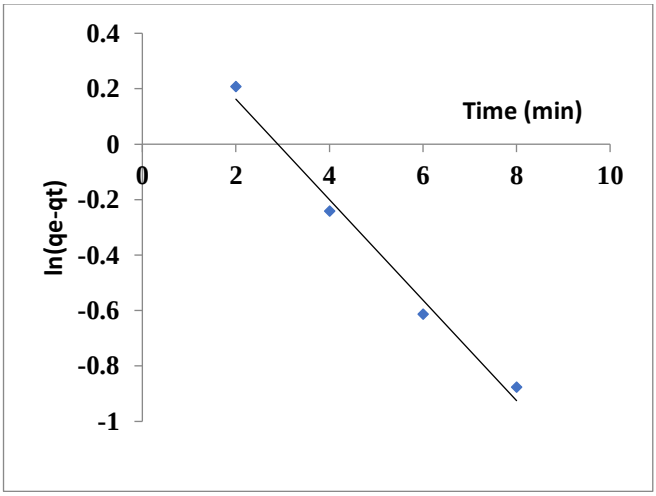

Fig.12: Pseudo first order model for the adsorption of MG on walnut shells
(m=3g/L, C=10mg/L and T=25°C).

3.3.2. Pseudo second order kinetics model (PSO)

This model was proposed by Ho and McKay in 1998 [34]. It was adopted to explain the sorption kinetics at a wider time interval, and can be described by the linearized form presented by the following relation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{Q_e} \qquad (4)$$

Where, t contact time; k_2: constant of adsorption speed of the kinetics of pseudo-second order; q_t and q_e: adsorption capacities respectively at the moment t and at equilibrium.

Fig.13 illustrates the pseudo-second order kinetics.

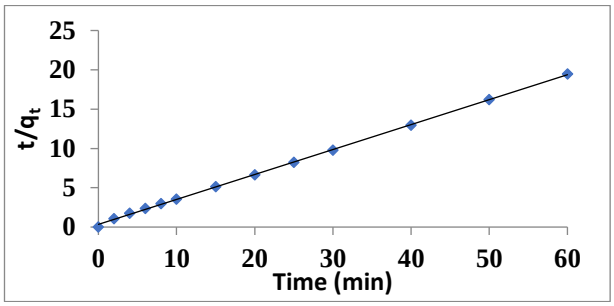

Fig.13: Pseudo second order model for the adsorption of MG on walnut shells.

Table 1: Parameters of the adsorption kinetics of MG on walnut shells.

Models						
$q_{e,exp}$ (mg.g^{-1})	PFO			PSO		
	$q_{e.cal}$(mg.g^{-1})	k_1	R^2	$q_{e,cal}$ (mg.g^{-1})	k_2	R^2
3.073	1 ,688	0,181	0.986	3,154	0,293	0.999

The study of the linear regressions presented in Fig (12 and 13) represented in Table 1 shows that the correlation coefficients (R^2) for the PSO kinetic model better describes the process of adsorption of MG on walnut shells. In addition, the theoretically calculated values ($q_{e,cal}$) by this model agree very well with those of the experiment ($q_{e,exp}$).

3.4. Adsorption isotherm

The establishment of adsorption isotherms enables to calculate the maximum quantity adsorbed by the solid and also the identification of the type of adsorption. The experimental obtained results show that the isotherm is of type L, which corresponds to the classification of Gilles [35]. This last, indicates a growth of adsorption when the concentration of the adsorbate increases (Fig. 14).

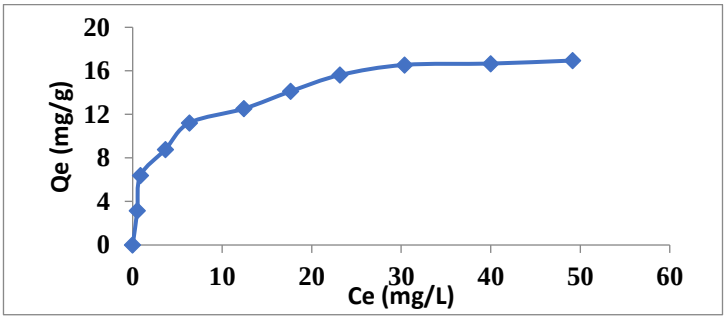

Fig. 14: Adsorption isotherms of MG ions on raw walnut shells.

3.4.1. Langmuir isotherm

The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions [36]. The Langmuir equation in the linear form is expressed as Eq. (4):

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \qquad (5)$$

The experimental results of the removal of MG according to the Langmuir equation are shown in Figure 15 which shows a linear distribution.

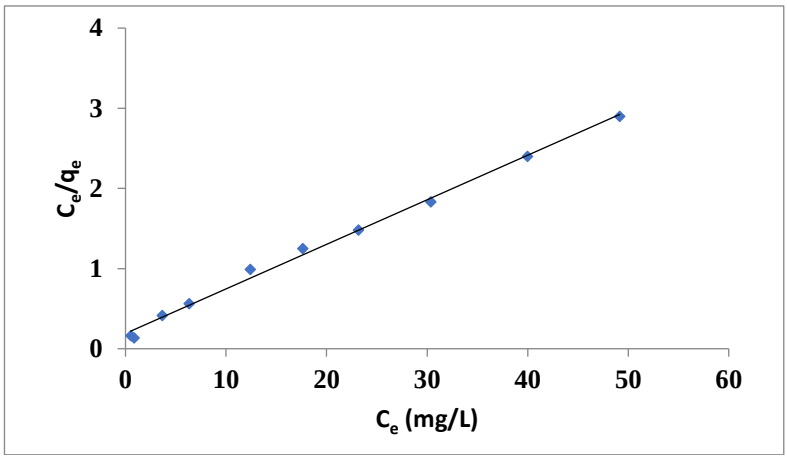

Fig.15: Linear form of the Langmuir model of the MG on walnut shells

An essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor R_L [37, 38]:

$$R_L = \frac{1}{1 + R_L C_0} \qquad (6)$$

where C_0 is the initial MG concentration (mg L^{-1}). The value of R_L indicated the isotherm of the Langmuir type. RL the value shows that the adsorption is variable in nature: unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$

Table 2: The calculated values of the separation factor R_L.

