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Application of raw and roasted date seeds for dyes removal from aqueous solution

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- ✓ Methyl Orange (MO);
- ✓ Response surface methodology (RSM);

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Abstract

The present study concerns the adsorption in aqueous solution of methylene blue (MB) and methyl orange (MO) on raw date seeds powder (RDS), roasted date seeds (RoDS), carbonized date seeds (CDS) and commercial activated carbon (CAC) taken as a reference. Infrared spectroscopy has been used to characterize the aforementioned adsorbents. The adsorption tests were carried out by varying the mass of the adsorbent, the initial concentration of the adsorbate and the pH of adsorbate solution. The optimum removal conditions have been determined using the surface response methodology to fit retention rate. Optimal dyes (5 mg/L) removal occurs at pH 5 with sorbent dose of 75 mg/L. Results of adsorption on various examined materials show that raw and roasted date seeds are effective sorbents for removing MB from aqueous solution. The infrared analysis reveals that the functional groups involved in the adsorption exist in RDS and RoDS but not in CDS. MB is adsorbed in multilayers on heterogeneous surfaces. The adsorption process of the MB on the examined adsorbents is controlled by the chemisorption.

1. Introduction

Date, fruit of date palm, is one of the main agricultural products in many Moroccan regions, mainly along the valleys of Ziz and Draa. Dates and its derived products are an important source of income for aboriginal people and contribute to the economic development of these regions.

Under the Morocco green plan launched in recent years, the date palm has benefited from subsidies for rehabilitation and intensification of existing palms and the creation of new modern plantations. Therefore, the production of dates is increasing that packing and processing operations of this product result in a number of by-products such as seed, for example. This fruit processing by-product commonly named ‘‘date by-product’’ used as traditional herbal coffee in some countries, are currently employed for limited purposes such as animal feed. Date seeds are of an important research interest due to their high nutritional value and contents of functional ingredients including dietary fiber and phenolic compounds [1]. Exploring valorization is a critical need to find suitable applications for potential recycling of this waste. Date seeds, mainly composed of cellulose, hemicellulose, and lignin, are effective material that could be used as an adsorbent for the removal of both organic and inorganic pollutants from aqueous solution [2, 3]. The succesfull use of these low cost sorbents is essentially due to oxygenated functional groups which are present in the lignocellulosic materials such as cellulose and phenolic compounds.

Furtheremore, dyes are frequently employed in many industries, such as textile, paper, and tannery, which use large volumes of water. As a result, a considerable amount of colored wastewater are generated. The presence of this non biodegradable pollutant in natural water is then not suitable, that it's removal is of ever-increasing interest. Taking into account these considerations, date–pits powder is used as an adsorbent for the removal of color from aqueous medium, precisely methylene blue and methyl orange.
To examine the interactions between adsorption parameters and to limit the number of tests to perform, our choice fell on the response surface methodology (RSM) [4, 5] in view of its performance in determining optimal operating conditions for multi-parameter systems.

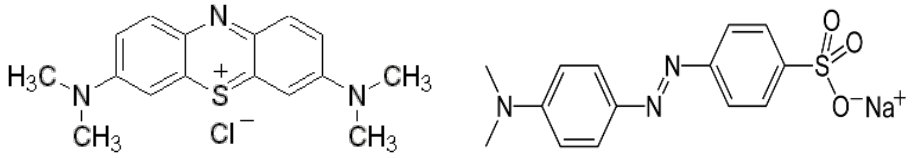
2. Materials and experimental methods

2.1. Adsorbents

The adsorbents used in this work are the raw date seeds (RDS), roasted date seeds (RoDS), carbonized date seeds (CDS) and commercial activated carbon (CAC) taken as reference. The date seeds examined are the seeds of the Boufeggous Moroccan variety from the region of Errachidia. These date seeds are previously washed with distilled water and then dried in an oven at 60°C for 24 hours. They are then crushed using a micro-grinder in their natural state and then sieved, the particle size retained for the adsorption tests is between 0.5 and 2 mm. The roasted and carbonized date seeds (RoDS, CDS) are obtained after torrefaction and carbonization of the powder of the date seeds respectively at 243 and 440°C for a few minutes under a nitrogen flow rate of 60 cm^3/min.

2.2 Adsorbates

Examined adsorbates in this work are methylene blue (MB) and methyl orange (MO) which are two widely used dyes in textile industry. Methylene blue is an organic compound of chemical formula $C_{16}H_{18}N_3SCl$ (figure 1a). Its molecular mass is equal to 319.85 g/mol. It is an organic molecule belonging to the family of the Xanthenes. It is a cationic dye $C_{16}H_{18}N_3S^+$. Methyl orange is an organic compound of chemical formula $C_{14}H_{14}N_3NaO_3S$ (figure 1b). Its molecular mass is of 327.33 g/mol. It is an anionic dye $C_{14}H_{14}N_3SO_3^-$.



