

Modeling and characterization of malachite green adsorption onto date palm petioles

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ARTICLE INFO

Article History :

Received : dd/mm/yyyy

Accepted : dd/mm/yyyy

Key Words:

Optimization;
Malachite Green;
Box-Behnken design;
Sorption.

ABSTRACT/RESUME

Abstract: To achieve the elimination of malachite green from aqueous solution by using date palm petioles, three factors were been varied: the initial concentration of dye, the mass of adsorbent and the stirring speed.

The optimization of these factors gave us an almost elimination of dye ($Y_{exp.} = 99.40\%$) under the following optimal conditions: the initial concentration of Malachite green $[MG]_0 = 30ppm$; the mass of adsorbent $m_{ads} = 0.26g$ and the stirring speed $SS = 199rpm$.

I. Introduction

The discharge of colored industrial effluents in the receiving environment causes serious problems. Among the widely used dyes and the most rejected in the nature we found the malachite green dye. This dye is widely used in several industries such as textile, paper, wool, plastics, agrifood and cosmetics to color their products [1-2]. It also used in aquaculture industry worldwide as inhibitor of protozoal ectoparasitoses and mycoses of fish and their eggs [2-6].

Malachite green has been considered to be highly toxic agent from human's health which causes irritation of the respiratory tract, gastrointestinal tract and skin [7]. It also threatens aquatic life and it has adverse effects on the liver, gills, kidneys, intestine, gonads and pituitary gonadotrophic cells [8].

To fight against this danger which menace life in general, several treatment methods have been considered such as: degradation using ultrasonic irradiation [9], and sunlight irradiation [10], photocatalytic degradation [11], photo-degradation [12-13], biosorption onto wheat bran [14], hen feathers [15], micro algae *Cosmarium* sp. [16], dead leaves of plane tree [6], potato peel [17-18], wood apple [19] and oil palm trunk fibre [8]. The use of the solid waste products from agriculture gives an importance to sorption process.

The application of the unactivated and activated (chemically or thermally) palms waste as biosorbent in the treatment of effluent has been studied by several researchers in these last years [20-24].

Therefore, the objective of this study was to evaluate the adsorption potential of date palm petioles for malachite green (MG) dye.

To have a total elimination of malachite green, we chose to apply the Box-Behnken design. For this, three factors were varied such as: the initial dye concentration (between 10-30ppm), the mass of the adsorbent (0.1-0.3g) and the stirring speed (between 0-400rpm).

II. Experimental

II.1. Preparation and characterization of adsorbent

In the present study, the date palm petioles used were collected from the Algerian Sahara (Oued Souf). Initially, date palm petioles were grinding into small size and washed several times with tap water until the disappearance of the reddish color, after they washing with double-distilled water to remove any foreign materials and impurities than they dried in sunlight for 48 h to remove moisture (fig. 1).

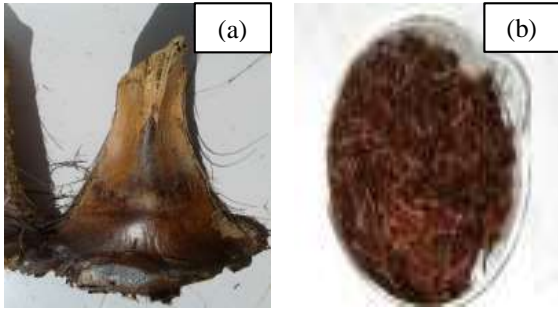


Figure 1. The adsorbent used in this study before (a) and after preparation (b)

The physical-chemical characteristics composition of date palm petioles (table 1) are given by using a various analytic techniques. It has been found that the fibers had a homogeneous aspect, with a rough surface and an outer lignin rich layer around the fibers. It was also found that this adsorbent has a more at least porosity and a value of pH_{ZPC} equal to 8.04 which gives a basic character to the adsorbent. Using a graduated cylinder with a capacity of 100 mL, the apparent density can be measured by determining the weight occupied by a data palm petioles.

$$d_{app} = \frac{P_1 - P_0}{100 \rho_{water}} \quad (1)$$

Or

P_1 : Weight of the filled graduated cylinder (in g);
 P_0 : Weight of the empty graduated cylinder (in g).

