

Removal in batch mode experiment of Methylene Blue onto trimming Wood of Orange Tree – Equilibrium and Kinetics Studies –

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ARTICLE INFO

Article History:

Received : 05/02/2018

Accepted: 28/03/2018

Key Words:

Adsorption,
Methylene blue,
Isotherms,
Kinetics,
Ligno-cellulosic wastes,
Modeling.

ABSTRACT/RESUME

Abstract: In the present study, adsorption of Methylene Blue (MB) from aqueous solution was investigated using an adsorbent derived from Trimming Wood of Orange Tree (WOT). The used adsorbent was analyzed using FT-IR and SEM techniques. The adsorption of MB was carried out using a batch system and the effects of adsorbent dose, initial pH, ionic strength, contact time, initial concentration and temperature on the adsorption capacity of adsorbent were investigated. Kinetic parameters, rate constants, equilibrium adsorption capacities and determination coefficients, for each kinetic equation were calculated and discussed. It was shown that the adsorption of MB onto WOT could be described by the pseudo-second order kinetic. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin models. Adsorption of MB onto WOT followed the Langmuir isotherm for all temperatures studied and the maximum MB uptake was observed as 48.78 mg/g at 293 K. The evaluation of thermodynamics parameters such as the negative Gibbs free energy and negative enthalpy change indicated respectively the spontaneous and exothermic nature of the sorption process.

I. Introduction

One of the most serious environmental problems is the existence of toxic compounds in wastewater, like dyes and pigments. These substances are widely used in manufacturing processes such as paper, plastics, printing inks and others [1]. Their

presence in wastewater, even at low concentrations, cause serious harm to the aquatic life reducing light penetration which hinders photosynthetic phenomena and affect the food web [2]. Some of them are known to be carcinogenic and highly toxic to living beings [3] due to the presence of complex aromatics, metals and chlorides [4]. Several

technologies for dye wastewaters treatment have been reviewed in different works, but they have not been widely applied at large scale and are limited by their high operational costs [5]. Over the last decades, the treatment by activated carbon is considered to be one of the most promising techniques for wastewaters treatment. Many researchers have developed different activated carbons based agricultural wastes for dyes removal such as: orange peel [6], sponge loofa [7], avocado kernel seeds [8], pine wood [9], Euphorbia rigida [10], Apricot Stone [11] and others. However, adsorption by activated carbon is limited by its higher cost and the need for its regeneration. Recently, there is a big interest to reduce the cost preparation of activated carbon by valorizing agricultural by-products as adsorbent without any chemical or physical activation. These non-conventional wastes, abundant, inexpensive, requiring little processing, have been proved the success for dyes removal. Recently, a number of low-cost adsorbents have been examined [12-16], whose lignocellulosic waste took an important place on several dyes removal studies [17]. In Algeria, orange tree wastes are a large expansion in the agricultural sector. There are great quantities of wood orange tree throwing after trimming operation (or pruning) and their use is only limited to its combustion on site. Instead of eliminating them, it is recommended to treat these branches for a possible reuse. There are not reports on the valorization of raw wood orange tree trimming waste as adsorbent for the dye removal from aqueous solution. The valorization of wood orange tree trimming as green adsorbent, without any chemical or physical modifications, used in the present study was carried out with the aim to optimize conditions such as initial dye concentration, pH, particle size, contact time, adsorbent dosage, agitation speed and temperature. Besides this, the equilibrium adsorption data were fitted to various equations to obtain constants related to the adsorption phenomena. Equilibrium and kinetic analysis were conducted to determine the factors controlling the rate of adsorption, the optimization of various parameters in dye recovery and to find out the possibility of using this material as low-cost adsorbent for dye removal.

II. Materials and methods

II.1. Adsorbent preparation and characterization

The sample of Wood Orange Tree trimming (pruning) (WOT) was collected from an agriculture area of an orange tree plantation, situated near KADIRIA (northeast area of ALGERIA). The sample was cut into pieces, milled, sieved in particle size range from 0.50 to 0.63 mm. The WOT fibers were intensively washed with distilled water and dried in an oven at 105 °C for 48 h.

Characterizing raw WOT, several analyzes were made. The amounts of humidity and ash were determined by the gravimetric method. The point of zero charge (pH_{PZC}) was determined by stirring 0.15 g of WOT with 50 mL of NaCl solution (0.01 N) at different initial pH (2-12) for 24 h [18]. Initial and final pH_s were measured by using a Jenway 3010 pH-meter. To determine which functional groups were responsible for dye uptake, a Fourier Transform Infra-Red spectroscopy (FT-IR) analysis for raw WOT was performed using FT-IR Bruker Alphas spectrometer. Scanning electron microscopy (SEM) was used to study the surface morphology of the raw WOT fibers, using Philips Esem XL30 with tungsten filament.

