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Removal of Malachite Green Dye From Aqueous Media using *Helianthus Annuus* Seeds Shells as Eco-Friendly Adsorbent: Optimization, Equilibrium, and Kinetic Studies

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Abstract

The fat diffusion of organic dyes in our environment has become a very serious ecological problem, which needs the improvement of new and low-cost methods for their elimination from aquatic media. In this In this approach, we studied the use of the *Helianthus annuus* seeds shells as natural, low-cost and eco-friendly adsorbent for the removal of the malachite green (MG) from aqueous media. The *Helianthus Annuus* seeds shells (HA-Ss) were characterized using various techniques such as FTIR, SEM, and ATG. The sorption tests were performed according to the Batch system, under the effects of four physicochemical factors, including the adsorbent mass (0.0025 and 5 $g.L^{-1}$), medium pH (1-10), MG initial concentration (10-50 mg/L), and temperature (25-45°C). The removal optimal condutions were found to be 2.5 g/L of *Helianthus annuus* seeds shells, 20 mg/L as MG initial concentration, and pH 7 for 60 minutes of contact time with a removal efficiency up to 99%. Several kinetic models including pseudo-first order and pseudo-second order were used to describe MG adsorption mechanism, the modeling studies indicated that adsorption mechanism follows the pseudo-second-order kinetic model, and the adsorption isotherms follow the Freundlich model with Q_e reached 7.69 mg/g.

Keywords: Removal; Adsorption; Malachite green, *Helianthus annuus*, seeds shells; eco-friendly adsorbent.

1. Introduction

In last few years, the removal of organic dyes and pigments from water resources has become an essential environmental process; this problem is generated by the fat utilization of these substances in the world wild [1–4]. For example, the discharges from plastic, papers, textiles, wood, and leather industries are contaminated by important quantities of organic colorants[5]. These compounds are

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characterized by various chromophore groups related to aromatic rings, in particular, Safranin, malachite green, eosin, basic Fuchsin, acid Fuchsin, crystal violet, and rodamine B[1,5–7].

Malachite green is one of the triphenylmethane dyes; it is a nonbiodegradable recalcitrant colorant. The high toxicity of substance related to its dangerous effect on ecologic system, especially for the aquatic organisms[1,7–9]. The toxicity of the malachite green is devolved during bioaccumulation and it can be transported in various media, e.g., sediments, foods, and water resources [5]. Many of studies confirmed that the MG can be metabolically reduced by the aquatic organisms to LMG (leucomalachite green). For example, when fish exposed to MG reach the consumer, the amount of leucomalachite green present in the fish is expected to be higher than that of Malachite green. Other studies avowed that the malachite green has a high harmful degree to animals such as rabbits, mices and rats[1,9]. The toxic data showed that the median lethal dose LD_{50} for rats and mice are estimated to be 80 mg kg^{-1} and 275 mg kg^{-1}, respectively [1,9]. In other side, the pollution by malachite green leads to several dangerous effects for humans, including digestive system irritation, sensitivity, mucous membrane irritation and bladder, nausea, and vomiting [1,9]. Consequently, it is necessary to treat the discharges contaminated by this compound before they are discharged via the wastewater system. Therefore, various techniques were improved to eliminate malachite green from aqueous media, including advanced oxidation, adsorption, microbial biodegradation, photo-degradation, ozonation, and photocatalysis [1,7–11]. Nevertheless, the majority of these processes are energy-consuming and expensive technologies, especially when applied for treating large amount of polluted water. The adsorption technique appears to be well suited to eliminate this dye because of its proven effectiveness in removing organic pollutants and also for economic reasons, using low-cost adsorbents such as fibers, leaves, shells, clays, and sand [5,12].

Agricultural wastes such as *Helianthus annuus* seeds shells (HA-Ss) are considered as low-cost and eco-friendly adsorbents, these bio-adsorbents are available in large quantities and have proven to be effective in industrial effluents [13–15]. Many researchers have been done to investigate the efficacy of *Helianthus annuus* seeds shells as a bio-adsorbent for dyes removal [13]. Other researchers have focused on the study of the adsorption of heavy metals using this material [13–15]. *Helianthus annuus* seeds shells have good adsorption characteristics due to its constituent composition of hemicelluloses, lignin and celluloses, which contain groups of substituent's such as hydroxyl, amine and acid groups that may react with the organic dyes [13–15].

In this study, we interested to the removing of malachite green from aqueous media using *Helianthus annuus* seeds shells as eco-friendly adsorbent. To attain an appropriate removal efficiency of this dye, the effect of four physicochemical factors including, the HA-Ss powder mass, solution pH, MG initial concentration, and medium temperature, was studied in batch system. Also, the regeneration

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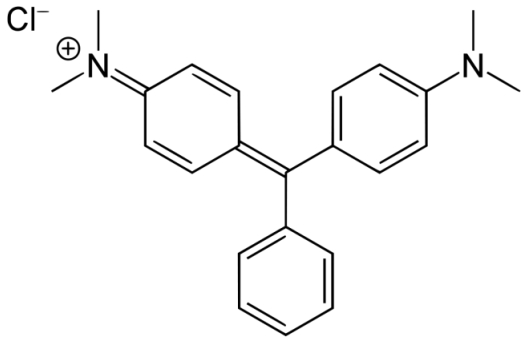
of used HA-Ss powder was realized in the aim to reutilisation of this bio-adsorbent for other adsorption operations.

2. Experimental

All solutions used in adsorption tests were made by dissolving chemicals of analytical grade reagent (Fluka) in distilled water. A stock standard solution (500 mL) of malachite green (Table 1) was prepared by melting 500 mg of $C_{23}H_{25}ClN_2$ in of distilled water. The solutions pH was adjusted using aqueous solutions (0.1 mol/L) of NaOH and HCl. The used *Helianthus annuus* seeds shells were collected from northeastern corner of Algeria (Annaba region).

