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Three Level Design to Estimate Dyes Adsorption Parameters using Oenological By-Product as Adsorbent

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Abstract

In this study, Grape Marc (an oenological by-product) obtained from local winemaking was used as an adsorbent. Two ways are used to determine Methyl Blue (MB) and BEMACID Red (BR) dyes adsorption parameters' effects on adsorbent efficiency. In a kinetic way, the batch mode tests the effects of different parameters: solution pH, contact time, initial dyes concentration, and sorbent weight. The statistical way used response surface methodology with three-level designs. In the batch mode, the high dyes removal of 95% and 91.8% were observed at pH = 6 and pH =2 for BM and BR dyes respectively for initial dyes concentration of 50 mg/L. The pseudo-second-order kinetic model could better define the experimental data with a high determination coefficient $R^2 = 0.99$. Also from the kinetic study, the two empirical correlations reflect the weak effect of sorbent weight on the external mass coefficient for the BR dye $k_{f\ BR\ dye} = 2.2.10^{-6} M^{0.618}$. While the statistical results show positive effects of pH on adsorption capacities values for the BR dye removal and negative effect toward the second dye (MB). The two mathematics formulas generated by the BBD model are tested in a confidence level greater than 95% (p-value < 0.05) and the dependence percentage between the factors and the response is 99% and 98% for MB and BR dye respectively. In summary, the GM has a high affinity towards MB dye compared to BR dye and the statistical way gives more adsorption information compared to the classical way.

Keywords: Adsorption, Optimization, Three-level design, Grape Marc waste, Textile dye, Statistical study

1 Introduction

The frightening problem in developing countries is environmental pollution. Several industries (textile industry, leather, cosmetics, paints, food, ceramics, construction wax, paper, etc) which use dyes have recognized in recent years a rapid development that classifies them among the major sources of pollution of ecosystems [1- 3]. Water pollution is mainly due to the release of untreated colored water from the industries, surface runoff, and sewage leakage and overflows [4]. The effluent liquid discharged into water changes the nature of the water making them unfit for human use and agricultural purposes [5]. Also, this discharge affects the plants and animals present in the water bodies by inhibiting the penetration of sunlight into the water stream [6]. The complex aromatic molecular structure of the dyes present in wastewater makes them more stable and difficult to treat. Effluent treatment can be done by physical, chemical, and biological methods such as electrochemical treatment like electro-reduction, electrolysis, chemical precipitation, coagulation, and advanced oxidation process using hydrogen peroxide or ozone [3, 5]. The predominant drawback is that these techniques are complex in design, non-cost-effective, high electricity cost, sludge formation, and health hazards are a matter of concern, while the decolorization using adsorption is eco-friendlier and requires low-cost investment, and is easy to perform. Various natural adsorbents are cost-effective such as: Sawdust [7], Garlic peel [8], Rice husk [9], Pomelo (Citrus grandis) peel [10], Jack fruit peel [11], Date stone [12], Wood wastes [13], Cotton [14], Seeds [15], Coffee husk [16]. The rate and efficiency of dye biosorption are affected by diverse process parameters so it is necessary to optimize the parameters for the effective degradation of dyes. Which include initial pH solution, temperature, dye concentration, biomass concentration, static-agitation, and time [17]. Minimization of cost and realizing time with an increase in the efficiency of the biosorption would be favored by the optimization of these parameters [18]. For the first time, the only used optimization method was a mono-parametric study (one factor at time OFAT) [19]. The disadvantages of this method were consumption of products, of realizing the time, and of ineffective which concerns the interaction between factors. To overcome the drawbacks associated with the OFAT; poly parametric study or Design of Experiments based on the statistical design was used as an alternative method to optimize several factors at the time. This study (DOE) propounds a minimum number of experimental trials whatever the number of factors to be studied and increase the efficiency of any process. There are several methods for the optimization and modeling available with composite statistical designs like Central Composite Design (CCD, Box-Behnken design (BB), and Plackett-Burman design (PBD) [20]. The most common design used for the process parameters optimization by the scientific communities is PBD and Response surface

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methodology (RSM) (BBD and CCD). To predict the resultant responses under defined conditions based on the interactions between independent variables and dependent variables an effective statistically designed methodology RSM can be used. The objective of the present research work was to obtain the significant parameters affecting the dyes biosorption onto Grape Marc (GM) using statistical methodology RMS. A classical dye Methylene blue and industrial dye ETL were used in this study. Also, the aim was to optimize the responses to maximize the efficiency of the process using the design of three-level BBD with a low number of experimental runs. In the batch mode the effect of the initial pH solution, the contact time, initial dyes concentration, and sorbent weight are tested using kinetic study. The pHz, SEM, and IR analyses of the adsorbent were performed.