(a) (b)

Figure 1: Molecular structure of MB (a) and MO (b)

2.3. Adsorbents characterization

2.3.1. Infrared characterization

The apparatus used for the characterization by infrared spectroscopy is a Bruker-Tensor 27, which operates in reflection mode. This apparatus is equipped with a Globar source that emits radiation in the region of mid-infrared and of a DLaTGS detector. In the unity of Attenuated Total Reflection (ATR), enough of the sample is placed, without prior preparation, on the diamond crystal, which allows the acquisition between 4000 and 500 cm^{-1} in wave number. The number of scans is 20 with a resolution of 4 cm^{-1}. The device is controlled by OPUS software.

2.3.2. Point zero charge

The point of zero charge (pHpzc) is determined by solid addition method [6, 7]. This method consists in introducing 50 ml of a solution containing NaCl 0.1 into closed vials and adjusts the initial pH of each of them to a value between 2 and 12 by addition of NaOH or HCl (0.1 M). Each bottle receives then 50 mg of material to characterize. Obtained suspensions are kept under stirring at room temperature for 24 hours and the pH of the filtrates corresponds to the final pH (pH_f). The plot of the final pH (pH_f) as a function of the initial pH (pH_i) is given in figure 2. pHpzc corresponds to the intersection of bisector straight line with titration curves ($pH_f = f(pH_i)$). One can note that the pH of the suspension solution, pHs, measured immediately after the addition of 50 mg of adsorbent in 50 ml of NaCl 0.1, is 5.6.

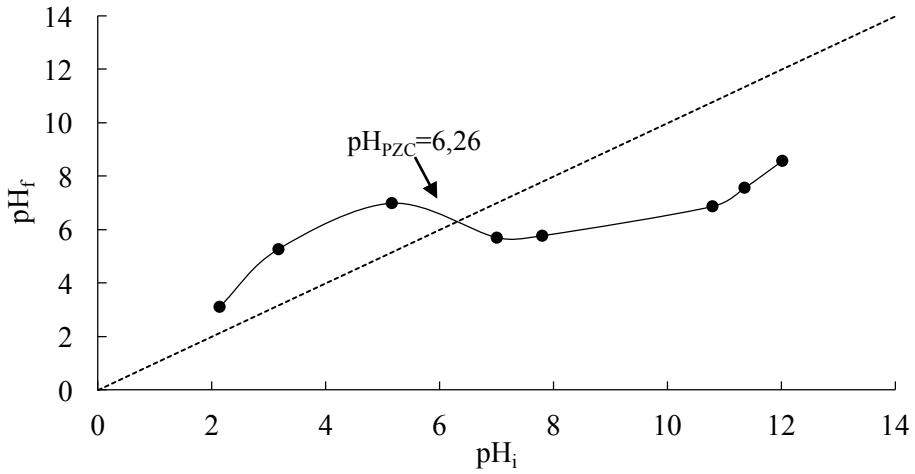


Figure 2: Titration curve (pH_f)=f(pH_i)) obtained in NaCl 0.1M as supporting electrolyte

As shown from figure 2, the pH value of the intersection point corresponding to pH_{PZC} or isoelectric point, is of 6.26. So, the surface charge of date-seed particules is positive at pH below 6.26, and negative at pH above 6.26.

2.4. Experimental protocol of the kinetics and isotherms of the adsorption

Sorption experiments were conducted at room temperature, by a batch method, using suspension volume of 50 ml. Adsorption of dyes is carried out at various concentrations, for well-determined pH and RDS dosage. After a contact time of 1h, the supernatants are filtered and analyzed for aqueous dyes using UV-visible spectrophotometry method. The adsorbance of Methyl Blue, and Methyl Orange is measured at 664 nm and 464 nm respectively, by a spectrophotometer 1600 MAPADA. The adsorbed dyes is calculated from the difference between the concentrations before and after equilibrium with date seeds.

The sorption efficiency is evaluated by adsorption capacity q_a (mg/g) or the retention rate R % given by the following equations:

$$q_a = \frac{(C_0 - C_e)V}{m} \qquad \text{(Eq.1)} \qquad\qquad R\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad \text{(Eq.2)}$$

Where V(L) is the suspension volume, C_0 and C_e are, respectively, the initial and the equilibrium concentrations of the adsorbate ($mg.L^{-1}$).

2.5. Response surface methodology (RSM)

Used response surface methodology is based on central composite design matrix (CCD) [5, 8]. The optimal operating conditions are determined for three parameters which are initial dyes concentration, RDS dosage and pH of adsorbate solution. The limits of variation of these parameters are recorded in table 1.