II.2. Batch mode adsorption studies

The working Methylene Blue (MB) solutions were prepared by diluting the stock solution (1000 mg/L) to give the appropriate concentrations. The adsorption experiments were performed in batch mode by contacting 100 mL of MB solution at initial concentration C_0 with an appropriate WOT mass. The tested parameters were WOT dosage (1-10 g/L), initial solution pH (3-10), ionic strength (NaCl and CaCl₂: 0.01-0.10 mol/L), contact time (0-360 min) and initial MB concentration (10-100 mg/L). For predetermined time intervals, aqueous samples were taken and residual concentration of MB (C_t) was measured using UV/visible spectrometer at 664 nm.

The percentage of MB adsorbed and the amount of MB adsorbed at time t were calculated using Eq. 1 and Eq. 2 respectively.

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} * 100 \quad (1)$$

$$q_t \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_t)}{m} * V \quad (2)$$

The adsorption isotherms were conducted by shaking for 24 h and using different concentrations of MB (10-100 mg/L) at different temperatures (293-309.5 K). The amount of MB adsorbed onto WOT at equilibrium (mg/g) was calculated using the following expression Eq. 3:

$$q_e \left(\frac{\text{mg}}{\text{g}} \right) = \frac{(C_0 - C_e)}{m} * V \quad (3)$$

Where C_0 , C_t and C_e are concentrations of MB at initial time, t time and at equilibrium time (mg/L) respectively, V is the volume of the MB solution (L), m is the dried mass of WOT (g).

II.3. Adsorption kinetics and isotherms models

The kinetic study is important for the adsorption process because it describes the uptake rate of adsorbate, and controls the residual time of the whole process. Two kinetic models namely the,

pseudo first order and pseudo second-order are selected in this study for describe the adsorption process.

The pseudo-first order equation [19] is given in equation Eq.4:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} \cdot t \quad (4)$$

The pseudo-second order model [20] is expressed by the equation Eq.5:

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t \quad (5)$$

For the pseudo-second order, the initial adsorption rate h (mg/g.min) is expressed by the equation Eq.6:

$$h = K_2 q_e^2 \quad (6)$$

Where q_t (mg/g) is the amount of metal adsorbed on the adsorbent at various times t (min), K_1 the rate constant of the pseudo-first order kinetic (min^{-1}), K_2 the rate constant of the pseudo-second order kinetic (g/mg.min). The slope and intercept of the plots of $\ln(q_e - q_t)$ vs t was used to determine the first-order rate constants K_1 and q_e . The slope and intercept of the plot of t/q_e vs t was used to determine the second-order rate constants K_2 and q_e .

An empirically found functional relationship common to most adsorption process is that varies almost proportionally with $t^{1/2}$, the Weber-Morris plot (q_t vs $t^{1/2}$), rather than the constant time t [21] Eq.7.

$$q_t = K_{in} \cdot t^{1/2} + C \quad (7)$$

Where K_{in} is the intraparticle diffusion rate constant ($\text{mg/g.min}^{1/2}$). Values of intercept C gives an idea about the thickness of boundary layer. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface.

To fit the experimental isotherm data of MB adsorption onto raw WOT, three isotherm models were applied: Langmuir, Freundlich and Temkin models.

Langmuir isotherm [22]:

The non-linear linear forms of the Langmuir isotherm are represented by the following equations respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

$$\frac{C_e}{q_e} = \frac{1}{q_n} C_e + \frac{1}{K_L q_n} \quad (9)$$

Where C_e is the equilibrium concentration (mg/L), q_{max} is the monolayer adsorption capacity (mg/g) and K_L is the constant related to the free adsorption energy (Langmuir constant, L/mg).

Equilibrium parameter for Langmuir isotherm called separation factor (R_L) was expressed as Eq. 10. The values of this parameter indicate the shape of the isotherm which: $R_L > 1$ is unfavorable, $R_L = 1$ is linear, $R_L = 0$ is irreversible and finally $0 < R_L < 1$ is favorable.