2 Materials and Methods

2.1 Adsorbent and adsorbates

Grape Marc waste (GM) was obtained as industrial waste from a local winery in Ain Temouchent west of Algeria. Samples (Pomace and Stems) were washed several times using distilled water to remove impurities and until the rinse water was clear (the black color was disappeared). The biomass was air-dried prior then dried in an oven at 80°C up to constant weight. The dried biomass was ground to a fine powder, sieved to obtain average sizes (500 µm). BEMACID Red (BR) one of the ETL dyes family, has certain market parameters: moderate cost and high fixing capacity, classified it in the list of the most used dyes in the textile industry in Algeria. Methylene blue (MB) cationic dye supplied by Sigma Aldrich was used as an adsorbate. This organic molecule belongs to the Xanthine family. With C.I. n°52015 and molecular weight 319, 85 g/mol. The dye chemical structure is as follows (Fig. 1)

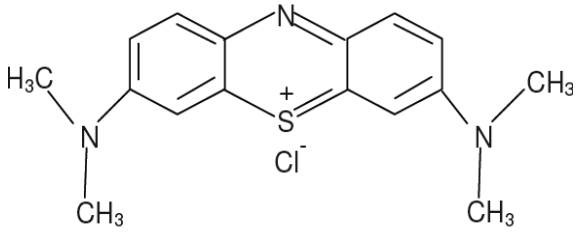

Fig. 1: Chemical structure of MB dye

A Stock solution of 1000 mg/L of each dye was prepared by dissolving accurately weighed samples of dyes in a liter of distilled water for each dye. The experimental solutions were prepared by diluting the stock solution of both dyes with distilled water to the desired concentration.

2.2 Experimental methods

Adsorption performances of two cationic dyes were studied in batch mode presented by the one factor at time (OFAT) method. Effects of different parameters were studied by controlling the value of initial pH solution from 2 to 11, contact time from 5 to 60 min, sorbent weight: 50 mg and 100 mg, and initial dyes concentration 50 mg/L and 30 mg/L. The mixtures were stirred at 300 rpm. The equilibrium concentrations of the solutions were determined using a UV-Vis spectrophotometer (HACH DR 2000) at 664 nm and 500nm for MB and BR dyes respectively. The percentage removal (R %) and the equilibrium quantity adsorbed q_e (mg/g) of the two dyes on GM were calculated using the following equations [21].

$$R\% = \frac{(C_0 - C_t).100}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e).V}{m} \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of dyes at time t respectively, m (g) is the mass of biomass, and V (L) is the volume of samples dyes solution. The desired pH value of each solution was adjusted by adding 0.1-0.01 M HCl and/or 0.1-0.01 M NaOH using pH- meter (SCHOTT CG711). The point of zero charges of GM was estimated according to the method described in our previous study [22]. The functional groups on the surface of the adsorbent were characterized by FTIR analysis. The structure and morphology of GM were characterized by Scanning Electron Microscopy (SEM).

2.3 Three-level Box-Behnken Design (BBD)

To cover the entire statistical adsorption surface, the response surface method (RSM) provides superb design tools and aims to optimize the process through experimental runs analysis. Due to its ability to estimate the parameters of the quadratic polynomial model and to detect the lack of fit of the model compared to other RSM designs, the BBD three-level design was used to evaluate the parameters' effect on the removal efficiency [20]. The BBD design is based on the following quadratic polynomial regression model:

$$Y = \alpha_0 + \sum \alpha_i X_i + \sum \alpha_{ii} X_i^2 + \sum \alpha_{ij} X_i X_j \quad (3)$$

where α_0 is the constant coefficient, α_i, α_{ii}, and α_{ij} are the regression coefficients and X_i and X_j indicate the independent variables, Y is a dependent variable. In this paper, the dependent variable represents the adsorption capacities for the two dyes (Y_{MB} and Y_{BR}). All the essays were repeated three times and data were analyzed by analysis of variance (ANOVA).