Table 1: Independent variables and their coded levels for the central composite design

Factor	Code	-1	0	+1
RDS Dosage (mg)	X_1	25	50	75
pH of adsorbat solution	X_2	3	7	11
Initial concentration of adsorbat (mg/L)	X_3	5	12.5	20

The sequential approach consists of three parts: factorial plan $N_F=2^k$, axial points $N_a=2k$ and (plan) points to the Center N_0. For our modelling, the used central composite matrix is to three factors (K = 3) with three points at the center, which corresponds to 17 tests in total ($Ne=N_F+N_a+N_0=2^k+2k+N_0=2^3+2(3)+3=17$). The matrix constructed from these data is given in table 2 with the values of the retention rates experimentally obtained after realization of 17 experiments. It should be noted that the obtained retention rates are significant in both acidic and basic mediums for MB, while it shows that the used material is not a good adsorbent for MO (table 2). The coefficient with one factor represents the effect of the individual factor, while the coefficients with two factors and with second-order terms respectively represent the interaction between two factors and the quadratic effect. The positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect [9].

Table 2: Experimental design matrix for dyes removal by RDS

Run	*RDS dosage (mg)*	*pH*	*Initial concentration ($mg.L^{-1}$)*	*Retention rate (%)*	
				MB	**MO**
1	17.82	7	12.5	41	23
2	25	3	5	49	20
3	25	3	20	33	-25
4	25	11	5	91	9
5	25	11	20	81	-35
6	50	2	12.5	50	38
7	50	7	2.84	73	-23
8	50	7	12.5	84	22
9	50	7	12.5	80	15
10	50	7	12.5	85	20
11	50	7	22.15	81	20
12	50	12.14	12.5	78	16
13	75	3	5	95	23
14	75	3	20	65	-22
15	75	11	5	76	-5
16	75	11	20	80	-42
17	82.18	7	12.5	90	19

The regression equation that follows from the constructed matrix is as follows:

$$Y = 78{,}92 + 11{,}08.X_1 + 10{,}86.X_2 - 3{,}86.X_3 - 5{,}29.X_1^2 - 6{,}05.X_2^2 + 1{,}78.X_3^2 - 11{,}83.X_1X_2 - 0{,}04X_1X_3 + 5{,}01X_2X_3 \quad \text{(Eq.3)}$$

The retention rate values predicted by JMP® 11 program, studied response, are compared with the experimental values (table 2, figure 3). The accuracy of the model developed depends on the values of R^2 and σ, which are respectively the regression coefficient and the standard deviation. In our work, the estimated values of R^2 and σ are respectively of 0.85 and 10,96 (figure 2), indicate that there is good agreement between the experimental and the predicted values in MB removal.

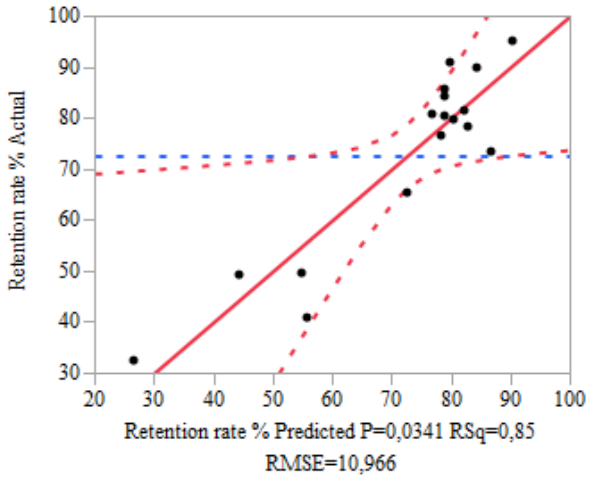


Figure 3: Predicted versus experimental MB Removal (%R) of RDS

In the imposed limits of the three examined parameters, desirability and performance changes obtained by the prediction profiler of JMP® 11 software are represented in figure 3. The optimization indicates that the retention rate decreases when the MB concentration increases, while it increases with the mass of the adsorbent. Moreover, the retention rate is almost stable for pH values less than 7 and decreases beyond this value. The optimum conditions which emerge from the methodology of the experimental surfaces are 75 mg of sorbent dose, 5 mg/L of dye concentration and a pH of dye solution equal to 5. This pH value is quite similar to that of the pH of the solution (paragraph 2.3.2.).