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

Freundlich isotherm [23]:

For Freundlich isotherm model, the general form is given by Eq.11, and the linear form is presented by Eq. 12.

$$q_e = K_F C_e^{1/n} \quad (11)$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (12)$$

Where K_F is the constant indicative of the adsorption capacity of the adsorbent (L/g) and $1/n$ constant shows adsorption intensity of dye onto the adsorbent. For a suitable adsorption system, $1/n$ value varies between 0 and 1.

Temkin isotherm [24]:

Eq. 13 and Eq. 14 present the general and linear forms, respectively, for Temkin isotherms model.

$$\frac{q_e}{q_m} = \frac{B_T}{q_m} \ln(A_T \cdot C_e) \quad (13)$$

$$q_e = B_T \ln C_e + B_T \ln A_T \quad (14)$$

Where B_T is the constant related to the heat of adsorption (mg/g), A_T is Temkin isotherm constant (L/min).

II.4. Statistical test for the Isotherms data

Because of the inherent bias resulting from linearization of isotherm models, the non-linear regression Root Mean Square Error (RMSE) (Eq. 15) and Chi-Squares (X^2) (Eq. 16) test are used as criteria for the fitting quality. The smaller RMSE, X^2 values indicates the better curve fitting [25].

$$RMSE = \sqrt{\frac{1}{N-2} \cdot \sum_1^N (q_{e,exp} - q_{e,cal})^2} \quad (15)$$

$$X^2 = \sum_1^N \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (16)$$

Where $q_{e(exp)}$ (mg/g) is the uptake experimental, $q_{e(cal)}$ (mg/g) the calculated value of uptake using a model and N the number of observations in the experiment (the number of data points).

II.5. Thermodynamic study

The various thermodynamic parameters, standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were determined using Eq. 17 and Eq. 18 [26]. The linear plot of $\ln K_d$ against $1/T$ allow the determination of ΔH° and ΔS° .

$$\Delta G^\circ = -RT \ln K_d \quad (17)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (18)$$

Where R is the universal gas constant (8,314 J/mol.K), T the absolute temperature in Kelvin and K_d is the thermodynamic constants equilibrium of MB adsorption on WOT were determined from the intercept of the linear plots of $\ln \frac{q_e}{C_e}$.

III. Results and discussion

III.1. The WOT characterization

The raw WOT consists of small amounts of ash (3.08 %) and possesses certain moisture content (30.21 %). The pH_{PZC} of WOT is equal to 5.15. Therefore, the surface charge carried by WOT will be positive for pH smaller than 5.15 and negative beyond. The FT-IR spectra represented in **Fig.1**, display a number of adsorption peaks which identify some functional groups. The intense absorption bands around 3600 and 3100 cm^{-1} indicates the presence of -OH and -NH groups. The peak 2900 cm^{-1} is assigned C-H bands. The peak at 1737.22 cm^{-1} corresponds to carbonyl C=O stretching and can be attributed to the hemicellulose and lignin. The absorption band corresponding to 1504.01 cm^{-1} represents C=C or C=N vibrations in aromatic region. The peaks 1457.98, 1421.98, 1369.89, 1322.28 and 1231.28 cm^{-1} may represent C-C stretching vibration of carboxylic acid and alcohols. The peak 1030.66 cm^{-1} is assigned C-C, C-O or C-N bands. These results indicated that WOT adsorbent presented different functional groups as hydroxyl, carboxyl and carbonyl which may be potential adsorbent sites for MB uptake. The Scanning electron microscopy (SEM) image (**Fig. 2**) shows that the WOT fibers have considerable numbers of heterogeneous pores where there is a great possibility for the MB adsorption.

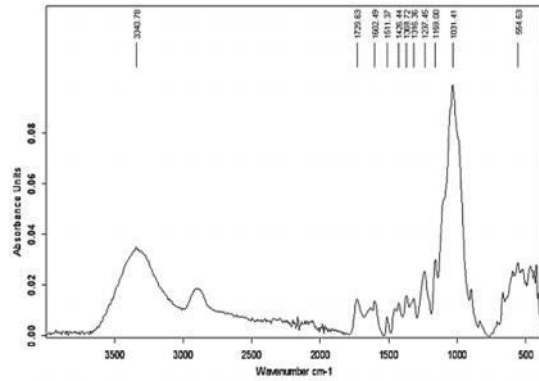
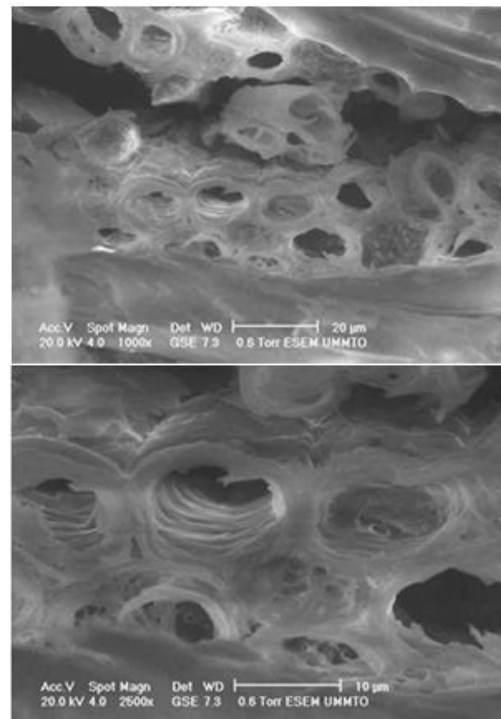