3 Results and discussions

2.4 Grape Marc Waste characterization

To identify the functional groups present in the surface of industrial waste adsorbent GM and which are responsible to remove cationic dyes, the FTIR presented in Fig. 2 was analyzed. GM is cellulosic biomass.

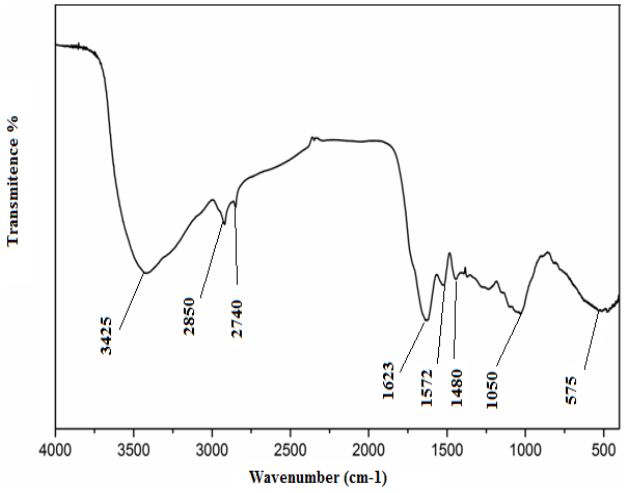

Fig. 2: FTIR spectra of Grape Marc in the range from 4000 to 500 cm^{-1}

The broad intense band at 3425 cm^{-1} (which typically occurs in the range of 3200 to 3600 cm^{-1}) corresponds to the O–H group of acids [22]. The vibration band C–H of cellulose is located at 2850 $cm^{-1}$and 2740 cm^{-1} [23]. The peak around 1623

cm^{-1} is characteristic of the stretching vibration of C=O of the carboxylic acids of hemicelluloses present in the biomass [24]. The C–H deformation and aromatic ring vibration were observed at the peak of 1480 cm^{-1} [23]. The peak at 1050 cm^{-1} corresponds to the C–OH stretching vibration [22], the band between 575 and 510 cm^{-1} represents C–N–C scissoring that is only found in protein structures [25]. As shown in Fig. 3, the morphologies of the GM were analyzed by scanning electron microscopy (SEM). From Fig. 3 it can be seen that there are holes that present pores and which indicate that the adsorbent has a porous surface.

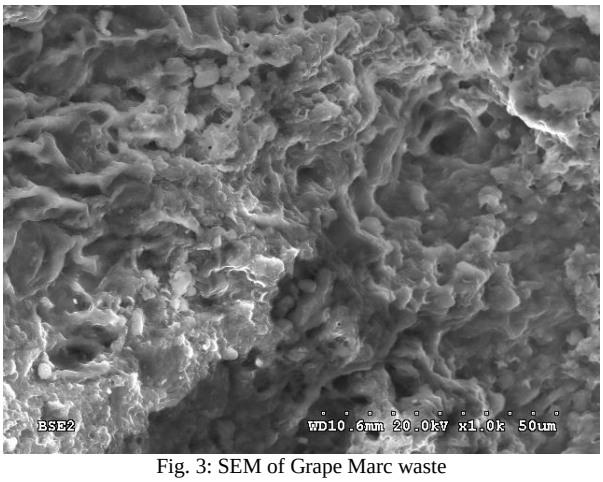

Fig. 3: SEM of Grape Marc waste

3.2 Adsorbent pH_{pzc}

To understand the adsorption process is important to find the pH_{pzc} of the adsorbent surface. The pH drift method was used [22]. The intersection of the pH initial curve (pHf_1) and final pHf plot gives the pH_{pzc} value (Fig. 4). This parameter was found to be equal to 7.4. For pH solution value less than the pH_{pzc} value ($pH < pH_{pzc}$) the adsorbent surface is positively charged, and at the reverse case ($pH > pH_{pzc}$) the surface of the adsorbent becomes negatively charged which eliminate acidic dyes. The same determination methods of pH_{pzc} were used for different biomass as the viscose-based activated carbon fiber felts were found to be equal to 5.09 [26].