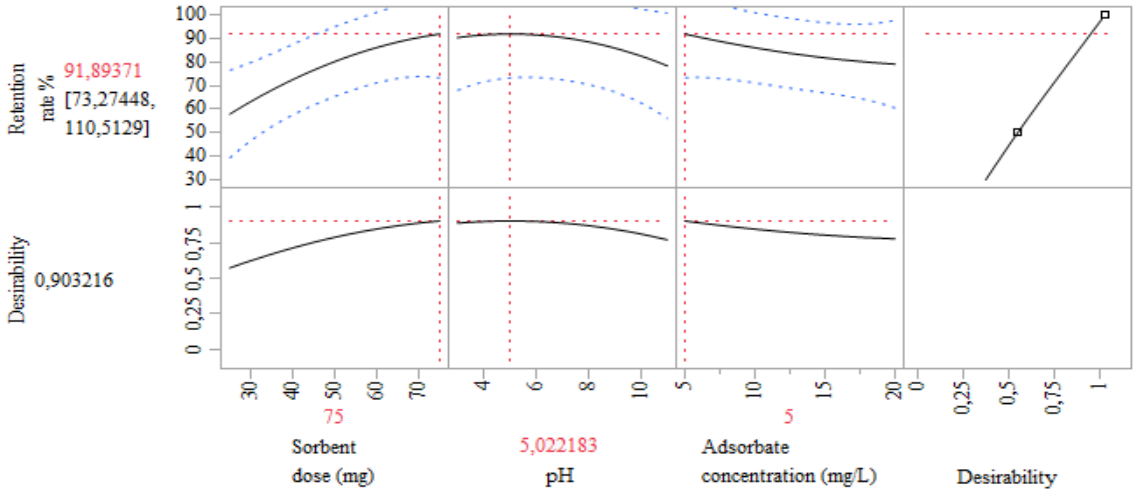
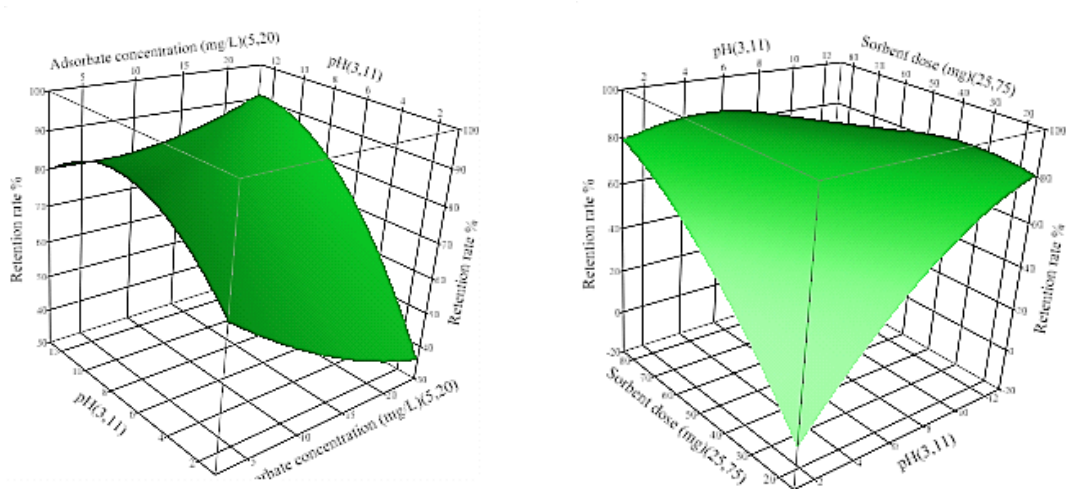


Figure 4: Prediction profiler outputs of JMP®11 software after maximization of the desirability

The three-dimensional response surface plots related to pH-concentration and pH-mass interactions obtained from the experimental design are given in figure 5. Figure 5a shows that the mass of the adsorbent and the pH of the solution are the factors which significantly affect this response, according to the gradient of slope in the 3-D response surface plot.



(a) *(b)*

Figure 5: Three-dimensional response surface plots for RDS/MB system : a) pH-concentration, b) pH-sorbent dose

3. Results and discussions

3.1. Adsorption kinetic

Figure 6 represents the results of the adsorption kinetics of methylene blue on raw date seeds, Roasted date seeds, carbonized date seeds and on commercial activated carbon. Thus, maximum retention rates, equilibrium time were deduced from the curves are recorded in table 3.

The effect of contact time on retention rate is shown in figure 6. From these results, the kinetic curves follow a similar trend, retention rate increases rapidly with contact time reaching a steady, maximum value after about 2 to 15 min. The maximum retention rate is obtained for RoDS, and CAC sorbents. This phenomenon could be explained by the existence of easily accessible adsorption sites, followed by diffusion to the less accessible sites before reaching adsorption equilibrium where all the sites are occupied.

Moreover, the results show that the retention rate of MB by the raw date seeds is of 70 % after 5 minutes. The adsorption improves with the roasted date seeds and becomes practically equivalent to that on the commercial activated carbon. In terms of adsorption on carbonized date seeds, the retention rate is lower than on the other samples (table 3). This is due to the fact that the functional groups responsible for the adsorption exist in the raw and roasted date seeds but not in the carbonized one as appears from the infrared spectra (figure 7). Indeed, carbonization leads to the loss of the functional groups involved in the adsorption. The same observation was made with coal derived from lignin [10, 11].