Figure 1. FT-IR spectra of raw WOT.

Figure 2. SEM images of raw WOT



III.2. Effect of WOT dosage

The amount of used adsorbent plays an important role in adsorption process. **Fig. 3** presents the variation of percentage removal and adsorption capacity of MB by varying WOT dosage from 1 to 10 g/L. MB removal increases from 81.6 to 95.4 % for an increase in WOT dosage from 1 to 10 g/L. However, the amount of MB adsorbed decreases from 20.4 to 2.4 mg/g. The removal enhancement can be due to the availability of more adsorption active sites and to the increase in surface area. However, the adsorbed capacity decrease may be due to the overlapping and accumulation of binding sites [27]. The same phenomena have been observed in other previous studies of MB adsorption by spent coffee ground [2], castor seed shell [28] and spent tea leaves [29].

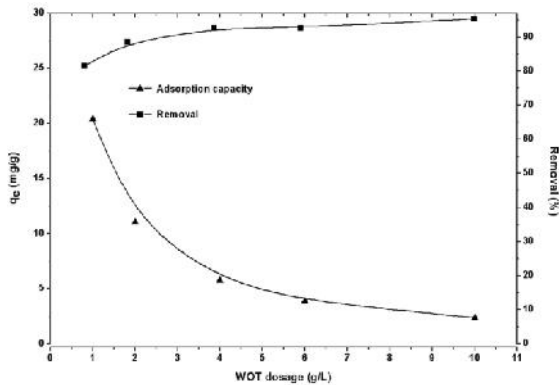


Figure 3. Effect of the WOT dose on the adsorption capacity and percentage removal of MB (particle size = 0.50-0.63 mm, $C_0 = 25$ mg/L, time = 180 min, pH solution)

III.3. Effect of initial solution pH

From Fig.4, the increase in solution pH from 3 to 4 increases the adsorption capacity of MB from 3.7 to 5.4 mg/g, corresponding to an increasing of removal percentage from 58.5 to 85.7 %. Thereafter there is no significant change. At acidic pH range (lower than WOT pH_{PZC}), lower MB adsorption is probably due to the presence of H^+ ions excess competing with the cation groups on the MB for adsorption sites. At basic pH range (higher than WOT pH_{PZC}), the WOT surface is negatively charged, which favors electrostatic interactions with MB (cationic dye) molecules [30]. This, however, did not explain the slight decrease of dye adsorption at higher pH values [17]. Our results are similar to those observed for MB removal onto cotton wastes [3], fallen phoenix tree's leaves [31] and rice husk and rice husk ash [32]. MB solution has natural pH between 6 and 7 and at this pH, adsorption of MB dye is maximum with the WOT. Hence, pH of MB dye solution has not been varied in further experiments.

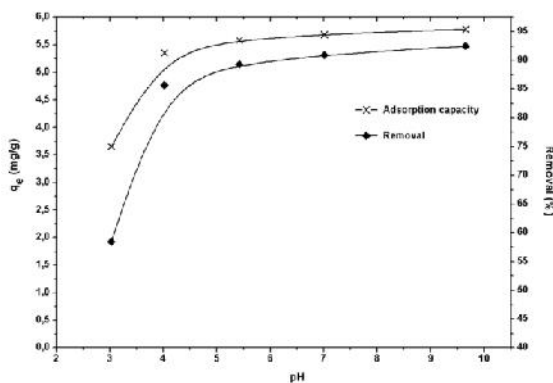


Figure 4. Effect of the initial pH on adsorption capacity and percentage removal of MB onto WOT (particle size = 0.50-0.63 mm, $C_0 = 25$ mg/L, WOT dose = 4 g/L, contact time = 180 min)