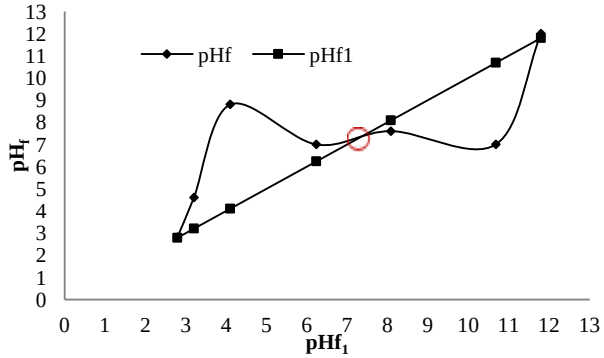

Fig. 4: pHpcz of Grape Marc

3.2 Results of kinetic study optimization

3.3.1 Effect of initial pH solution and dye concentration on MB removal

As shown in Fig. 5, the MB amount adsorbed increase from 74 to 96% when the pH solution increase from 2 to 6 and decreases again from 96 to 66 % when the pH increases from 6 to 11 for MB dye concentration of 30 mg/L. The same observation concerning the MB removal dye is found for the other dye concentration (50 mg/L). Also and through Fig. 6, BR dye removal has a different behavior than these of the MB dye, where the BR amount decreases from 91% to 10% when the solution pH increase from 2 to 11 for an initial dye concentration of 30 mg/L. The BR amount dye removal is very important for low initial dye concentration. The same observation was saved for MB dye removal for the two concentrations. Two high yield values of MB dye removal are observed at pH = 4 with 96% and 95.6% at pH = 6 and to keep the economic aspect of the process, the optimal value used in this study was pH = 6 for the dye MB and for BR dye the maximum yield of 91% was found for pH= 2, which represent the optimum value was used for the remaining steps of this paper. The optimum pH value is less than the pH_{pzc} (6<7.4 for MB dye and 2 <7.4 for BR dye) so the adsorbent surface is positively charged favoring the adsorption of anionic groups of the two dyes (the color of the adsorbent surface is changed). According to the results, the elimination of the MB dye is favorable in a weakly acidic medium; on the other hand for the BR dye, the strongly acidic medium is favorable. The same observations and conclusions are reported by other researchers when the apricot stone source waste as adsorbent was used to remove MB dye [27], around the same pH solution value (pH=5.8) was found when sugar can bagasse was used as a sorbent [28]. The results obtained indicate that the pH plays an important role in the behavior of the two dyes in the solutions. For tested the effect of these parameters on adsorption capacities for the two dyes, twenty-four experiments were realized and the found values of the removal yield dyes concern just the studied points and not all the points of the studied domain between 2 to 11.

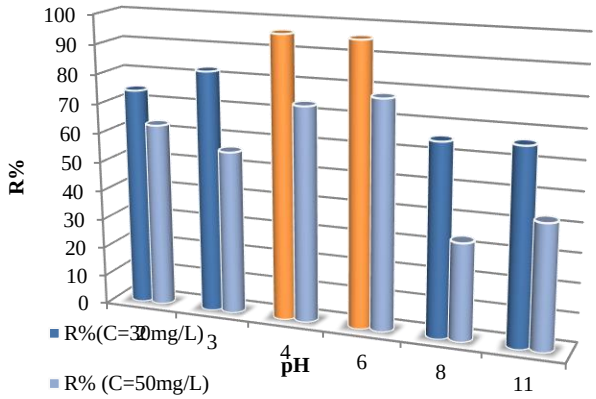

Fig. 5: Effect of initial pH on the removal of the MB at different dye concentrations