Table 1. Physicochemical properties of malachite green.

Chemical Structure	
UPAC Name	4-{[4-(Dimethylamino)phenyl]phenylmethylidene}-N,N-dimethylcyclohexa-2,5-dien-1-iminium chloride
Molecular Weight	364,911 g/mol
Water Solubility	66.6 g/L
pKa1	1.3
pKa2	12.5
λ_{max}	617 nm

2.1. Preparation and characterization of bio-adsorbent

The selected bio-adsorbent (*Helianthus annuus* seeds shells) was prepared following a well-defined protocol. The HA-Ss were washed several times with distilled water, and then dried in air for 10 days [13,16]. The dried samples were powdered well and sieved by an appropriate mesh sieve; only particles of sizes between 250-315 µm were used in adsorbent tests. The collected powder was dried in the oven at 100°C and stored in desiccators until use[13,16]. The dry powder was characterized by

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different methods such as FTIR, BET, SEM, and TGA technique. The seeds shells infrared spectroscopy spectrum was obtained using a Shimadzu Spectrometer (FTIR 8700, Japan) 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}. Their surface morphology was also characterized using Quanta (200 FEI) scanning electron microscopy and the analysis of shell powder samples were conducted in attached X-rays microanalyses. Additionally, the thermogravimetric analysis (TGA) was performed on the Mettler Toledo Stare TGA system, at a heating rate of 10°C min^{-1} (30 ml. min^{-1}) up to 600°C under N_2 flow gas atmosphere.

2.2. Batch adsorption studies

During the study of adsorption of MG on the HA-Ss powder, batch tests were conducted in room temperature 25±0.2°C. The batch adsorption experiments were conducted by mixing 20 mL of MG and 50 mg of HA-Ss powder in glass container tubes. Afterwards, these tubes were posed in rotatory shaker on initial concentration of 20 mg L^{-1} at 50 rpm during 120 min at pH 7. 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 MG adsorbed amount per gram adsorbent at equilibrium (Q_e, mg/g), was calculated by the flowing equation [5,17,18]:

$$Q_e = \frac{(C_0 - C_e)V}{m} \qquad (2)$$

Where C_0 and C_e are the malachite green initial concentration at time 0 and at equilibrium, respectively (mg/L), V is the solution volume in L and W is the used mass of adsorbent (g) [5,7,17,18]

The effectiveness of elimination of MB is calculated by equation (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 adsorbed MG, q_e, was calculated using equation (2).

$$Q_e = \frac{V(C_0 - C_e)}{m} \qquad (2)$$

Where q_e ($mg.g^{-1}$) is the capacity of adsorption at equilibrium; C_0 and C_e are, respectively, the initial and equilibrium concentrations ($mg.L^{-1}$); V (L) is the volume of the solution; m (g) is the mass of the adsorbent[5,17–19].

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3. Results and discussions

3.1. Bio-adsorbent characterization

The *Helianthus annuus* seeds shells are composed of cellulolytic materials, lignin, and pentosans covering the kernel, which accounts for 80% of its full weight, which makes it a flexible and durable bio-tsorbent[15,16,20]. The HA-Ss infrared spectrum (Figure.1) shows different peaks that are assigned to different functional groups and bands. Sunflower shells are lignocellulosic materials with a chemical composition of hemicelluloses, lignin and celluloses. The 3352 cm^{-1} band is assigned to the N-H and –OH stretch mode[15,16,20]. The bands at 2940, 2862 cm^{-1} are attributed to the C-H of the aromatic components and to the stretching vibration C-H. The peak at 1747 cm^{-1} is due to carboxyl groups or ester C = O and to 1629 cm^{-1} of amide binding N-H. The peak of absorption appearing around 1617 cm^{-1} is attributed to the vibrations of the aromatic ring of lignin and 1114 cm^{-1} is attributed to alcohols -C-O and carboxylic acids. The bands at 1388 and 1173cm^{-1} are respectively due to shear CH_2 and stretching of the C-N amines[15,16,20].

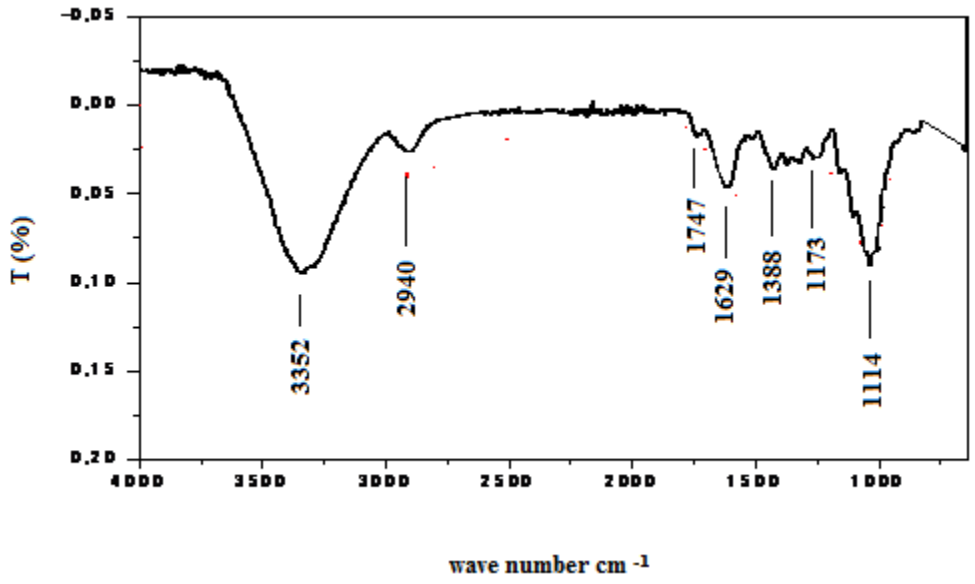

Figure. 1: Spectres FTIR of *Helianthus annuus* seeds shells powder.