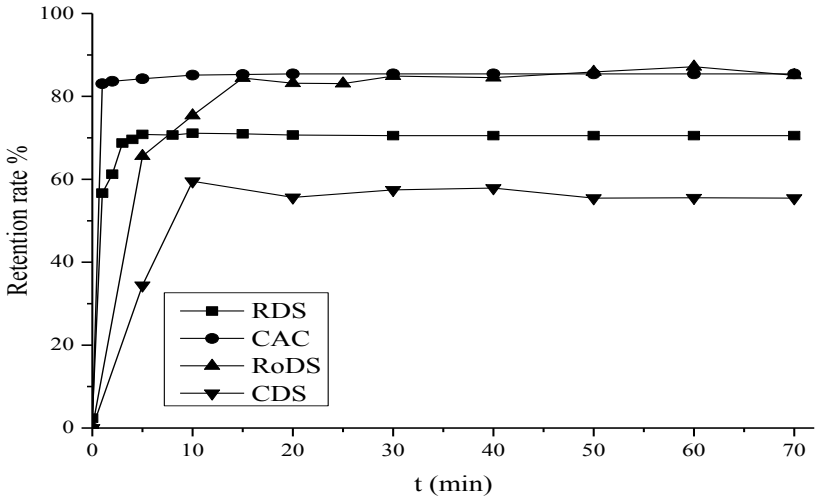


Figure 6: Adsorption kinetics of MB onto RDS, RoDS, CDS and CAC

Table 3: Retention rate and equilibrium time of MB on RDS, RoDS, CDS and CAC

Adsorbent	RDS	RoDS	CDS	CAC
Retention rate (%)	70	84	55	85
Equilibrium time (min)	5	15	20	10

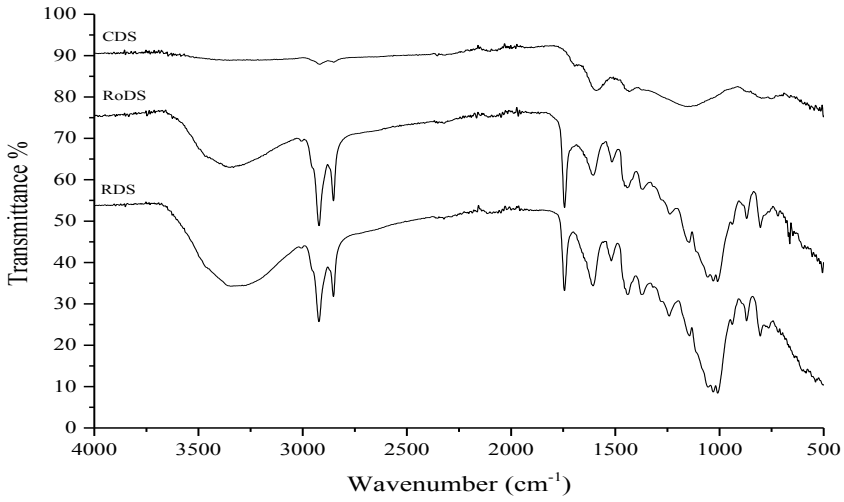


Figure 7: Infrared spectra of RDS, RoDS and CDS

Finally, the adsorption capacity of MB on roasted date seeds has improved of about 14 % than that on raw date seeds. El Messaoudi and al. [12] are the only ones, to our knowledge, to have used Moroccan raw date seeds and their derivative obtained not by heat treatment but rather a chemical in the adsorption of MB. El Messaoudi and al. [12] found that the adsorption capacity of MB by NaOH-chemically treated date seeds does not exceed 2 % compared to that on the raw date seeds.

3.1.1. Kinetic models

The plots of the kinetic models of the adsorption of methylene blue on the raw and roasted date seeds are shown in figure 8, for the pseudo-first order, pseudo-second order, intra-particle diffusion and the Elovich model. The values of the correlation coefficients, the mathematical expression of each model as well as the corresponding kinetic parameters deduced from the slope and the ordinate at the origin of the different traces are grouped in table 4.

