A *LJEST*

Adsorption methyl orange in aquatic solution using local palm stems from Laghouat region

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ARTICLE INFO	ABSTRACT/RESUME
Article History : *Received : 14/07/2020* *Accepted : 13/12/2020* **Key Words**: *Adsorption;* *Palm stems,* *Methyl orange,* *Kinetics,* *Isotherms.*	**Abstract:**This study consists of evaluating the biosorption on a local material, palm stems from the Laghouat region. In order to optimize this process, several parameters such as: pH, contact time, initial dye concentration and ionic strength were also studied. Monitoring of the kinetics of direct absorption of methyl orange by palm stems and the isothermal study. The results of the batch biosorption tests confirmed the ability of this material to adsorb the studied dye with an equilibrium time of 120 min at pH 4. The modeling shows that the biosorption of the elements considered takes place in a monolayer according to the Langmuir isotherm with a maximum adsorption quantity of methyl orange is estimated at 8.67 mg/g under the optimal conditions obtained.

I. Introduction

Water is essential to life, without it there would be no possible life on earth because all living things need water to exist. Water is one of the five essential elements for life and it is essential for the development of all life [1].

The protection of water is a considerable stake for our future; we are all concerned if we wish to continue to live in good condition, for that however we must all be careful not to use this blessing abusively.

The various human activities of the industrial, urban or agricultural type cause the pollution of water because of the discharges of many toxic products [2, 3]. Among these released products are mineral pollutants such as cobalt, copper, nickel, chromium, lead and zinc, which are detected in waste streams from mining operations, tanneries, electronics.electroplating, batteries and petrochemical industries [4,5] and organic pollutants such as synthetic dyes used in the textile industry which are discharged directly into the aquatic environment without any prior treatment [6,7].

Following this great threat to the environment, a lot of work has been done on water pollution control.

And several depollution techniques have been developed, we can cite precipitation [8], membrane filtration [9], ion exchange [10], liquid extraction [11], electrodeposition [12], advanced oxidation processes [13], biological processes [14] and adsorption which is considered to be one of the most widely used treatment techniques [15, 16] to remove certain classes of pollutants from water, in particular those which are not readily biodegradable. The removal of dyes is one of the groups of pollutants that is currently a problem.

In the course of research, several unconventional adsorbents have been investigated as agricultural wastes which can be obtained and used as adsorbents with inexpensive [17].

Dyes such as methyl orange have a reputation for being toxic and persistent in the environment, as the latter is classified among the azo dyes that cause methemoglobinemia, characterized by the impediment of oxygen transport in the blood. Medical studies have also shown that the presence of methyl orange in water causes irritation of the digestive and respiratory systems, as well as irritation of the eyes and skin [18].

The objective of this study is the use of palm stems as a local biosorbent in the Laghouat region to eliminate methyl orange (MeO) in aqueous solution.

II. Materials and methods

II.1. Preparation of biosorbent

The biosorbent chosen is the local palm stems of the Laghouat region of Algeria designated by TPL. The preparation of this biosorbent involves 5 steps: Boiling a quantity of TPL with distilled water for 30 min; Filtration then rinsing with distilled water; Drying in an oven at 378 K for 24 h and then crushing and screening. Then kept for adsorption tests.

Characterization of the adsorbent

TPL biosorbent is characterized by Fourier Transform Infrared (FTIR) spectroscopy before and after adsorption using the model 4200-FTIR device JASCO, Japan.

II.2. Preparationofadsorbate

A stock solution of methyl orange at a concentration of 1000 mg/L was prepared. The resulting aqueous solution was diluted with distilled water to obtain.

Methyl orange dosage

The exact concentrations of the methyl orange solutions were determined by UV-visible absorption spectrophotometer (UVILINE 9400). For this, the calibration curve was plotted using the measurement of the absorbance of a solution at the wavelength $\lambda = 465$ nm.