III.4. Effect of ionic strength

The effect of salt concentration was studied by addition of NaCl and $CaCl_2$ to the MB solution. As seen in Fig. 5, when the salt concentration increased from 0 to 0.1 mol/L, the value of adsorption capacity decreased from 5.8 to 3.2 and 2.4 mg/g for NaCl and $CaCl_2$, and the removal decreased from 92.6 to 51.5 and 37.7 % for NaCl and $CaCl_2$, respectively. The decreasing of adsorption efficiency with the salt concentrations increasing, can be related to the competitive effect between MB ions and cations from the salts (Na^+ and Ca^{2+}) for the sites available for the adsorption process [33]. The influence of NaCl on removal of MB was weaker than $CaCl_2$ because unit mole univalent Na^+ contributed less positive charges than unit mole divalent Ca^{2+} [34].

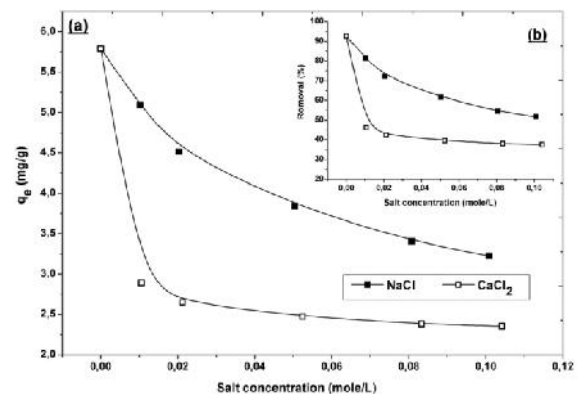


Figure 5. Effect of ionic strength on the adsorption of MB onto WOT (particle size = 0.50-0.63 mm, $C_0 = 25$ mg/L, WOT dose = 4 g/L, pH solution)

III.5. Effect of initial concentration of MB and contact time

Kinetic studies were carried out in order to determine the equilibrium contact time for different MB initial concentrations (10-100 mg/L) and results are presented in Fig. 6. This figure shows that the process of MB adsorption is quick from the beginning and slow down to finally reaches to equilibrium. In addition, we can note that when initial concentration increase from 10 to 100 mg/L, the equilibrium adsorption capacity increases from 2.4 to 22.5 mg/g. At higher concentrations, the excess dye molecules are not adsorbed by the WOT, due to the saturation of the limited binding sites on WOT surface. The similar findings were reported in the literature [35].

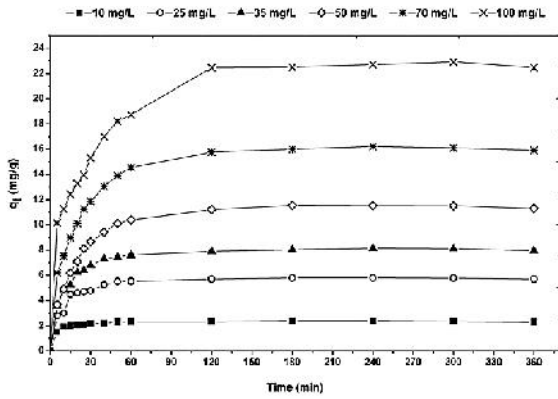


Figure 6. Effect of MB initial concentration and contact time on the adsorption of MB onto WOT (particle size = 0.50-0.63 mm, WOT dose = 4 g/L, pH solution)

III.6. Adsorption kinetic

Three different kinetic models, pseudo-first order, pseudo-second order and intra-particle diffusion, were used to interpret the obtained experimental data. Fig.7 (a) and Fig.7 (b) present the linear plots of the pseudo-second order and the pseudo-first order models, respectively. The kinetic constants (q_{e1} , K_1 , q_{e2} , K_2) were determined and the corresponding linear regression coefficient (R^2) values are given in Table 1. We can note, from the results, that the pseudo-second order model fits better than the pseudo-first order with higher determination coefficients ($R^2 > 0.99$). In addition, the experimental adsorption capacity (q_{exp}) values are very close to the model calculated values (q_{e2}),

verifying the high correlation of adsorption to the pseudo-second order model.