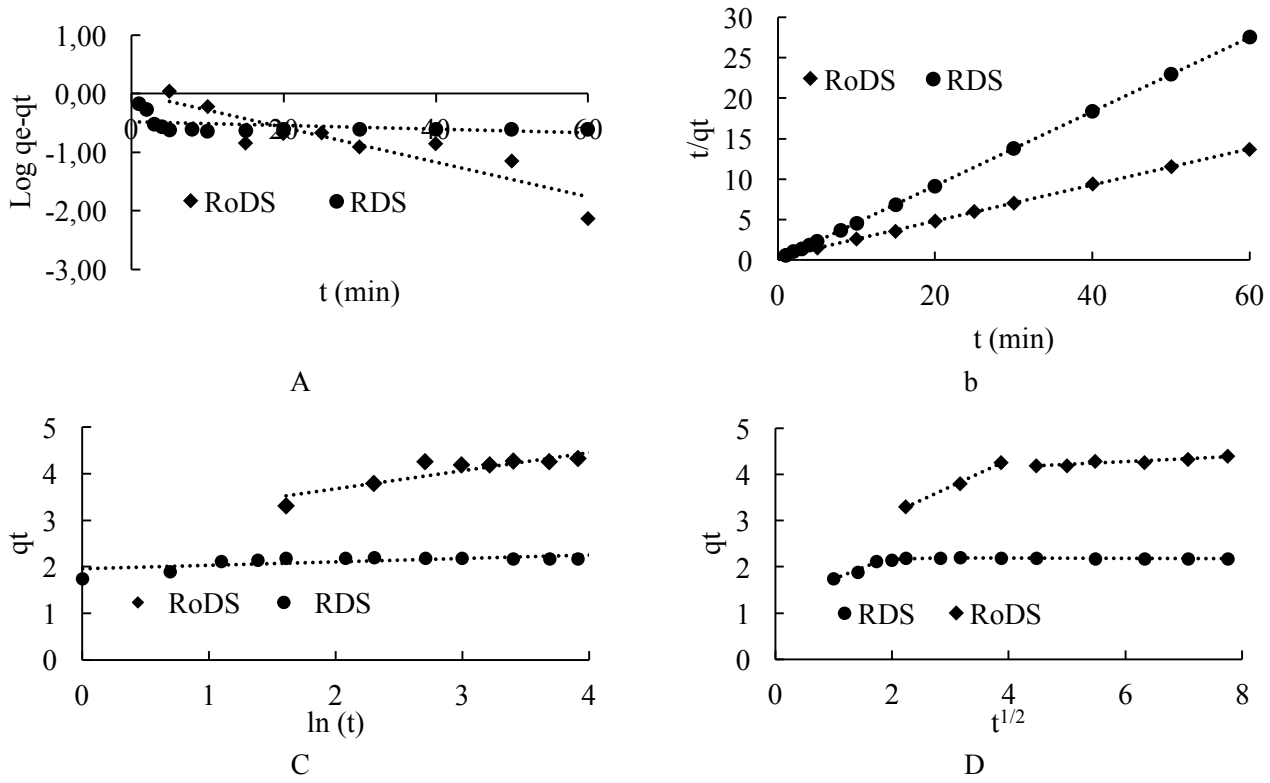


Figure 8 : Pseudo-first-order (a), pseudo-second-order (b), Elovich (c) and intra-particle diffusion (d) kinetic models of MB adsorption onto RDS and RoDS

Table 4 : Kinetic models parameters

kinetic models	Parameters		*Adsorbent/ Adsorbat*	
			RDS/MB	RoDS/MB
pseudo-first-order [15] $\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t$ (Eq. 4)	R^2		0.813	0.1806
	k_1 (min^{-1})		0.068	$7.36.10^{-03}$
	q_m (mg/g)		1.038	0.328
pseudo-second-order [13] $\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$ (Eq. 5)	R^2		**1**	**0.9996**
	k_2 ($g.mg^{-1}.min^{-1}$)		0.160	0.144
	$q_{e\ theo}$ (mg/g)		2.187	4.480
	$q_{e\ exp}$ (mg/g)		2.43	4.40
	$\Delta q = q_{e\ theo} - q_{e\ exp}$ (mg/g)		0.243	0.08
intra-particle diffusion [16] $q_t = K_d \times t^{1/2} + C$ (Eq. 6)	Type I	R^2	**0.9542**	**0.9971**
		k_d ($mg.g^{-1}min^{-0.5}$)	0.5031	0.5779
		I	1.2301	2.0011
	Type II	R^2	0.4041	**0.8903**
		k_d ($mg.g^{-1}min^{-0.5}$)	0.0296	0.0596
		I	2.1083	3.9145
	Type III	R^2	0.7526	-
		k_d ($mg.g^{-1}min^{-0.5}$)	-0.0039	-
		I	2.227	-
Elovich [17] $q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt$ (Eq. 7)	α (mg/g min)		$9.82.10^9$	694.41
	β (g/mg)		13.12	2.576
	R^2		0.5161	0.8073

With : q_t and q_e : the amount of adsorbed dyes, respectively, at a time t and at equilibrium time (mg/g),
t : contact time (min),
K_1, K_2 and K_d: rate constants respectively for kinetic equation of pseudo-first-order (min^{-1}), pseudo-second order ($g.mg^{-1}.min^{-1}$) and intraparticle diffusion ($mg/g\ min^{1/2}$),
I : intercept which reflects the boundary layer effect (mg/g).
α (mg/g min) is the initial rate constant and the parameter β (g/mg) is related to the extent of surface coverage and activation energy of chemisorption

Examination of the different traces in figures 8a, b and c shows that the kinetics of the adsorption of MB on RDS and RoDS is of the pseudo-second order type, since values of the correlation coefficient corresponding being very close, and even equal to 1 (table 4). Moreover, the amount of adsorbed dyes at equilibrium time and calculated by the pseudo-second order model are consistent with those obtained experimentally (table 4). This would indicate that the adsorption process is mainly controlled by chemisorption [13]. This result is in agreement with the pHpzc and pHs measurements. Thus, the contribution of an electrostatic effect to the MB uptake by the RDS, and RoDS sorbents, is negligeable for pHpzc > pHs [14].
In terms of intra-particle diffusion (figure 8d), it is done in two and three steps respectively for the RoDS/MB and RDS/MB systems. For these systems, diffusion is involved in the process but is not the limiting step because the traces of the different stages do not pass through the origin. The resistance to external mass transfer is more important for RoDS than to RDS because the values of the ordinates at the origin C indicate that the adsorbed solute is more abundant on the boundary layer of the RoDS than on that of the RDS (table 4). Although the model of intraparticle scattering indicates that the adsorption mechanisms of MB are complex, it is possible to suggest that resistance to transfer would be manifested by a higher equilibrium time with RoDS than with RDS (table 3).