III. Results and discussion

III.1. IR spectroscopyanalysis

Fourier transform infrared spectroscopy (FTIR) is performed in order to determine the functional groups characterizing this local biosorbent (Fig. 1 and Table. 1).
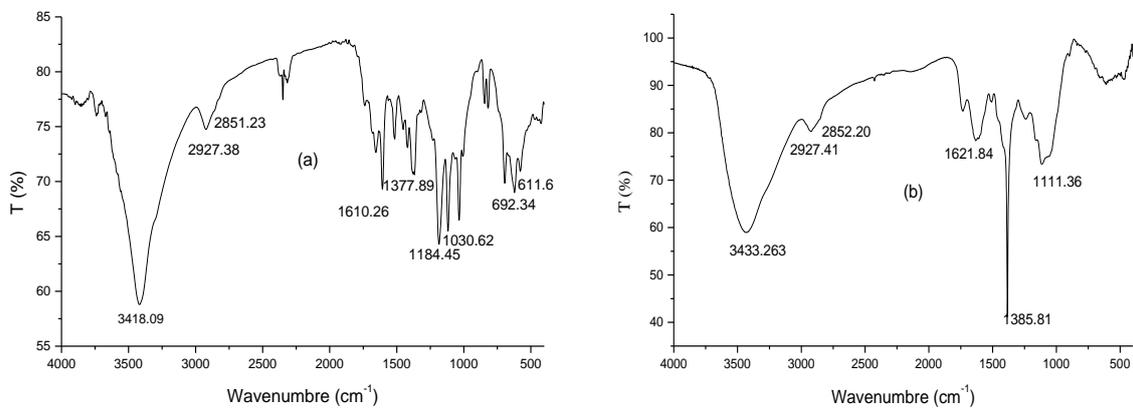

Fig. 1. IR spectrum of TPL adsorbent: (a) before; (b) after adsorption of MeO.

The corresponding typical IR functional groups are listed in Table 1 before and after adsorption allow to say that: remarkable variations in the intensities of the bands and the disappearance of the bands such as 1030.62; 692.34 and 611.6 cm-1, many similar results have been observed but on other lignocellulosic biomaterials [19].

Table 1. IR spectral characterization of TPL biosorbent before and after adsorption.

The wavenumber band (cm⁻¹)		Assignment	
Before	After	Bonding	Groups
3418.09	3433.263	N-H, O-H	hydroxyl or amine groups
2927.38 et 2851.23	2927.41 et 2852.20	C-H	aliphatic chains
1610.26	1621.84	C=O	carboxylic groups
1377.89	1385.81	C=C	aromatic groups
1184.45	1111.36	C-O-C	ether groups
1030.62	--		
692.34	--		
611.6	--		

III.2. Adsorptiontests

III.2.1. Effectofsolution pH

PH is an important factor in any adsorption study, as it can influence the adsorbent and adsorbate structure as well as the adsorption mechanism.

In this work, we studied the adsorption efficiency of methyl orange by varying the pH from 1.5 to 8 using an acid solution H_2SO_4 (0.1 M) or a basic solution NaOH (0.1 M) according to the desired pH.

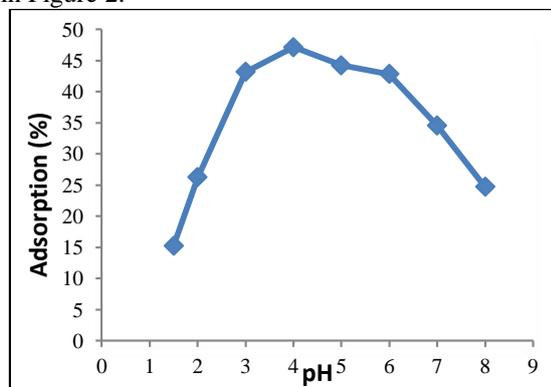The results obtained during these tests are presented in Figure 2.