There are several methods for the determination of the real density, only the most used is that of the graduated cylinder.

The principle consists of a series of weighings (3 times) and the absolute volume of the material is equal to the volume of water displaced.

Put in a graduated cylinder a volume V_0 of water.

Weigh a mass m of the adsorbent (about 2g) and introduce it into the graduated cylinder such that the water reaches the end of the upper graduation. Identify the air bubbles carefully. Read the new volume V_1 . The absolute volume was $V_1 - V_0$.

The real density is calculated by the following relation:

$$d_{real} = \frac{m}{V_1 - V_0 \rho_{water}} \quad (2)$$

Avec $\rho_{water} = 1g/cm^3$ à $20^\circ C$.

The notion of permeability induces that of material porosity. The porosity of an aggregate or a rock is the volume of voids contained by the total volume V_1 (void + solid).

$$\varepsilon (\%) = 1 - \frac{\rho_{app}}{\rho_{abs}} \times 100 \quad (3)$$

The humidity is a fairly important parameter for the preservation of our adsorbent. Indeed, measurements were examined to determine the humidity of our adsorbent. In a first step, we weigh

2g of adsorbent (P_1), then we put it in an oven at $105^\circ C$ for 1 hour, then we put it in a desiccator for 30 min in order to weigh it again (P_0). The manipulation is repeated 3 times.

$$H (\%) = \frac{P_1 - P_0}{P_1} \times 100 \quad (4)$$

Table 1. Physical-chemical characteristics of the adsorbent

Size (μm)	between 160 μm and 180 μm
Apparent density (g/mL)	0.09
real density (g/mL)	0.23
Porosity (%)	59.61
pH_{ZPC}	8.04
Humidity (%)	13.45

An environmental FEI Quanta 250 SEM is used to examine the morphology of date palm petioles before using as adsorbent without treatment.

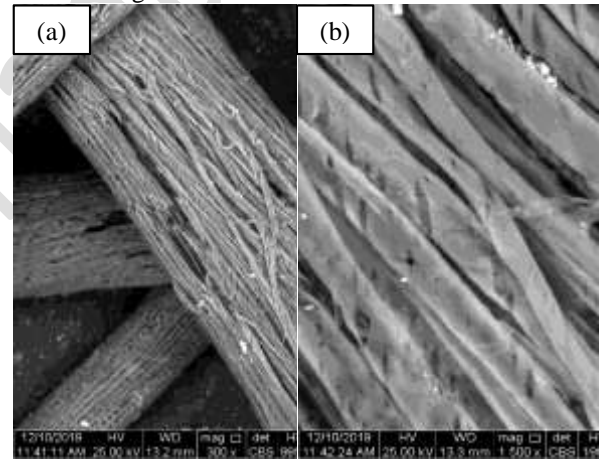


Figure 2. SEM micrographs of date palm petioles: (a) 300 μm , (b) 50 μm .

The SEM images shown in Figure 2 represent the adsorbent before use. Indeed, these images tell us about the structure of the adsorbent. It was found that the structure of this adsorbent is heterogeneous fibers with the presence of a significant number of pores.

The composition of date palm petioles without treatment is given in table 2 and figure3.

Table 2. The composition of date palm petioles without treatment

Element	C	O	Mg	Ca
% of	52.56	46.78	0.42	0.24

Based on EDAX analyzes, the chemical composition of the adsorbent was determined. In

fact, we find that this adsorbent consists of 52.56% of C, 46.78% of O, 0.42% of Mg and 0.24% of Ca.

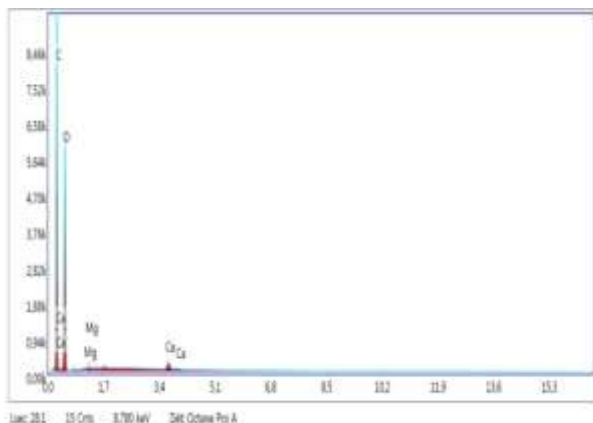


Figure 3. EDAX of date palm petioles

II.2. Adsorbate: Malachite green (MG)

Malachite green dye (MG) was purchased from Merck and used without further purification. The characteristics and chemical structure of the dye are listed in table 3 and figure 4 respectively.