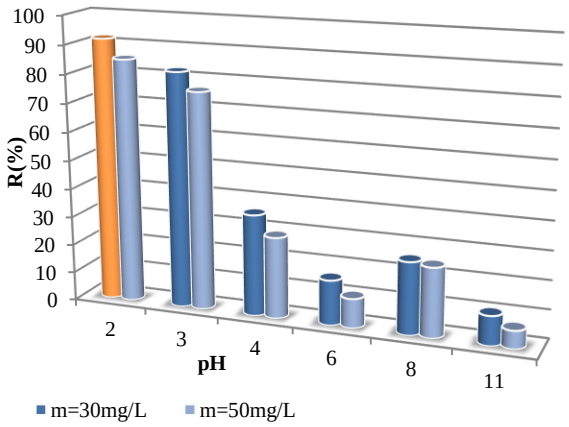

Fig. 6: Effect of initial pH on the removal of the BR at different dye concentration

3.3.2 Effect of contact time and sorbent weight on MB dye removal

As shown in Fig. 7, a very fast step during the first five minutes is observed in the biosorption process of BM dye. After this step, the biosorption slightly increased up to 10 min. Thereafter, the reached equilibrium biosorption was observed within 30 min; which means that all adsorption sites are saturated by the MB dye. The same curve indicates the effect of the sorbent weight; when the weight of the sorbent increases from 50 mg to 100 mg, the adsorption capacities decrease from 48 mg/g to 45 mg/g. This can be explained by the existence of the collision and aggregation between the adsorbents particles. The same results were also observed by the adsorption of MB dye onto Salvadora persica stems ash [29] and Ficus carica bast [30]. The optimum contact time and weight sorbent values are 30 min and 50 mg respectively for MB dye. From Fig. 8, the three steps observed during the MB dye adsorption (fast, medium, and slow) are also illustrated during the BR dye adsorption but with different slopes. The negative effect of adsorbent weight on the MB dye adsorption capacity is also observed on the BR dye adsorption capacity. In our previous study concerning the BR dye removal, the brewery waste gives an important adsorption capacity and affinity towards this dye compared to the obtained results in this paper.

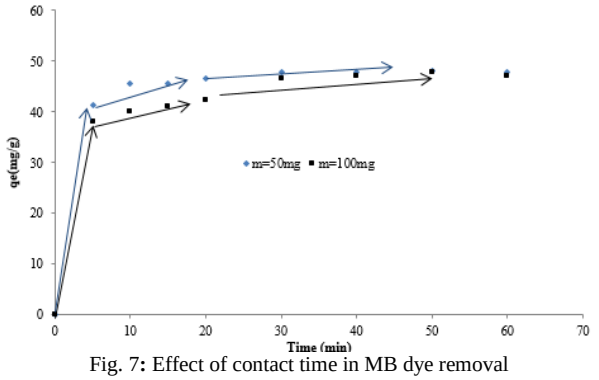

Fig. 7: Effect of contact time in MB dye removal

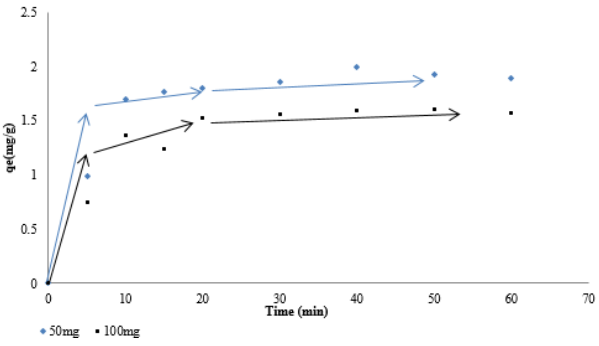

Fig. 8: Effect of contact time in BR dye removal

3.3.3 Kinetic results modelization

The adsorption mechanism of dye removal from an aqueous solution by any adsorbent can be described by kinetic models and by analyzing controlling rate removal dye [21]. The following equations (pseudo-first-order, Eq. (4); pseudo-second-order, Eq. (5) and intraparticle diffusion Eq. (6) [21] were selected to appropriate the experimental kinetic data.

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}\, q_e - k_1.t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

$$q_e = k_d.t^{1/2} + C \quad (6)$$

where q_e and q_t correspond to the amount adsorbed per unit mass of adsorbent (mg/g) at equilibrium and at time t, respectively, k_1, k_2, and k_d correspond to the rate constant for pseudo-first, pseudo-second-order kinetics, and intraparticle diffusion models. All models are illustrated in Figs. 9, 10, and 11. The determination and comparison of the correlation coefficients R^{22} and the values of the calculated adsorbed amounts indicate the conformity between experimental data and the kinetic model.