Fig. 2. Influence of the pH of the solution on the adsorption of methyl orange under the conditions: [MeO]= 15 mg/L, contact time= 120 min, m= 1.0 g and T= 293 K.

The result described in Figure 2 shows that the adsorption of MeO evolves from initial pH 2 to pH 4.0 and then decreases over the pH range 4 to 8. This is attributed to the protonation of TPLs, H^+ ions provide a significant force of electrostatic attraction between the surface of the TPLs and the dye molecules leading to maximum adsorption. At a pH above 4, the degree of protonation of the surface of the adsorbent is lower, which will cause the diffusion and adsorption to decrease, due to electrostatic repulsion. The lower adsorption of the dye in alkaline media can also be attributed to the competition of hydroxide ions (OH^-) with anionic dye molecules for the adsorption sites.

in Figure 3, show that the adsorbed amount of methyl orange increases rapidly in the first 15 minutes and remains constant after 120 minutes, indicating a state of equilibrium.

This shows that the adsorption equilibrium of the dye by the adsorbent used is very fast. Indeed, the remaining unoccupied exterior sites are difficult to occupy, this is due to the formation of repulsive forces between the MeO molecules and the surface of the solid.

In addition, MeO molecules are medium in size and can be readily diffused into internal pores until saturation, which will reduce mass transfer between liquid phase and solid phase over time. These lead to a decrease in the adsorption rate and a plateau is

observed which corresponds to the equilibrium state after 120 min.

III.2.2. Effect of contact time and initial concentration

It is known that the initial concentration of the pollutant and the contact time are parameters very influencing the adsorption. The effect of contact time on the adsorption of MeO by TPLs has been studied at different initial concentrations.

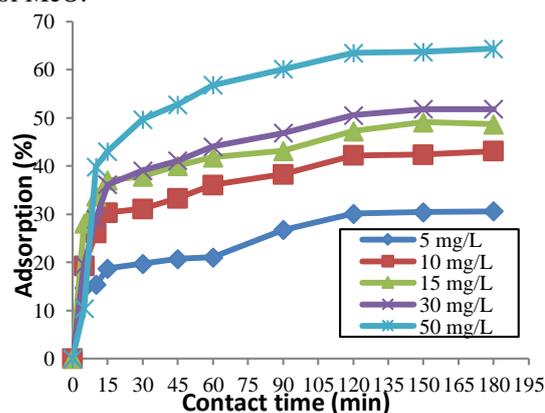Figure 3 shows the results of the effect of contact time and the initial concentration on the adsorption of MeO.

Fig. 3. The effect of the contact time and the initial concentration on the adsorption of MeO under the conditions: m = 1.0 g and T = 293 K.

The characteristic curves of the adsorption kinetics at different times, illustrated in Figure 3, show that the adsorbed amount of methyl orange increases rapidly in the first 15 minutes and remains constant after 120 minutes, indicating a state of equilibrium.

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III.2.3. Effect of ionic strength

The ionic strength of the aqueous medium is represented by the presence of all the conductive elements in solution, this can be sodium salts, calcium, etc. It is determined by measuring the conductivity in order to study the competitive adsorption effect between medium salinity and MeO on local palm stems.

This study was carried out using NaCl electrolyte solutions at different concentrations. The results obtained are presented in figure4.
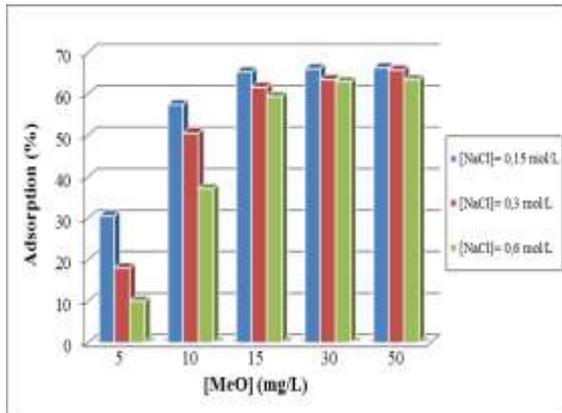

Fig. 4. Influence of the ionic strength of the solution on the adsorption of MeO under the conditions: [MeO] = 15mg/L, contact time= 120 min, m= 1 g and T = 293 K.