Table 3. The physical and chemical characteristics of MG dye

Generic name	C.I. 42000; Basic Green 4
Color index number	42000
Abbreviation	MG
Molecular formula	$C_{25}H_{26}N_4O_2$
Purity (%)	≥ 90
Molecular weight (g/mol)	374
λ_{max} (nm)	618
Melting point	144-150°C
pH value	2.4 (10g/L, H ₂ O, 24°C)
Solubility in water	110 g/L at 24°C

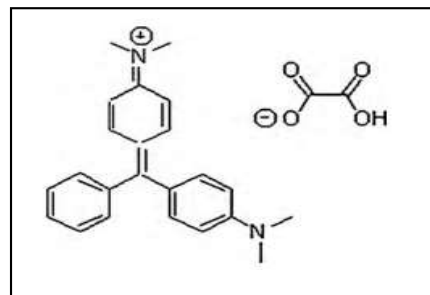


Figure 4. Chemical structures of malachite Green.

II.3. Adsorption tests (Batch equilibrium and kinetic studies)

Adsorption experiments were performed in a beaker of 250 mL capacity. Temperature of 25 ± 2 °C was kept constant using a thermostatic bath. The experiments were performed by contacting a certain mass of adsorbent with 100 mL of desired concentration of cationic dye.

The residual concentration of the MG was analyzed by the spectrophotometric method using a visible spectrophotometer (CecoMAM) set at a wavelength of 618nm, corresponding to a maximum absorbance determined experimentally.

Dye removal yield ($Y_{exp.(\%)}$) was obtained by equation 5:

$$Y_{exp.(\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (5)$$

Where C_0 and C_f are the initial and the equilibrium liquid-phase concentrations of MG (ppm) respectively.

III. Results

The factors selected for this study and their levels are shown in Table 4. Applying the Box-Behnken design, it was found that the influence factors in this phenomenon are: the stirring speed, the initial concentration of dye $[MG]_0$ and the weight of adsorbent m_{ads} .

The results of the eliminated percentage of MG ($Y_{exp.}$ and $Y_{theor.}$) are presented in table 5.

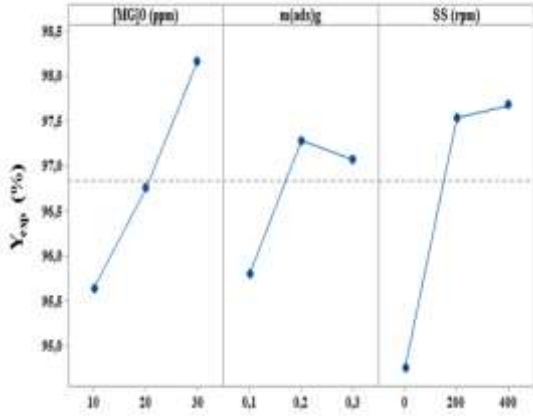


Figure 5. Main effects plot of parameters for yield.

Table 4. Experimental domain of each factor

Parameters	[MG] ₀ (ppm)	m _{ads} (g)	SS (rpm)
Minimum	10	0.1	0
Middle	20	0.2	200
Maximum	30	0.3	400

Table 5. Experiment Results of removing MG by experimental matrix Box-Behnken.

Ordre Std.	[MG] ₀ (ppm)	m _{ads} (g)	SS (rpm)	Y _{exp.} %	Y _{th.} %
14	20	0.2	200	97.91	98.08
12	20	0.3	400	97.97	97.49
1	10	0.1	200	96.28	95.61
9	20	0.1	0	92.81	93.29
13	20	0.2	200	98.14	98.08
5	10	0.2	0	92.33	92.52
11	20	0.1	400	97.45	96.93
6	30	0.2	0	99.09	97.90
7	10	0.2	400	97.13	98.31
10	20	0.3	0	94.75	95.27
2	30	0.1	200	96.63	97.34
4	30	0.3	200	98.74	99.40
15	20	0.2	200	98.20	98.08
3	10	0.3	200	96.80	96.10
8	30	0.2	400	98.14	97.96

Figure 5 shows the effects of factors in the study domain. For the initial concentration of dye [MG]₀, it can be seen that the increase in this parameter favors elimination where yields above 90% were achieved. In contrast, for the factors the mass of the adsorbent (m_{ads}) and the stirring speed (SS), it was found that in the middle of the chosen domain a good removal efficiency was achieved [6, 17].