The morphological structure of *Helianthus annuus* seeds shells is shown in Figure.2 at various magnifications. The SEM images show clearly that the HA-Ss surface is characterized by high porosity due to the presence of large number of small holes as mesopores and macropores with sizes in the range (10 -30 µm), these holes promote the transport of chemical species in all directions through the HA-Ss (diffusion phenomenon), which may be conducive to the retention of pollutants that may be suitable for the retention of pollutants. However, the SEM images of HA-Ss after the adsorption show the presence of new layer due to the appearance of MG molecules adsorbed on the surface of *Helianthus annuus* seeds shells[16,21,22].

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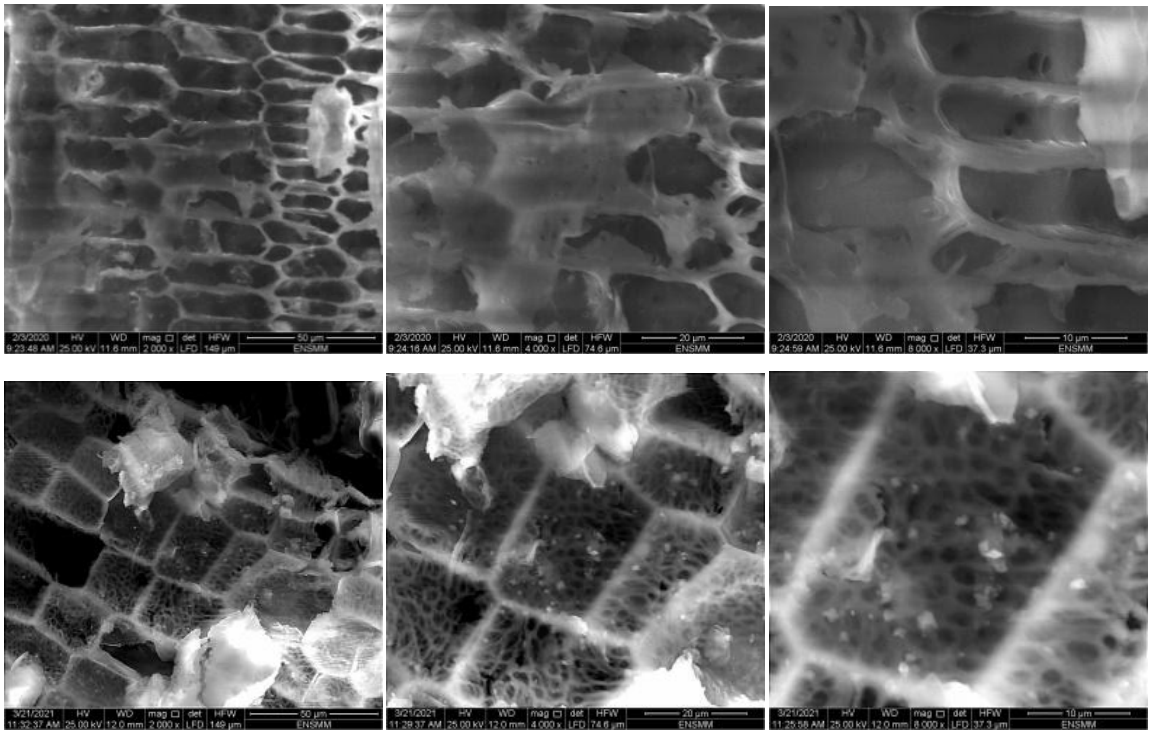

Figure 2: Scanning electron microscope images of *Helianthus Annuus* seeds shells at various magnifications before and after MG adsorption.

The ATG plot shows five phases of mass loss as shown in Figure 3. The first step from 25°C to -120°C corresponds to a loss of approximately 11.55% of the weight of HA-Ss sample due to dehydration of this sample *Helianthus annuus* [16,21–23]. The second weight loss is 11.96% was observed in temperature range of 120-250°C, which corresponds to the depolymerization of hemicellulose. the third step 250-327°C with the highest loss of 40.59%, it indicates the degradation of celluloses[16,21–24], the fourth step 327-500°C with the loss of 26.46%, corresponds to the degradation of lignin and the fifth step 500-600°C correspond to carbon residues 6.96% [16,21–24].

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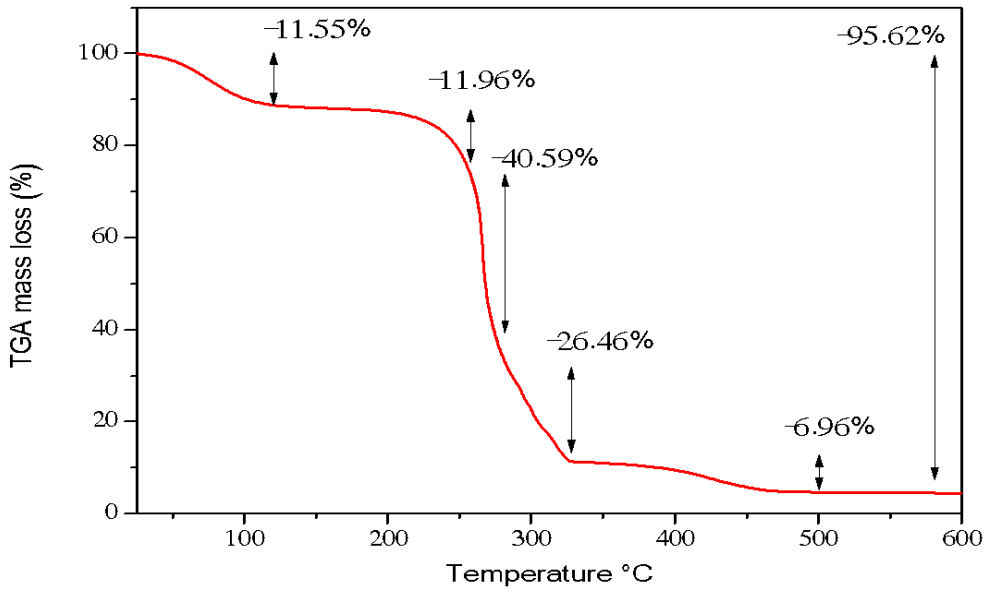

Figure 3: The ATG plot of the *Helianthus Annuus* seeds shells powder.