As seen from Fig. 8, the plots of q_t against $t^{1/2}$ are not linear over the whole time range and give three straight-line with different slopes and intercepts values. The values of $K_{in(i)}$, $C_{(i)}$ and the corresponding linear regression coefficient R_i^2 obtained from the first and second linear portions are listed in Table 1. The higher correlation coefficients R^2 are correspond to the second phase (0.94-0.99). In addition, $C_{(i)}$ parameter is different than 0 and the straight-line does not pass through origin implying that adsorption of MB onto WOT was affected by some other mechanisms [17].

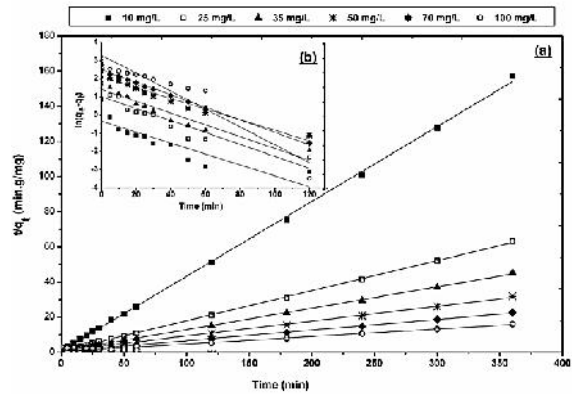


Figure 7. Application of pseudo-second order (a) and pseudo-first order (b) to the MB adsorption onto WOT for different MB initial concentrations

Table 1. Pseudo-first order, pseudo-second order and intra-particle diffusion parameters of MB adsorption onto WOT for different initial concentrations

Initial concentration (mg/L)	10	25	35	50	70	100	
q_{exp} (mg/g)	2.387	5.79	8.025	11.538	15.981	22.501	
Pseudo-first order	K_1 (min ⁻¹)	0.030	0.032	0.032	0.029	0.034	0.049
	q_{e1} (mg/g)	0.71	2.77	4.09	8.05	12.07	26.85
	R^2	0.76	0.86	0.90	0.95	0.99	0.90
Pseudo-second order	K_2 (g/mg.min)	0.258	0.034	0.020	0.008	0.006	0.003
	q_{e2} (mg/g)	2.34	5.84	8.20	11.86	16.61	23.69
	R^2	0.99	0.99	0.99	0.99	0.99	0.99
	h (mg/g.min)	1.413	1.159	1.345	1.125	1.655	1.684
Intra-particle diffusion	K_{id1} (mg/g.min ^{1/2})	0.322	0.989	1.134	1.606	1.839	1.538
	C_1 (mg/g)	0.815	0.359	1.082	-0.027	1.913	6.516
	R_1^2	0.91	0.78	0.97	0.99	0.99	0.98
	K_{id2} (mg/g.min ^{1/2})	0.084	0.309	0.442	0.755	1.22	1.251
	C_2 (mg/g)	1.684	3.216	4.302	4.421	5.2	8.943
	R_2^2	0.97	0.95	0.94	0.97	0.99	0.98

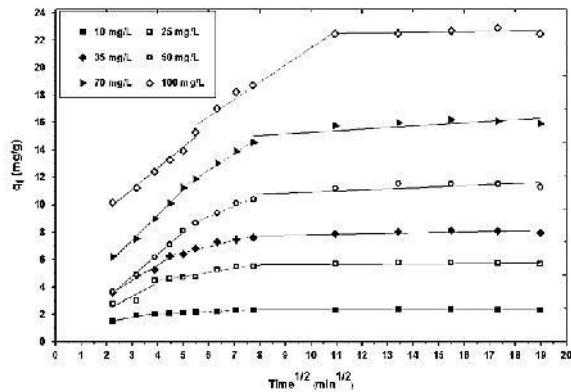


Figure 8. Application of intra-particle diffusion model for MB adsorption onto WOT for different MB initial concentrations

III.7. Isotherm study

The equilibrium experimental data for MB adsorption onto WOT at different temperature (293, 298, 303 and 309 K) were fitted using Langmuir, Freundlich and Temkin isotherms (Fig.9). The calculated parameters characteristics of each isotherm model are given in Table 2. It can be seen from the results illustrated in Table 2 and Fig. 10, that Langmuir isotherm fits better than Freundlich and Temkin isotherms with higher correlation coefficients ($R^2 \sim 0.99$) and the smaller RMSE, X^2 values indicates the better curve fitting. For all studied temperatures, we can note that the evolution of R_L is including between 0.057 and 0.490, which belonging in the range of 0-1, indicating that MB adsorption onto WOT is a favorable process.