According to the graph in figure 4, we notice that there is not a significant difference in the evolution of the adsorption rate between the salts used at different concentrations, so we conclude that the Na$^+$ ions found in low quantity cannot occupy all active sites of the adsorbent.

On the other hand, if the solution has a high concentration of salts used, there will be competition between the Na$^+$ ions and the adsorbate to occupy the adsorption sites.

III.3. Kinetic study

The objective of this study is to determine the order and the model which well describe the kinetics of adsorption of MeO by palm stems as well as the time required to reach the equilibrium state of adsorption and the rate constants of adsorption of methyl orange.

The pseudo-first order model was proposed by Lagergren [20] which is expressed by the following integrated relation (1):

$$Ln(q_e - q_t) = Ln(q_e) - k_1 t \quad (1)$$

With: qe: Amount of solute adsorbed at equilibrium (mg/g); qt: Amount of solute adsorbed at time t (mg/g); K$_1$: First order speed constant (in min^{-1})

The application of this model for a given system can be verified by examining the linearity of the line obtained by plotting Ln (qe–qt) as a function of t. The intercept and the slope of the line are used to calculate qe and K$_1$.

The pseudo-second order model makes it possible to characterize the adsorption kinetics by taking into account both the case of rapid binding of solutes to the most reactive sites and that of slow binding to the sites of low energy [21] which is expressed by the following relation (2):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

With K$_2$: Second order speed constant (g.mg^{-1}.min^{-1}).

The adsorbed amount at equilibrium qe and K$_2$ can be determined experimentally from the slope and the y-intercept of t/qt = f (t).

The results of linear regression of the two pseudo-first order and pseudo-second order models of the adsorption kinetics of MeO on TPLs are presented in Table 2.

Table 2. Kinetic parameters of MeO adsorption at 298 K.

C$_0$ (mg/L)	Exp.	Pseudo-first order			Pseudo-secondorder		
	q$_e$ (mg/g)	q$_e$ (mg/g)	K$_1$ (min^{-1})	R^2	q$_e$ (mg/g)	K$_2$ (g/mg.min)	R^2
10	2.21	5.897	0.0187	0.9642	2.27	0.0480	0.9916
15	2.90	5.297	0.0184	0.9561	2.93	0.0585	0.9947
30	4.60	4.249	0.0175	0.9645	4.82	0.0215	0.9959
50	13.28	2.596	0.0157	0.9291	15.01	0.0042	0.9761

According to the values of the correlation coefficients corresponding to the results found (Table 2) which are closer to unity for the pseudo-second order kinetic model than the pseudo-first-order kinetic model. This indicates that the pseudo-second order kinetic model well describes the adsorption of MeO on TPLs.

III.4. Isothermal study

For the isothermal study of the adsorption of MeO on TPL and it is known that there are several models of isotherms, In this work, the most common models of isotherm Langmuir [22] and Freundlich [23] have been adjusted to the experimental data which was calculated by the difference between the initial and final (measured) concentrations of methyl orange.