3.2. Optimization of main parameters affecting the malachite green Bio-sorption

3.2.1. Effect of the adsorbent dose on bio-sorption of malachite green

The effect of adsorbent mass on the adsorption percentage of MG onto the HA-Ss powde was studied by changing the quantity of adsorbent (0.0025–0.1g), at volume solution of 20 mL, temperature (25±0.2°C), pH 7 and contact time 120 min and initial concentration of 20 mg L−1. The obtained results are shown in Figure 4. The obtained results show that the% elimination of HA-Ss increases with increasing HA-Ss mass. Above a mass of 0.05g, the level tends to stabilize with the appearance of a saturation level (Figure 4). From Figure 5, it can be seen that the influence of increasing the amount of support is positive on the retention efficiency. This phenomenon is attributed to the increase in the available surface area and therefore active surface sites[25,26].

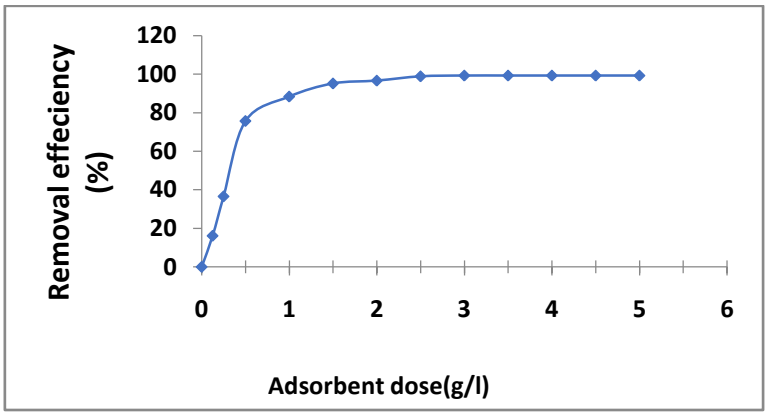

Figure 4: Effect of adsorbent dose on the bio-sorption of malachite green onto *Helianthus annuus* seeds shells ($[MG]_0$ = 20 mg.L^{-1}, contact time = 120 min, T°=25°C).

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3.2.2. Effect of the medium pH on the bio-sorption of malachite green

The medium pH has a remarkable influence on the pollutant adsorption process, as it directly influences the surface charge of the adsorbents and the nature of the ionic species of the adsorbates [27].

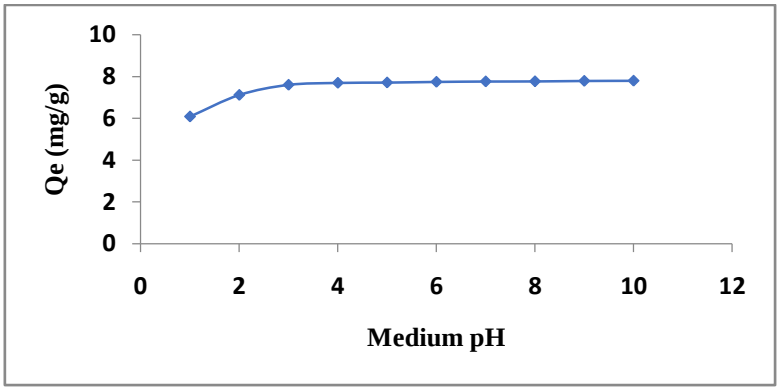

Figure 5: Effect of medium pH on bio-sorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5 g/l, $[MG]_0$ = 20 mg.L^{-1}, contact time = 120 min, T°=25°C).

Figure 5 shows the effect of pH on MG removal by HA-Ss powder. It is found that when the pH of the solution goes from 1 to 10, the adsorption quantity goes from 6.07 to 7.79 mg / g. It is therefore clear that an increase in pH favors the formation of the groups $R-NH^-$, $R-CO-NH^-$, $R-O^-$, $R-COO^-$, therefore an increase in negative electric charges at the surface of the MG which leads to an electrostatic attraction of the MG (R^+, Cl^-) due to its positive charge in solution[28] according to the following equation:

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

However, in an acidic medium, the functional groups amino, carboxylic, hydroxyl, etc. are protonated, and therefore its surface becomes positively charged [16,28,29]; hence electrostatic repulsion with MG which inhibits adsorption, this can be expressed by the following reactions:

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

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3.2.3. Effect of the medium temperature on bio-sorption of malachite green

Effect of temperature on the adsorption capacity of MG at 25°C, 35°C, and 45°C by HA-Ss powder was studied at pH 7, MG concentration 20 mg/L, and dose adsorbent 2.5 g/L. As shown in Fig. 6 the temperature has no effect on the capacity adsorption of MG on HA-Ss. This compartment can be due to the partial deactivation of the HA-Ss 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 [30,31].