3.2. Adsorption isotherms models

The MB adsorption isotherm models of the raw and roasted date seeds are shown in figures 9a, b, c and d respectively for the Langmuir, Freundlich, Temkin and Dubinin models which the corresponding parameters are given in table 5.

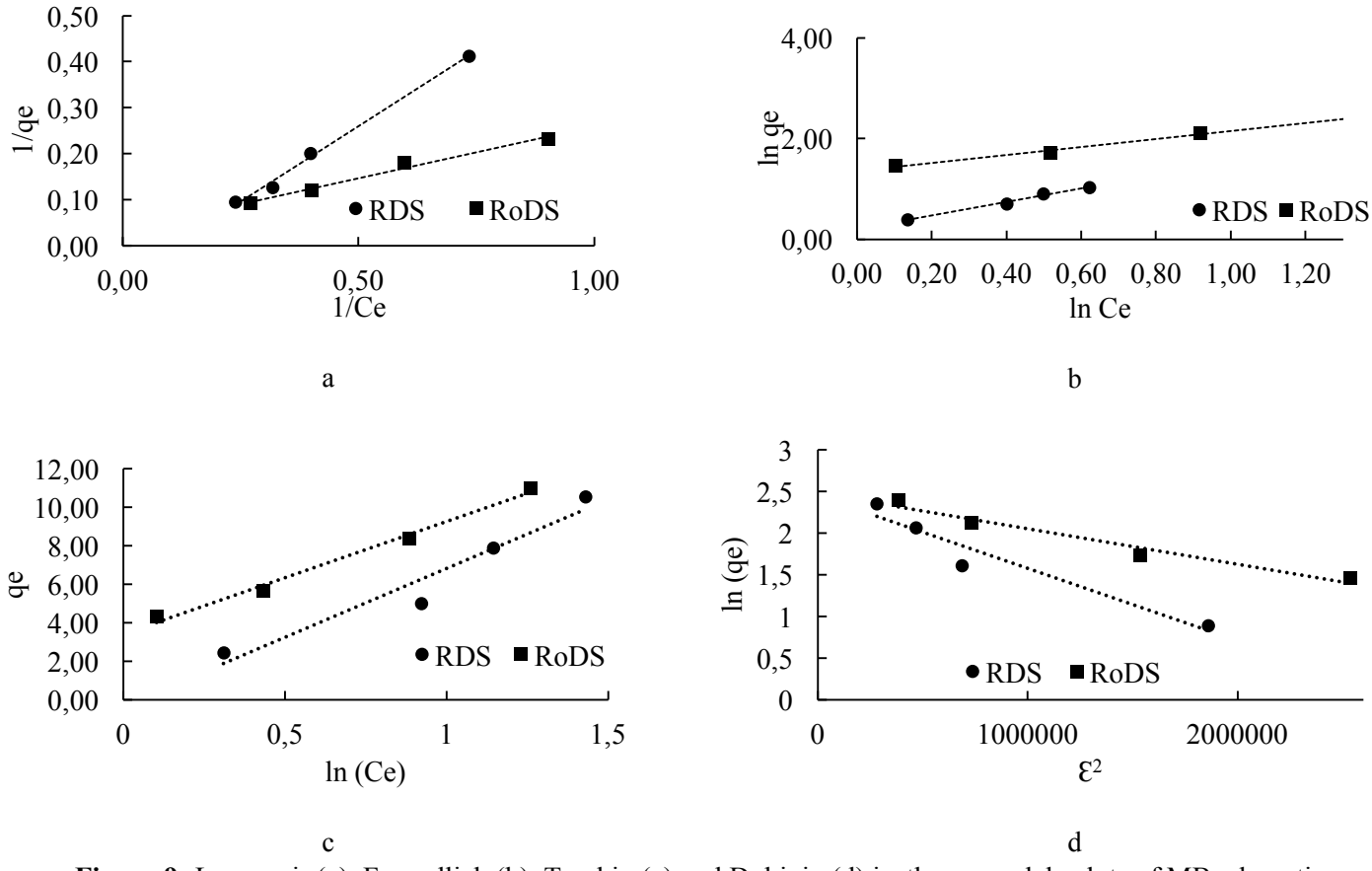


Figure 9: Langmuir (a), Freundlich (b), Temkin (c) and Dubinin (d) isotherm models plots of MB adsorption onto RDS and RoDS