For the description of the adsorption isotherms of this work, the parameters of the adsorption isotherms obtained using linear equations (3) for the Freundlich model and (4) for Langmuir were determined:

$$Ln(q_e) = Ln(K_f) + 1/n Ln(C_e) \quad (3)$$

With: qe: The quantity of adsorbate adsorbed per unit mass of adsorbent (mg/g), K$_F$: Parameter essentially linked to the maximum adsorption capacity (mg/g), Ce: the concentration of the adsorbate in the solution at equilibrium (mg/L), n:

Parameter linked to the coefficients of variation of the interaction energies with the recovery rate.

$$1/q_e = 1/q_{max} + 1/(b C_e \times q_{max}) \quad (4)$$

With: C_e: Concentration at equilibrium (mg/L), q_e: Amount adsorbed at equilibrium (mg/g), q_m: Maximum amount adsorbed at monolayer saturation or maximum adsorption capacity (mg/g), K_L: Adsorption equilibrium constant, dependent on temperature (L/mg).

The simulation of the results obtained by the Langmuir and Freundlich models is presented in Table3.

Table 3. Constants of different MeO adsorption isotherm.

T (K)	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	1/n	K_F (mg/g)	R^2
293	7.77	0.081	0.9799	0.6135	0.781	0.9732
303	8.19	0.058	0.9777	0.6454	0.635	0.9612
313	8.39	0.052	0.9869	0.6556	0.592	0.9680
323	8.67	0.047	0.9804	0.6706	0.555	0.9554

The different results obtained by the Langmuir and Freundlich models in Table 3, indicate that the Langmuir isotherm was best suited to the experimental results because the correlation coefficients (R^2) for the Langmuir isotherm was between 0.9777 and 0.9869 compared to 0.9554 and 0.9732 of the Freundlich isotherm. This means that the adsorption of MeO takes place by monolayer adsorption [24]. The calculated maximum adsorption capacity of MeO was 8.67 mg/g.

The Langmuir isotherm is applicable when there is a strong specific interaction between the adsorbate solute and the adsorbent.

III.5. Comparative study

In order to enrich this study, the results obtained for the adsorption capacity of this adsorbent were compared with those cited in the literature. Table 4 illustrates this comparative study.

Table 4. Comparative study of the adsorption of MeO on different adsorbents.

Adsorbants	Time balance	pH optimal	Kineticmodel	Isothermal	q_m [mg/g]	References
Olive sand	60 min	6	Pseudo-Second ordre	Langmuir	1.47	[25]
Ashes	40 min	6	Pseudo-Second ordre	Freundlich	3.62	[26]
Mango pits	40 min	6.8	Pseudo-Second ordre	Freundlich	5.71	[19]
Activatedcarbon	50 min	4	Pseudo-Second ordre	Freundlich	5.77	[27]
TPL	120 min	4	Pseudo-Second ordre	Langmuir	8.67	This study

The maximum absorption capacities (q_m) of methyl orange of some adsorbents reported in the literature were compared with those of the present study.

The comparison (Table 4) shows that the biosorbent used in this study has an interesting adsorption capacity compared to other adsorbents, this comparison indicates that this biosorbent prepared from TPL has a better efficiency compared to others in the elimination of methyl orange.

The different performances of the adsorption of methyl orange could be explained by the following factors: the heterogeneous nature and the chemical, structural and morphological composition of each adsorbent such as the structure, the functional groups and the specific surface.

IV. Conclusion

Methyl orange biosorption tests have confirmed the possibility of using TPL in water treatment.

-The characterization of this biosorbent has shown the presence of different functional groups (carboxylic, hydroxyl, etc.) on the surface of the biosorbent.

- The adsorption of methyl orange has a good yield in an acidic medium, on the other hand, the efficiency of this one is lower the higher the electrolyte concentration.

-The results of the kinetic study for this pollutant, show that the retention took place in 120 min, and it is controlled by the pseudo-second order model.

-The adsorption isotherm of methyl orange follows the Langmuir model well with a maximum adsorption quantity of 8.67 mg/g.
-The comparative study showed that the TPL adsorbent has a high capacity to remove methyl orange from aqueous solution, resulting in good adsorption efficiency at low cost.
Looking ahead, it will be very interesting to:
-Improve the performance of this material by chemical activation or heat treatment of optional sites.
-Test the effectiveness of this biomaterial against other pollutants.

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