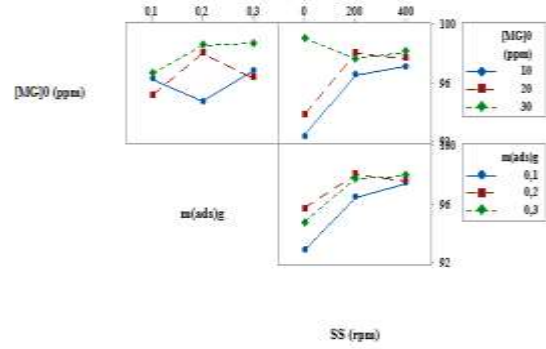


Figure 6. Main effects plot and interactions for yield.

The achieved yields in the different interactions are showing in the fig.6. For the first interaction between [MG]₀ and m_{ads} two weak interactions is found, the first between the two masses 0.2 and 0.3g at the maximum level for the initial dye concentration, and the second between [MG]₀-SS between 0 and 200 rpm at the same level for [MG]₀. There are also two strong interactions between 200 and 400rpm: the first at the medium level of [MG]₀ and the second at the medium level of the adsorbent mass.

It is interesting to note that high yield can be obtained when the initial concentration of MG is maximum.

III.1. Polynomial regression

The mathematical model expressing the removal efficiency of malachite green must take into account all the terms (linear, square and interaction). It is represented by equations 6 and 7 in uncoded and coded unit respectively.

Regression equation in uncoded units

$$Y_{exp. \%} = 85.56 + 0.199*[MG]_0 + 40.0*m_{ads} + 0.03907 *SS - 0.00022 *[MG]_0*[MG]_0 - 94.9*m_{ads}*m_{ads} - 0.000035*SS*SS + 0.394*[MG]_0*m_{ads} - 0.000718*[MG]_0*SS - 0,0177*m_{ads}*SS \quad (6)$$

Regression equation in coded units

$$Y_{exp. \%} = 98.083 + 1.258*[MG]_0 + 0.637*m_{ads} + 1.464*SS - 0.022 *[MG]_0*[MG]_0 - 0.949*m_{ads}*m_{ads} - 1.387*SS*SS + 0.394*[MG]_0*m_{ads} - 0.435*[MG]_0*SS - 0,353*m_{ads}*SS \quad (7)$$

III.2. ANOVA

From Table 6, it can be seen that among the factors studied the most significant factors are the initial concentration of the dye (P = 0.021), stirring speed (P = 0.012), SS² (P = 0.056) and the interaction effect between the [MG]₀ and the SS ([MG]₀ × SS) with the P value of 0.045 (P-value < 0.05) .

Table 6. Analysis of variance for yield

Source	DL	Sc. Seq.	CM		F	P
			adjust			
Regression	9	52.2253	5.8028	5.00	5.00	0.046
Linear	3	33.0485	11.0162	9.50	9.50	0.017
[MG] ₀	1	12.6623	12.6623	10.92	10.92	0.021
m _{ads}	1	3.2436	3.2436	2.80	2.80	0.155
SS	1	17.1426	17.1426	14.78	14.78	0.012
Quadratic	3	9.8175	3.2725	2.82	2.82	0.147
[MG] ₀ *[MG] ₀	1	0.0019	0.0019	0.00	0.00	0.970
m _{ads} *m _{ads}	1	3.3250	3.3250	2.87	2.87	0.151
SS*SS	1	7.1047	7.1047	6.12	6.12	0.056
Interaction	3	9.3592	3.1197	2.69	2.69	0.157
[MG] ₀ *m _{ads}	1	0.6221	0.6221	0.54	0.54	0.497
[MG] ₀ *SS	1	8.2379	8.2379	7.10	7.10	0.045
m _{ads} *SS	1	0.4993	0.4993	0.43	0.43	0.541
Error	5	5.8004	1.1601			
Inadequate adjustment	3	5.7522	1.9174	79.49	79.49	0.012
Pure error	2	0.0482	0.0241			
Total	14	58.0257				

III.3. Response surface and contour RSM

At a stirring speed of 200 rpm, the best malachite green removal yields are represented by yields greater than 99%. These best yields are located in the range of 0.2-0.3g of adsorbent mass and in the maximum level for the initial dye concentration [6, 17].