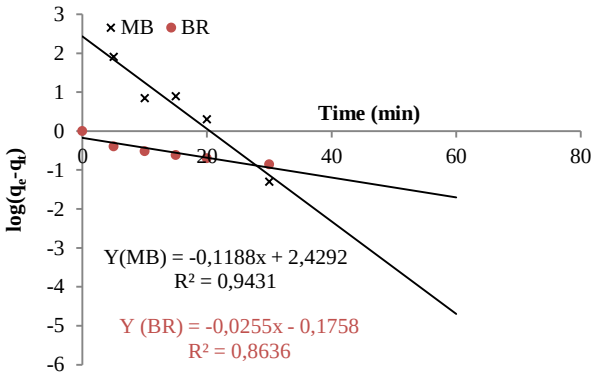

Fig. 9: Pseudo-first order plot for the adsorption of MB and BR on GM waste

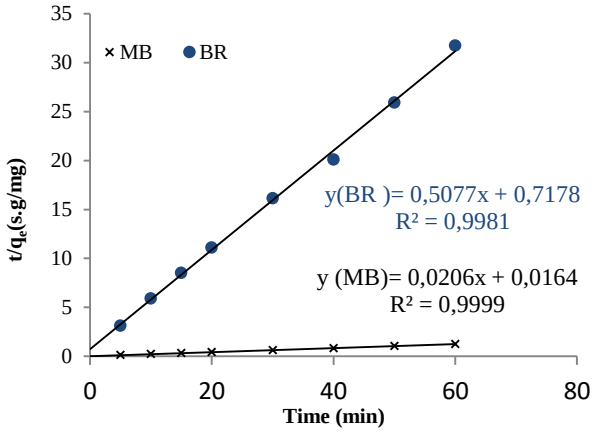

Fig. 10: Pseudo-second order plot for the adsorption of MB and BR on GM waste

From Table 1 and according to the high correlation coefficient values (R^2 up to 0.99) the adsorption of the two dyes is best described by the pseudo-second-order kinetic model compared to other kinetic models. Besides, the calculated value q_e 48.5 mg/g and 1.96 mg/g for MB and BR dyes respectively close with experimental q_{exp} value 48mg/g and 2.05 mg/L for MB and BR dyes respectively. These results indicate that the adsorption mechanism studied obeys the pseudo-second-order kinetic model, and gives the possibility to suggest that the adsorption mechanism can be controlled by the two modes of transfer (extern and interdiffusion). From Fig. 11, the linear fit between the q_t versus operating time ($t^{0.5}$) intersects with qe ax in 37.13 and 1.42 (C ≠ 0) for BM and BR respectively, this means that the two dyes removal kinetic be controlled by both transfer modes. This agrees with the first conclusion found from the pseudo-second-order application. The kinetic models were also validated for their appropriateness by normalized standard deviation Δq (%), which is given in Equation (7) [31].

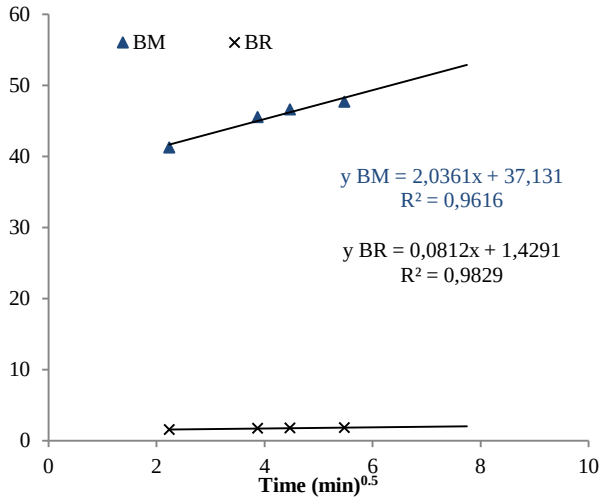

Fig. 11: intra-particle diffusion plot for the adsorption of MB on GM waste

$$\Delta q(\%) = 100\sum \frac{\left[(q_{ex}-q_{cal})/q_{ex}\right]^2}{N-1} \quad (7)$$