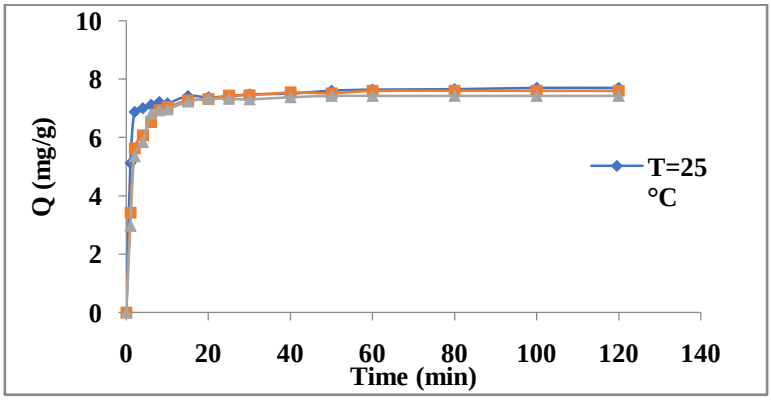

Figure 6: Effect of medium temperature on bio-sorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5g/L , $[MG]_0$ = 20 mg.L^{-1}, pH=7).

3.2.4. Effect of the initial concentration on bio-sorption of malachite green

To study the influence of the concentration of the adsorbent material on the binding of MG, tests were carried out with concentrations of 10 to 50 mg/l. The other parameters are kept constant.

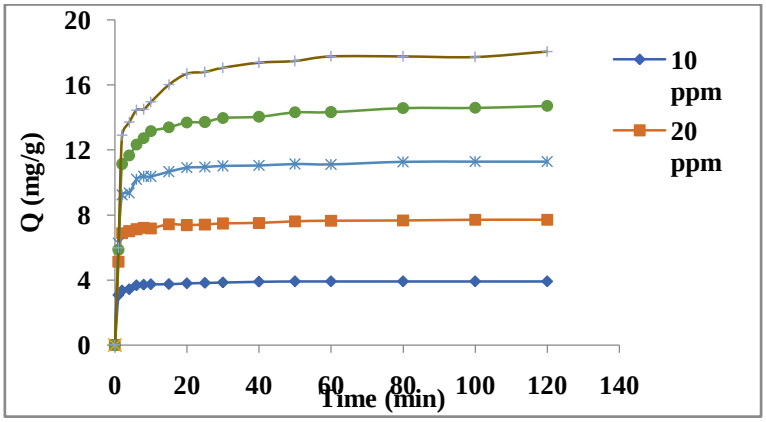

Figure 7: Effect of initial concentration on the bio-sorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5g/L , pH=7 and contact time = 120 min, T°=20°C).

Figure.7 shows that the adsorbed quantity of MG increases as a function of the initial concentration. This evolution can be explained by the existence of a strong concentration gradient in MG between the solution and the surface of the adsorbent [32]. 30

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3.3. Bio-sorption kinetic modeling

Numerous scientific studies related to the malachite green adsorption used various kinetic models in order to underline the essential parameters of adsorption kinetics. The kinetic models describe the reaction rates which make it possible to determine the contact time taken to reach the adsorption equilibrium [32]. This is an important step in any adsorption study. For this, we followed the adsorption kinetics for an initial concentration of 20 mg/l, with HA-Ss dose of 2.5 g/L as shown in figure 8.

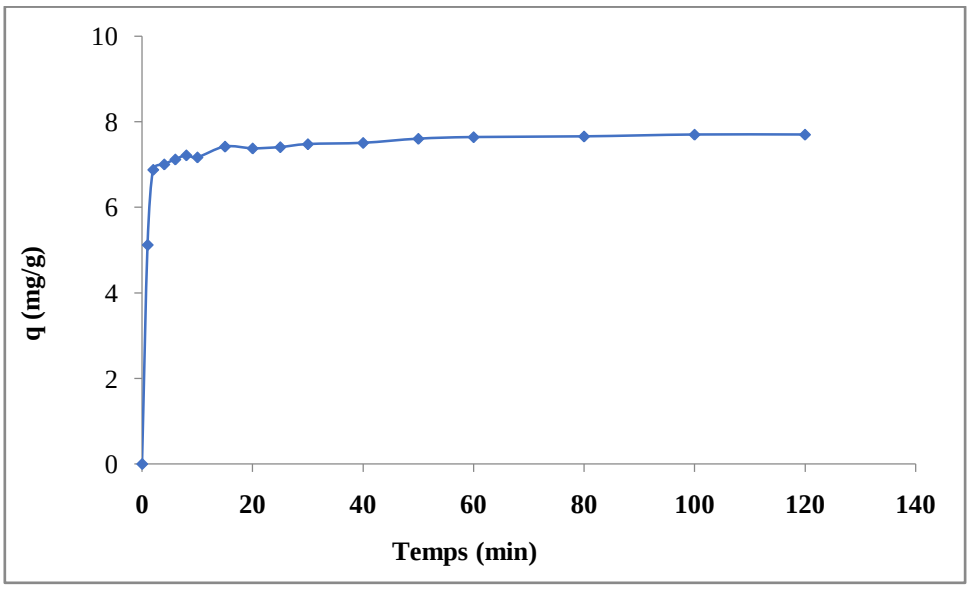

Figure 8: Kinetic of the bio-sorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5g/L , $[MG]_0$ = 20 mg.L^{-1} pH= 7, T°=25°C).

Based on the shape of the curve, we notice strong fixation early in the contact process and equilibrium and reached after 60 minutes of contact. The speed of adsorption can be explained by the fact at the start of adsorption, the number of active sites available on the surface of the adsorbent material, is much greater than that of the sites remaining after a certain time, at this level it is a pseudo-equilibrium between the speed of adsorption and desorption, the adsorption becomes relatively slower which gives the impression of equilibrium. In all of the adsorption tests, we opted for a time of 60 minutes to ensure that the equilibrium was established between the different phases.