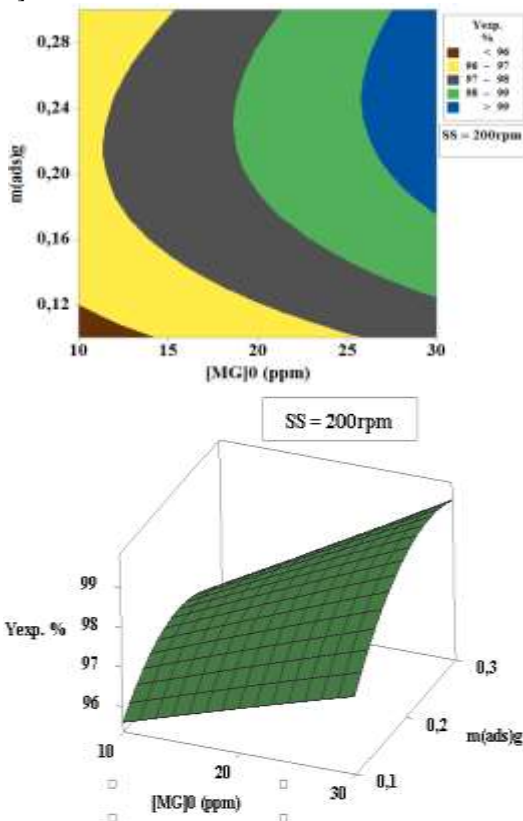


Figure 7. Response surface of yield according to [MG]₀ and m_{ads} (at m_{ads} = 200rpm).

At maximum of adsorbent mass, the best MG removal yields are located at maximum concentration for the dye and in the range of 80-280rpm for agitation speed.

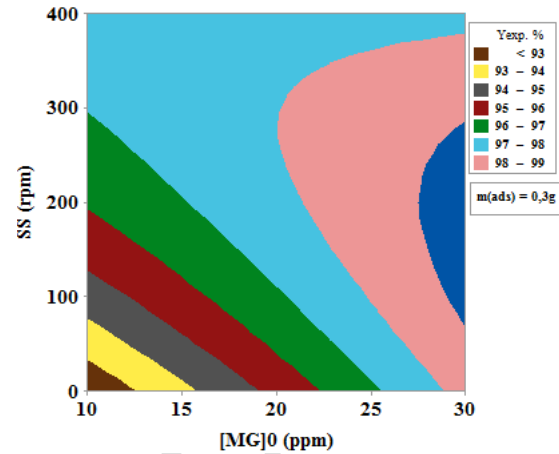


Figure 8. Response surface of yield according to [MG]₀ and SS (at m_{ads} = 0.3g).

Figure 8 shows that the region of best MG removal yields is represented by the response surfaces and contours at the middle of the field of the stirring speed and at the maximum level for the initial dye concentration [6].