C_0	10	20	30	40	50	60	70	80	90	100
R_L	0.257	0.0147	0.103	0.079	0.064	0.054	0.047	0.041	0.037	0.033

At From the data calculated in Table 3, the RL is greater than 0 but less than 1 indicating that the Langmuir isotherm is favorable.

3.4.2. Freundlich isotherm

Freundlich equation is an empirical model based on heterogeneous adsorption over independent sites. It assumes that the multilayer adsorption process occurs on a heterogeneous surface and the equation is written in linear form as follows [39]:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \qquad (7)$$

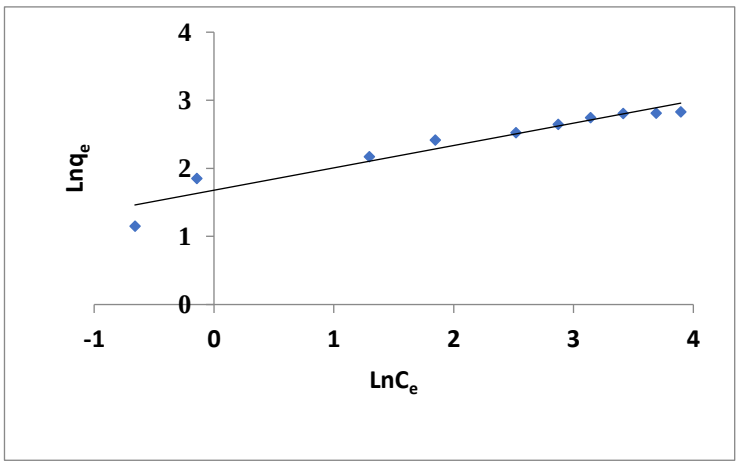

Fig. 16. Linear form of the Freundlich model of the MG on walnut shells

Where q_e : adsorption capacity of the solute per gram of adsorbent at equilibrium ($mg.g^{-1}$); where Q_e the amount of adsorbed per specific weight (mg/g); K_F Freundlich constants related to adsorption capacity; C_e the equilibrium concentration (mg/l); n Freundlich constants related to the adsorption intensity.

The values of K_F and n were determined from the intercept and slope of the linear plot of $\ln Q_e$ versus $\ln C_e$ in Fig. 16, respectively, and the results are presented in Table 4. The n value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption interpreted as a chemical process; if $n > 1$, then adsorption can be referred to as a physical process. n value in Freundlich within the range of 1–10 represents good adsorption [40].

Table 3: Isotherm parameters for MG onto walnut shells obtained by using the linear method

		Model					
		Langmuir			Freundlich		
Adsorbent	**q_{exp} (mg/g)**	**q_m (mg/g)**	**K_L (mg/g)**	**R^2**	**1/n**	**k_F (mg/g)**	**R^2**
walnut shells	16.948	18.18	0.289	0,995	0.328	5.354	0,926

The study of Langmuir and Freundlich adsorption isotherms are represented in Fig (15, 16) and Table 3. From these results, according to the values of R^2, q_m and q_{exp} (Table 3). It is clear that the Langmuir model is the better.

A comparison of adsorptive capacities of many of bio-adsorbents used for malachite green adsorption is shown in Table 4. The present work takes places in short time and at room temperature, therefore, it can be concluded that, walnut shells are considered as eco-friendly [41], efficient and effective bio-adsorbent for the removal of malachite green as compared with others studies reported in Table 4.

3.5. Comparison with other bio-adsorbents

Table 4: Comparison of the adsorption of the walnut shells for MG with other adsorbants

Used adsorbent	Capacity (mg/g)	Medium pH	Temperature K	Reference
Cellulose powder	2.422	7.2	298	[42]
Tamarind fruit shell	1.95	5	303	[43]
Commercial activated carbon	8.27	7	303	[44]
Neem sawdust	4.35	7.2	303	[45]
Helianthus Annuus seeds shells	7.69	7	298	[46]
walnut shells	16.94	6.8	298	This study

3.6. Conclusion

The purpose of this study was to find a use for walnut shells waste in removing a toxic dye called MG from water. The results showed that powdered walnut shells waste can effectively remove MG from water as an alternative adsorbent. The properties of the adsorbent material were analyzed using different techniques to better understand its effectiveness. The study found that the best efficiency rate was 93%. By studying the influence of various parameters such as pH, mass, initial concentration, stirring speed, and temperature, the optimal conditions for MG removal were determined. The pseudo-second order model was successfully used to fit the kinetic adsorption data. The adsorption of MG molecules with walnut shells biosorbent followed the Langmuir adsorption isotherm. This detailed study demonstrated that a low-cost and environmentally friendly bioadsorbent made from agricultural waste has great potential for removing MG dye from water, making it a possible alternative to commercial methods and a promising solution for removing other organic contaminants in the future.

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