It is important to indicate for raw and roasted date seeds, that the values of the correlation coefficients are very close to 1, in all the cases (table 5). However, the adsorbed amount calculated by Langmuir isotherm model in the case of RDS is negative because of the very low concentrations of dye. The determination of the parameters RL and b of this model is therefore impossible. A comparable result was obtained by Sakr and al. [18] during the adsorption of MB by the cactus powder. Always in the case of the Langmuir isotherm for RoDS, the calculated adsorbed quantity differs greatly to the experimental value (table 5). The Langmuir model therefore does not describe the experimental data of the adsorption of MB by RoDS.

In the case of the Freundlich isotherm, the values of K_F and those of 1/n indicate good adsorption capacity (table 5). This model satisfactorily describes the adsorption of MB on date seeds. The adsorption of MB is then done in multilayers on heterogeneous surfaces.
On the other hand, the B_T values estimated by the Temkin model (table 5) are very low indicating low interactions between the adsorbent and the adsorbate.
Finally, the high mean free energy value calculated from the Dubinin-Radushkevich model for both adsorbents (table 5) indicates that the mechanism is controlled by chemisorption.

Table 5: Parameters of the isotherms

Isotherms	Parameters	Adsorbent/adsorbate	
		RDS/MB	RoDS/MB
Langmuir [19] $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_mC_e}$ (Eq. 8)	$q_{m,cal}$ (mg.g^{-1})	**-15**	30.03
	b	-	0.146
	R_L	-	0.473
	R^2	**0.9953**	**0.9841**
Freundlich [20] $Ln(Q_e) = \frac{1}{n_f} Ln(C_e) + Ln(K_f)$ (Eq. 9)	$1/n_f$	1.3392	0.7947
	K_f	1.2188	3.875
	R^2	**0.9892**	**0.9913**
Temkin [21] $q_e = B_T LnK_T + B_T LnC_e$ (Eq. 10)	B_T (J/mol)	7.164	5.5973
	K_T (L/g)	0.9528	1.798
	R^2	**0.9373**	**0.9905**
	b_T (J/mol K)	345.83	442.63
Dubinin-Radushkevich [22, 23] $Lnq_e = Lnq_m - \beta\varepsilon^2$ (Eq.11)	E (K_J/mol)	$1.05.10^3$	$1.58.10^3$
	q_s (mg/g)	11.565	11.307
	β (K_J^2/mol^2)	9.10^{-07}	4.10^{-07}
	R^2	**0.9305**	**0.96**

Where
q_e and q_m are respectively the amount of adsorbed dyes at equilibrium time and maximum amount of adsorbate per unit sorbent (mg/g),
C_e is the equilibrium liquid-phase concentration (mg/L), residual equilibrium concentration
R: represent the gas constant (8.314 J/mol K),
T: absolute temperature (K)

ε is potential energy, it can be correlated as $\varepsilon = RTLn(1 + \frac{1}{1/C_e})$ (Eq. 12)

β the Dubinin-Radushkevich (DRK) isotherm model constant related to the adsorption capacity and gives the mean free energy *E* of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed by using the relationship: $E=1/\beta^{0,5}$ (Eq. 13)
K_L, K_F and K_T, are respectively Langmuir constant (L.mg^{-1}), Freundlich constant (mg$^{(1-n)}$L^n.g^{-1}) and Temkin constant (L. mg^{-1}) ,
R_L : dimensionless constant called separation factor or parameter of equilibrium $R_L = \frac{1}{1 + b \times C_0}$ (Eq.14)
B_T = Constant related to heat of sorption (J/mol) $B_T = RT/b_T$ (Eq.15), b_T = Temkin isotherm constant
1/ nf : factor of heterogeneity.
b (L.g^{-1}) is the Langmuir constant related to the affinity between adsorbent and adsorbate.

Conclusion

The date seeds of the Boufeggous Moroccan variety are used in the raw, roasted and carbonized states to remove methylene blue in aqueous solution. The parameters taken into consideration are the mass of the adsorbent, the initial concentration of the adsorbate and the pH of the solution. The optimal conditions for these three parameters, determined using the response surface method (RSM), are 75 mg RDS, 5 mg/L dye and a solution pH equal to 5.

The retention rate obtained by the roasted date seeds, comparable to that of the commercial activated carbon, is higher than that on the raw date seeds, which is higher on the carbonized ones. Infrared spectroscopy reveals that the functional groups involved in the adsorption phenomenon are present in RDS and RoDS but not in CDS.
Equilibrium data follow the pseudo-second order kinetic model where adsorption processes are governed by chemisorption for both RDS/MB and RoDS/MB systems. Freundlich model best represents the experimental values indicating that MB is adsorbed in multilayers on heterogeneous surfaces for both adsorbents.

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