where N is the number of data points, q_{exp} and q_{cal} (mg/g), are the experimental and calculated adsorption capacity, respectively. The smaller value of Δq (%) designates a better fit of the model. It is evident from Table 1 that the value of Δq (%) for the second-order model was found to be less than for the first-order model from 0.001 % to 8.05 % and from 0.027 to 6.85 for MB and BR dyes respectively; this is in accordance with the R^2 values attained for both models and confirm that the adsorption of the dye could be properly described by the pseudo-second-order kinetic model.

The value k_2 =0.0029 for BR dye is greater than the k_2 =0.0029 for MB dye and the two values found in this study is greater than the k_2 value found when MB dye was adsorbed by Ficus carica bast (k_2 =0.00019) [30] and by Cellulose Acetate Nanofibrous Membranes [32]. However, the sorption rate for the MB dye was found greater than the sorption rate of BR dye. Table 2 gathers some results of the adsorption capacity of the different adsorbents with those found in this research. As can be seen, the removal ratio of MB dye is higher than the reported values for the other adsorbents. This result may be due to the effect of surface area, morphology, surface structure, and functional groups. Nonetheless, this comparison is not precise, since the experimental conditions are different. Mcky 1986 [35] propose a general form to determine external mass transfer coefficient depending on the variation of the concentration by:

$$-\left[\frac{dC_t/C_0}{dt}\right]_{t\to 0} = K_f S_s \quad (8)$$

where S_s is the specific surface of MG which can be calculated by eq (9) and C_0, C_t were dyes concentrations at time 0 and t.

$$S_s = \frac{6m_s}{d\rho_s(1-\varepsilon)} \quad (9)$$

where: ε particle voidage, ρ_s solid density (g/cm^3), d particle diameter (m), and m_s concentration of adsorbent g/cm^3. Another form to determine this coefficient is proposed by [35]:

$$K_f = A(\text{variable})^B \quad (10)$$

The determination of the coefficient could be obtained by simply drawing a tangent to the curve, C_t / C_0 vs t, (Fig. 12 and 13).

Table 1: Kinetic parameter of the different models

Dye concentration	MB dye 50 (mg/L)	BR dye 50 (mg/L)
qe exp (mg/g)	48	2.05
Pseudo First Order		
k_1 (min^{-1})	0.1225	0.0255
q_e (mg.g^{-1})	11.91	0.85
R^2	0.975	0.863
Δq %	8.07	6.85
Pseudo second Order		
k_2 (g/mg.min)	0.0029	0.3590
q_e (mg/g^{-1})	48.5	1.96
R^2	0.999	0.998
Δq%	0.001	0.027
Intra particle diffusion		
k_d (mg/g.min)	2.0361	0.0812
C	37.131	1.4291
R^2	0.96	0.982

Table 2: The MB dye removal capacity in the kinetic study for different adsorbent

Adsorbent	$\mathbf{q_{exp}}$ (mg/g)	References
Wheat shells	17.92 at T=303K	[33]
Natural Saudi Red Clay	16.61 at T=298 K	[34]
Coffee husk	3.4 at T=298 K	[16]
Grape Marc	MB dye: 48.5 at T=298 K	This study
Grape Marc	BR dye: 2.05 at T=298 K	This study

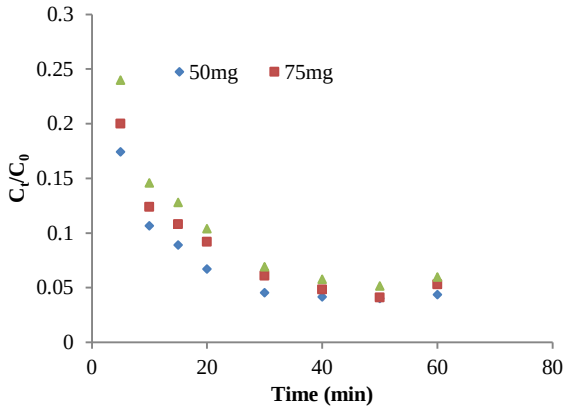

Fig. 12: Effect of adsorbent weight on external mass transfer coefficient for MB dye