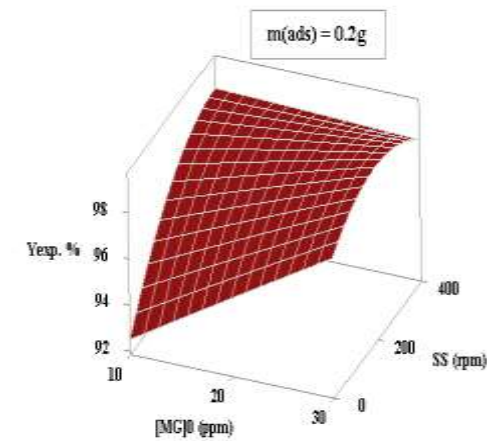
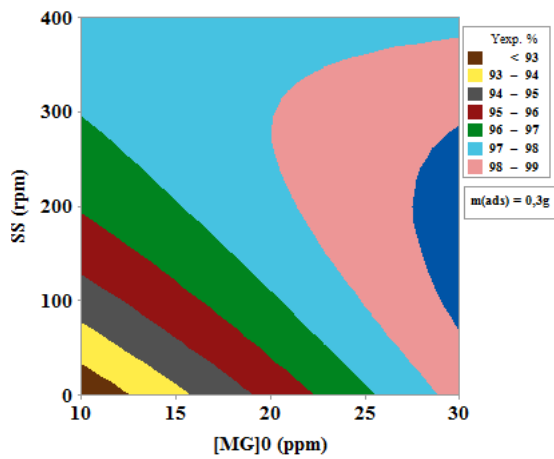


Figure 9. Response surface of yield according to $[MG]_0$ and SS (at $m_{ads} = 0.2g$).

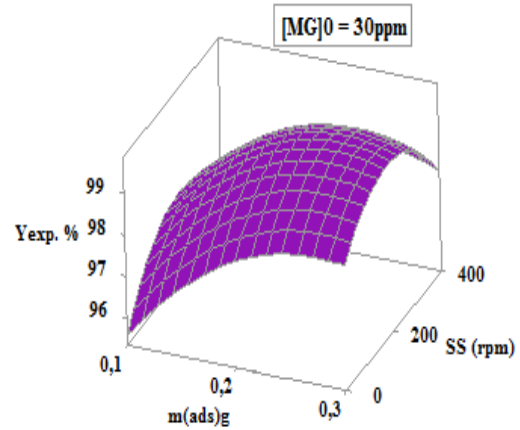
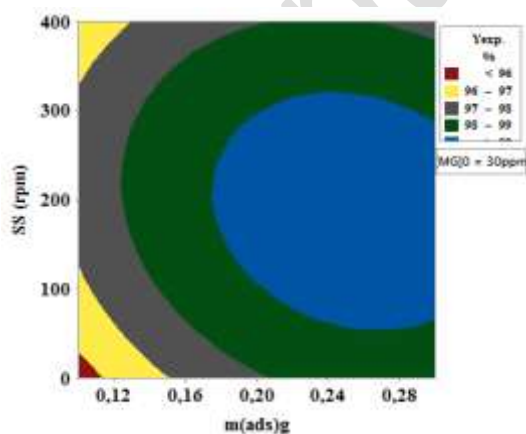


Figure 10. Response surface of yield according to m_{ads} and SS (at $[MG]_0 = 30ppm$).

At an initial concentration of MG (30 ppm), the results of the Response surface methodology (RSM) show that in the middle of the range of the stirring speed and in an interval of 0.18-0.3 g of palm petiole, the best removal yields of dye were obtained.

III.4. Optimization

Figure 11 show that the graphical representation of theoretical responses according to estimated responses shows a good linearity with a high correlation constant ($R^2 = 0.9189$).

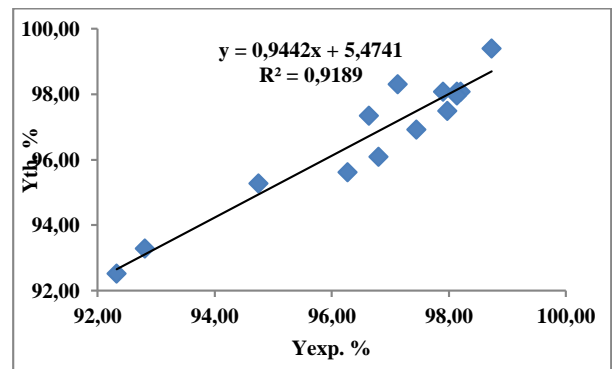


Figure 11. Correlation between theoretical and estimated yield.

The objective was to maximize the dye removal efficiency. A constraint was imposed on the $[MG]_0$, SS and m_{ads} . The experimental design can also be used to search for an optimum. The yield could be obtained with a value of 99.60% if the overall factors were 30ppm for the $[MG]_0$, 0.26g for m_{ads} and 190rpm for the stirring speed, corresponding to a desirability of 1.00. It was found that when the value of the desirability was high, the response was better and closes to the target response. A verification of the optimum conditions was carried

out twice in the same experimental setup. The removal efficiency of malachite green was performed with a mean yield of 99.40%.