The pseudo first order model is the oldest of the kinetic models, and was proposed by Lagergren (1898) [17,33,34]. This model makes it possible to describe the phenomena that take place during the first minutes of the adsorption process and it is more compatible with low concentrations of solute. The linear form of this model is represented by the following equation[17,33,34]:

$$ln(Q_e - Q_t) = ln\, Q_e - k_1 t \qquad (3)$$

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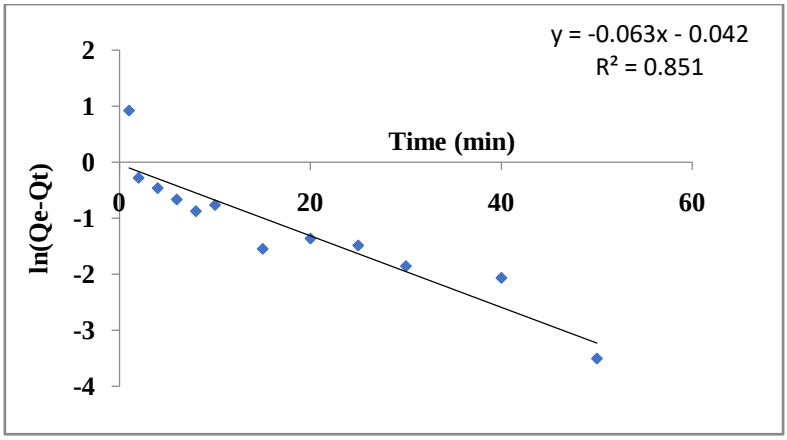

Figure 9: Plot of the pseudo--first-order of malachite green bio-sorption onto *Helianthus Annuus* seeds shells (HA-Ss dose = 2.5g/L , $[MG]_0$= 20mg/l, pH= 7 and contact time = 120 min, T°=25°C).

The pseudo second order kinetics model (PSO) was proposed by Ho and Mc Kay in 1998 [35,36]. It was adopted to explain the kinetics of sorption. It is assumed that the adsorption follows second order chemisorption, and can be described by the linearized form presented by the following relation:

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

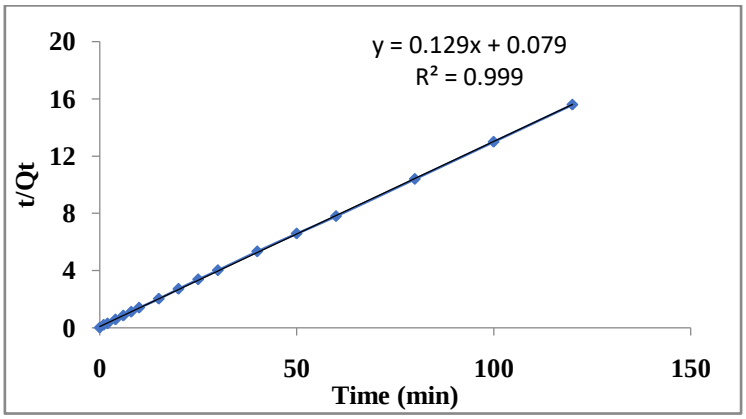

Figure 10: Plot of the pseudo--second-order of malachite green bio-sorption onto *Helianthus Annuus* seeds shells (HA-Ss dose = 2.5g/L , $[MG]_0$=20mg/l, pH= 7 and T°=25°C).

Tableau 2: Parameters of pseudo-first-order and pseudo-second-order kinetic models of malachite green bio-sorption on *Helianthus Annuus* seeds shells.

$Q_{e.exp}\,(\mathrm{mg}.g^{-1})$	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	$Q_{e.cal}\,(\mathrm{mg}.g^{-1})$	k_1	R^2	$Q_{e.cal}\,(\mathrm{mg}.g^{-1})$	k_2	R^2
7.69	0.958	0,063	0.851	7.7519	0,2106	0.999

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Figure. 10 illustrate the kinetics of the pseudo second order. The study of the linear regressions presented in Figures. 10 and shown in the Table. 2 shows that the correlation coefficients (R^2) for the PSO kinetic model better describe the process of adsorption of MG on HA-Ss. In addition, the theoretically calculated values ($Q_{e.cal}$) by this model agree very well with those of the experiment ($Q_{e.exp}$) [35,36].

3.4. Adsorption isotherm

Establishing adsorption isotherms allows us to calculate the maximum amount adsorbed by the solid and also to identify the type of adsorption. The quantity of MG at equilibrium Q_e is given by the following equation[35,36].

Establishing adsorption isotherms allows us to calculate the maximum amount adsorbed by the solid and also to identify the type of adsorption. The experimental results obtained show that the isotherm is of type L as shown in Figure 11, which corresponds to the classification of Gilles (Gilles 1960) [37]. The latter indicates an increase in adsorption with increases of malachite green concentration.

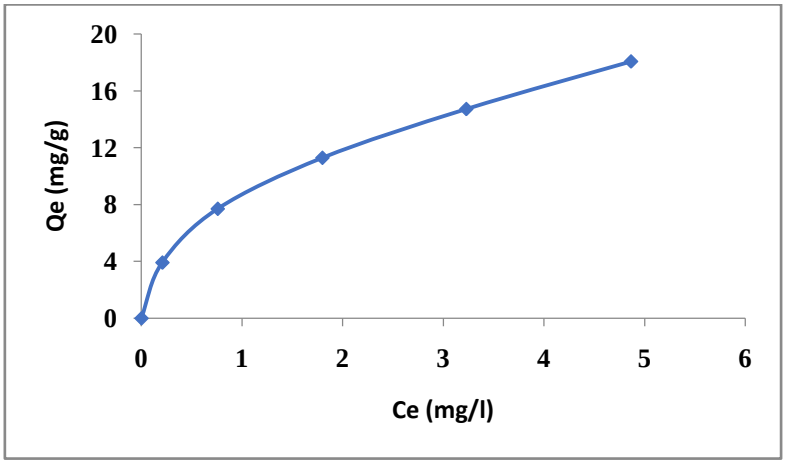

Figure 11. Isotherms for the of the bio-sorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5g/L, pH= 7, T°=25°C, 60 min as contact time).