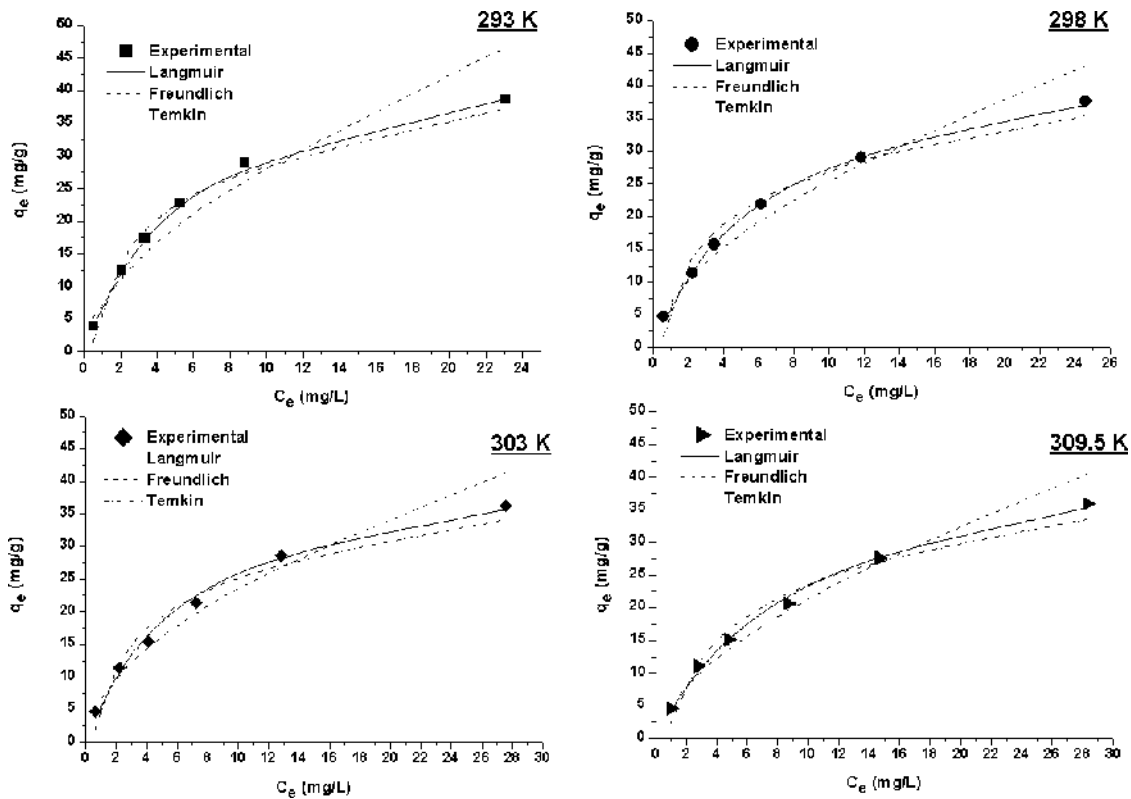


Figure 9. Comparison of various isotherm equations for the adsorption of MB onto WOT at different temperatures

III.8. Thermodynamic study

A calculation of fundamental thermodynamic parameters (ΔG° , ΔH° and ΔS°) is represented in Table 3. We notice that, the negative values of ΔG° for all temperatures indicate spontaneous nature of adsorption. ΔG° values were between -20 and 0 kJ/mol which indicate a physical adsorption process

[36]. The negative values of ΔH° and ΔS° indicate the exothermic nature of adsorption interaction and a decrease in randomness at WOT/MB solution interface, respectively [37].

III.9. Performances of the prepared WOT

It is instructive for a comparative purpose to report the values of the adsorption capacity of some adsorbents available in the literature. In Table 4,

it's given the different values of the Langmuir maximum adsorption capacity q_m of different lignocellulosic wastes cited in previous works. We can see that the Methylene Blue adsorption observed in this work is well positioned with respect to other researches. For our study, the maximum adsorption capacity q_m of MB at 293 K onto raw WOT (48.78 mg/g) is relatively interesting compared to other adsorbents. The differences of dye uptake are due to the properties of each adsorbent like the structure, the functional groups and the surface area.