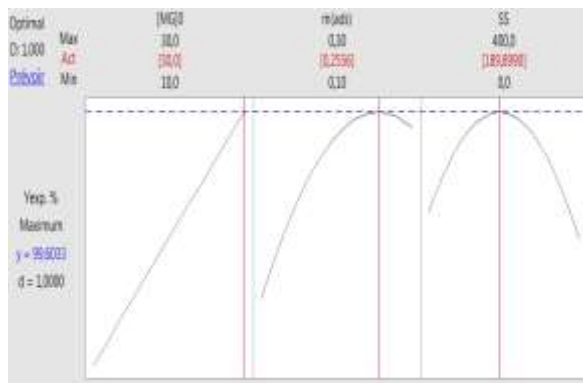


Figure 12. Optimization of the experimental parameters for the removal efficiency of MG.

III.5. Characterization of the sorbent

Scanning electron microscopy (SEM) analysis was carried out for the date palm petiole to study the surface morphology before and after MG adsorption.

From the results obtained, it can be seen that tests 5 and 9 show low elimination yields for malachite green. For this, we keep these tests for four (04) days in order to have a total elimination of the dye. The SEM images shown in Figure 13 give an idea of the removal of MG. From this figure, it can be seen that the dye was trapped in the pores of the adsorbent which makes the surface of the adsorbent charged with the dye and this is well represented in figure 13 (b) by white balls.

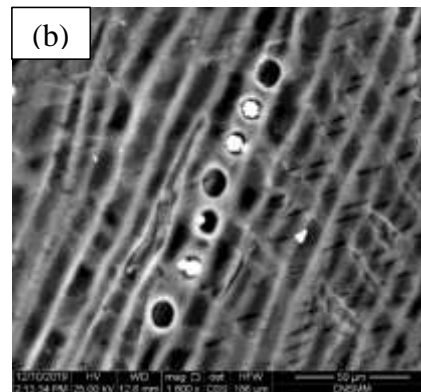
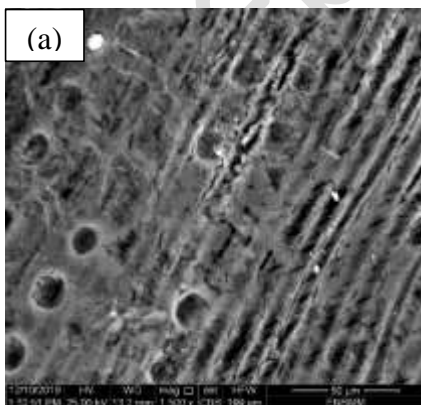


Figure 13. SEM micrograph of sorbent particle (a : test 5- b: test 9).

IV. Conclusion

To improve the yield of sorption of malachite green from wastewater and which was already optimized by an experimental design type Box-Behenken design, data palm petioles was used as a sorbent.

The factors studied are the initial concentration of malachite green, the mass of sorbent and the stirring speed. The response chosen was the extraction yield.

The analysis of variance ANOVA gives us the significant and non-significant factors. It was found that the initial concentration of the dye, stirring speed, SS² and the interaction effect between [MG]₀ × SS were the significant terms.

The regression was linear between the values of the theoretical and experimental performances. The fit was almost perfect because the correlation constant was equal to 0.919.

The optimization values gave a theoretical yield of 99.40 % where the overall factor were 0.26g for the m_{ads}, 30ppm for the initial concentration of malachite green and 199rpm for the SS. The model was therefore adequate to represent the process.

Conflict of Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Acknowledgements. We thank Prof. Abbas Boukhari Director of the LOMOP Research Laboratory and Dr Fethi Saoudi Head of the Process Engineering Department, Badji Mokhtar University of Annaba, for providing us with the

necessary material resources. The authors thank also the ENSMM-Annaba for the assistance provided in this research, represented in SEM analyzes.

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Please cite this Article as:

Bendebane S., Bendebane F., Bendebane H., Ismail F., Modeling and characterization of malachite green adsorption onto date palm petioles, *Algerian J. Env. Sc. Technology*, X:X (YYYY) XX-XX