3.4.1. Langmuir isotherm

The Langmuir adsorption isotherm assumes that the adsorption occurs by monolayer and that all the adsorption sites at the adsorbent level are homogeneous [38,39]. The linear form of Langmuir isothermal equation (11) is given by:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_L Q_m} \qquad (11)$$

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The experimental results of the removal of MG according to the Langmuir equation are shown in Figure 12 which shows a linear distribution. An essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor R_L [40,41]:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C_0 is the initial MG concentration (mg L^{-1}). The value of R_L indicated the isotherm of the Langmuir type. R_L 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 $R_L = 0$. At From the data calculated in Table 3, the R_L is greater than 0 but less than 1 indicating that the Langmuir isotherm is favorable.

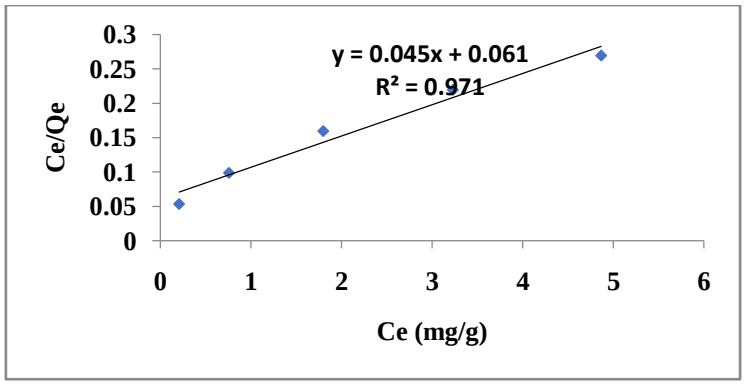

Figure 12: Langmiur Isotherms for the of the biosorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5g/L , pH= 7, T°=25°C, 60 min as contact time).

Table 3: The calculated values of the separation factor R_L.

C_0	10	20	30	40	50
R_L	0.119	0.063	0.043	0.032	0,026

3.4.2. Freundlich isotherm

The Freundlich isotherm has also been used to explain the observed phenomena[42–45]. It assumes that the multilayer adsorption process occurs on a heterogeneous surface and its linear form can be presented by equation (12):

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (12)$$

where Q e the amount of adsorbed per specific weight (mg/g); K Freundlich's constants related to adsorption capacity; C e the equilibrium concentration (mg/l); n Freundlich constants related to the adsorption intensity.

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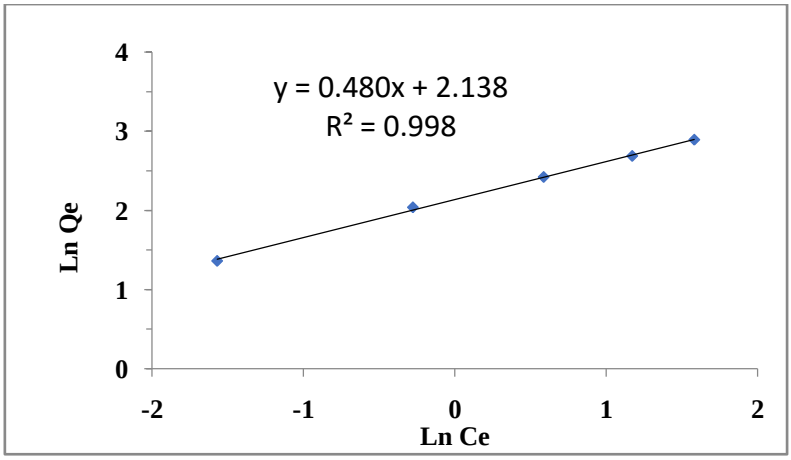

Figure 13: Freundlich isotherms for the of the bio-sorption of malachite green onto *Helianthus annuus* seeds shells (HA-Ss dose = 2.5g/L , pH= 7, T°=25°C, 60 min as contact time).

The study of the Langmuir and Freundlich adsorption isotherms, represented respectively by Figure 13 and Table 4, shows from the values of R^2 (0,998) that the Freundlich model is the best suited[42].

Tableau 4: Freundlich and Langmuir parameters of of malachite green bio-sorption on *Helianthus Annuus* seeds shells.

Experimental data	Langmuir model			Freundlich model		
q_{exp} (mg/g)	q_m (mg/g)	K_L (mg/g)	R^2	1/n	k_F (mg/g)	R^2
7.69	22.22	0.737	0.971	0.480	8.482	0.998

3.5. Comparison with other bio-adsorbents

A comparison of adsorptive capacities of many of bio-adsorbents used for malachite green adsorption is shown in Table 5. The present work takes places in short time and at room temperature, therefore, it can be conclude that, *Helianthus Annuus* seeds shells are considered as eco-friendly [46], efficient and effective bio-adsorbent for the removal of malachite green as compared with others studies reported in Table 5.

Table 5. Comparison of *Helianthus Annuus* seeds shells adsorption capacity with some adsorbent.

Used adsorbent	**Capacity (mg/g)**	**Medium pH**	**Temperature K**	**Reference**
Tamarind fruit shell	1.95	5	303	[47]
Cellulose powder	2.422	7.2	298	[48]

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Commercial activated carbon	8.27	7	303	[49]
Neem sawdust	4.35	7.2	303	[50]
Helianthus Annuus seeds shells	7.69	7	298	This study

3.6. Adsorbent regeneration

The restoration of the used adsorbents is considered an essential advantage of the adsorption technique; it was applied to minimize the high cost of the removal process and reduce environmental pollution [51]. This technique was based on the separation of the used adsorbent from the solution by filtration, cleaned with HCl solution (0.1 mol/L), then washed several times with distillate water, and dried in a vacuum at 105°C. The generated adsorbent was used again during successive experiments. Herein, the regeneration of HA-Ss performance was studied by determining the MG adsorption amount after each adsorption experiment.