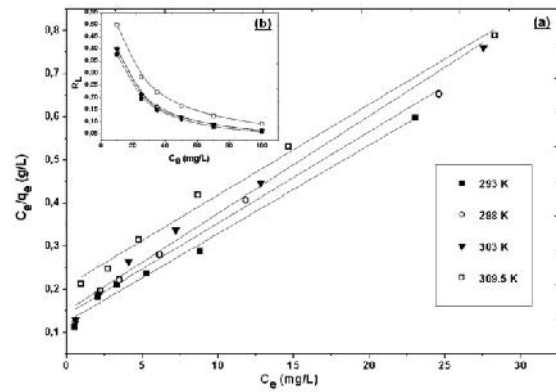


Figure 10. (a) Application of Langmuir model for MB adsorption onto WOT and (b) the corresponding R_L values

Table 2. Isotherm parameters obtained for adsorption of MB onto WOT

Isotherms	Parameters	Temperature values (K)			
		293	298	303	309.5
Langmuir	R^2	0.98	0.99	0.98	0.99
	K_L (L/mg)	0.165	0.147	0.150	0.101
	q_m (mg/g)	48.756	47.169	44.208	47.505
	RMSE	1.320	0.910	1.300	1.005
	χ^2	0.485	0.305	0.548	0.223
Freundlich	R^2	0.96	0.97	0.97	0.97
	K_F (L/g)	7.530	7.049	6.886	5.361
	$1/n$	0.581	0.565	0.540	0.604
	RMSE	4.703	3.056	2.791	2.556
	χ^2	2.384	1.152	0.963	0.950
Temkin	R^2	0.94	0.95	0.95	0.96
	B_T (mg/g)	9.464	9.029	8.405	9.253
	A_T (L/min)	2.207	2.055	2.110	1.326
	RMSE	3.066	2.507	2.398	2.169
	χ^2	8.255	5.881	3.972	2.917

Table 3. The thermodynamics parameters

Temperature (K)	$\ln K_d$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol.K)
293	2.67	- 6.53	- 40.72	- 0.116
298	2.34	- 5.79		
303	2.21	- 5.57		
309.5	1.80	- 4.63		

IV. Conclusion

This study has focused on the application of low cost adsorbent in water treatment. A natural wood waste, obtained from the trimming operation of orange trees, was used as adsorbent without any activation to retain methylene blue dye from aqueous solutions.

The adsorption process was studied as a function of selected parameters. It has been noticed that, the

MB removal increases with increasing pH solution, initial MB concentration and decreasing adsorbent dosage and salt concentration.

The results of the kinetic study show that, the adsorption process obeyed to the pseudo-second order model. The adsorption isotherm study shows that the adsorption isotherm of MB onto WOT follows the Langmuir model and the maximum adsorption capacity corresponding was 48.78 mg/g at 293 K.

Table 4. Comparison of Langmuir maximum equilibrium capacity for MB onto low- cost adsorbents and activated carbon

Adsorbent	Maximum adsorption capacity $q_m(\text{mg/g})$	References
Spend coffee grounds	18.7	[2]
Cotton stalk	13.71	[3]
Sawdust from saw mills	76.92	[17]
Sugarcane bagasse	30.7	[37]
Palm tree	29.5	[38]
Walnut sawdust	58.17	
Cheery tree sawdust	39.84	
Oak tree sawdust	29.94	[39]
Pitch-pine sawdust	27.78	
Modified wheat bran	25.18	[40]
Wheat shells	21.5	[41]
Banana peels	20.8	
Orange peels	18.6	[42]
Modified rice husk	29.15	[43]
Aleppo pine cones	93.57	[44]
Trimming Wood of Orange Tree WOT	48.78	This study

Determined thermodynamic parameters suggest that spontaneous and exothermic processes are involved. The results of the present investigation showed that WOT is a potentially useful adsorbent for the adsorption of dyes, an issue of environmental concern and the natural abundance of this food waste can provide an adsorption medium which could contribute to the treatment of wastewater. The comparison of the adsorption capacity of the prepared adsorbent with other adsorbents shows its attractive properties from industrial and economic interests.

This work in batch mode gave rise to satisfactory results, and our perspective will concentrate on the adsorption tests in column mode using industrial effluents treatment.

Acknowledgments The authors, thankfully, acknowledge the support obtained from the Research Laboratory of Alimentary Technology R.L.A.T, of BOUMERDES University, ALGERIA.

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Please cite this Article as:

Sifoun N., Abbas M., Yeddou A. R., Nouri L., Nadjemi B., Removal in batch mode experiment of Methylene Blue onto trimming Wood of Orange Tree – Equilibrium and Kinetics Studies, *Algerian J. Env. Sc. Technology*, 4:1 (2018) 654-663