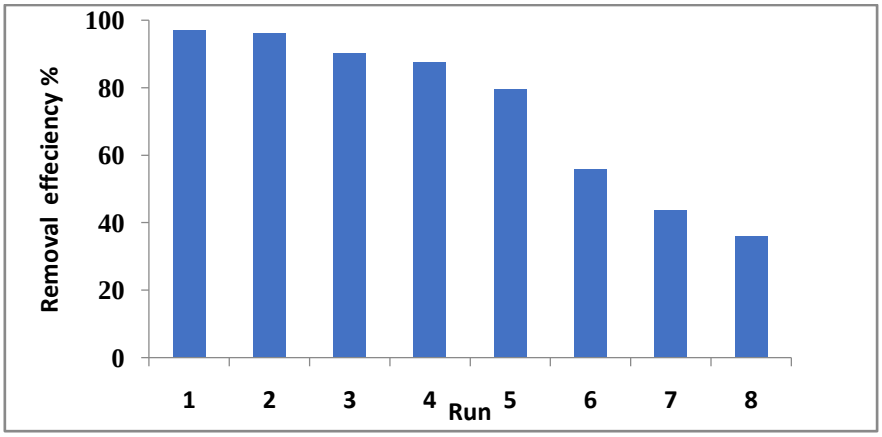

Figure 14: Evolution of adsorptive capacity of recycled *Helianthus annuus* seeds shells during the bio-adsorption of malachite green (HA-Ss dose = 2.5g/L, pH= 7, T°=25°C, 60 min as contact time).

Figure 14 shows that after three regeneration cycles, the MG adsorption efficiency slightly decreases from 97.01 to 90.35%, and after eight cycles of regeneration, the MG adsorption efficiency attains 35.85 %, which signifies that the retention capacity of *Helianthus Annuus* seeds shells is clearly affected. The rise in HA-Ss retention capacity can be attributed to the decrease of adsorption sites on its surface, due to the accumulation of the adsorbed MG molecules.

3.7. Applicability for treatment of real matrices

Numerous of adsorption studies have been focused on the removal of organic colorants from aqueous media using various adsorbents; however, a few of them involve effects water composition [6,52,53]. Therefore, the uses of real samples such as pure, surfaces, drinks, and seawater on the elimination of malachite green are of special interest. To inspect the effects of water composition on the adsorption

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removal process, the tests were realized using three contaminated samples obtained by melting malachite green in drink, pure, and seawater.

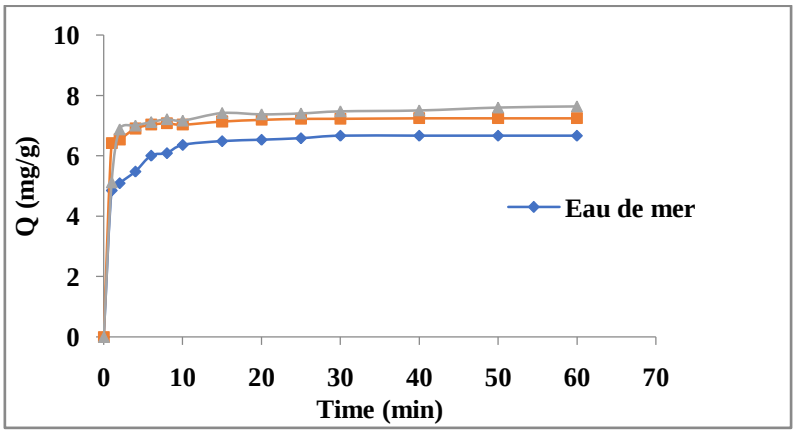

Figure 15. Effects water composition on the adsorptive removal of malachite green using Helianthus Annuus seeds shells as bio-adsorbent.

Figure 15 shows that the removal process in pure water is very rapid; with adsorption amount reaches 7.63 mg/g after 30 min of interaction, which is explained by the total removal of MG from the contaminated solution. Additionally, the removal rate becomes slow in the case of the adsorption of MG from fresh water, with removal efficiencies reached 7.24 mg/g. Nevertheless, in the case of seawater, the removal rate was strongly affected, with an adoption amount not exceeding 6.66 mg/g, even after 30 min. This observable fact can be explained by the harmful effect of some inorganic compounds in real samples (i.e. NaCl, $MgSO_4$, and KNO_3) which have been attached to the adsorbent surface and covered the active sites responsible for the uptake of the malachite green molecules[54–56].

3.8. Conclusion

The objective of this work was to study and the valorization of HA-Ss for the elimination of MG from aqueous solutions by adsorption in batch system. In order to better understand the adsorbent properties of HA-Ss, the material was characterized using different techniques. Overall, the best efficiency rate was found to be 90%. The study of the influence of the parameters (pH, mass, initial concentration, stirring speed, and temperature), made it possible to determine the optimal conditions. The adsorption kinetics are best described by the pseudo-second order model. According to Gilles' classification, the experimental results have shown that the isothermal shape is of type L and, according to the values of R^2, the Freundlich model is the best suited. The absorption isotherms of our adsorbent obey the Freudlich model The study of the absorption isotherms of Langmuir and

Freundlich, shows from the values of R^2 that the Freundlich model is the best suited. This work revealed that the shell of sunflower seeds is an ecologically effective natural waste that can be used successfully to remove Mg from wastewater.

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