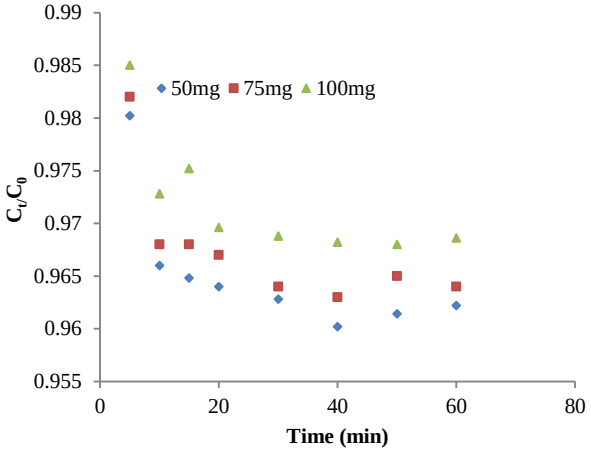

Fig. 13: Effect of adsorbent weight on external mass transfer coefficient for BR dye

From Fig. 12 and 13, the obtained results show that the slopes of the linear part of the curves for the lower adsorbent weight (50 mg and 75 mg) are almost the same compared to that obtained for the high adsorbent weight (100 mg). The plotting of the linear form of eq (10) generates a relationship that satisfied the experimental data for the two dyes:

$$k_{f\,MB\,dye} = 0.00037.M^{0.643} \quad (11)$$

$$k_{f\,BR\,dye} = 2.2.10^{-6}.M^{0.618} \quad (12)$$

From the coefficients values of the empirical correlation of k_f for the two dyes, it is found that the influence of adsorbent weight (M) on the mass transfer coefficient is positive and has a negligible effect for BR dye compared to MB dye. The obtained values of the empirical correlation coefficient are very weak compared to those obtained by Mamdouh (2008) [36].

3.2 Results of three-level BBD optimization

The three-level BBD methodology is a useful statistical tool to optimizing parameters of different processes [19-20], the four selected parameters affecting dye removal namely, initial pH solution, initial dye concentration, adsorbent weight, and contact time were selected as independent variables, and the dye adsorption capacity (Y) was considered as the dependent variable. Design expert 13 statistical software (evaluation version) was used to reach experiments design. In order to validate the predictive capability of the theoretical equation provided by the chosen design, three level-specific adsorption experiments were carried out, by varying the independent variables (time t, pH, initial dye concentration C and adsorbent weight m) within the range established in the experimental design (Table 3) and this by using different operational conditions performed in the 29 experiments established in the matrix of BBD design (Table 4).

Table 3: Levels of different independent variables used in the three-level BBD design

Variables	Levels		
	-1	0	+1
Time t (min)	10	30	50
pH	2	5	8
C (mg/l)	30	40	50
m (mg)	50	75	100

Table 4: Matrix of preparation conditions to the experimental design by BBD

Number of experiment	Time	pH	C	m
1	0	1	0	-1
2	0	0	0	0
3	0	-1	-1	0
4	1	0	1	0
5	-1	0	1	0
6	1	0	0	1
7	-1	0	0	1
8	1	-1	0	0
9	1	1	0	0
10	0	-1	0	1
11	0	0	-1	1
12	0	1	1	0
13	0	0	-1	-1
14	0	-1	1	0
15	0	1	-1	0
16	0	0	1	1
17	1	0	0	-1
18	-1	0	0	-1
19	0	0	1	-1
20	1	0	-1	0
21	-1	-1	0	0
22	0	0	0	0
23	-1	1	0	0
24	0	0	0	0
25	-1	0	-1	0
26	0	-1	0	-1
27	0	1	0	1
28	0	0	0	0
29	0	0	0	0

This software gives the possibility to test different models at the same time (linear, quadratic, and cubic) and according to the statistical values of Lack of fit, p-value, F-value and Mean square value the model is chosen. In our case, the quadratic model fits well the experiment data. R1 means the response for MB dye and R2 response for BR dye. From Tables 5 and 6, the difference between the Adjusted R^2 and Predicted R^2 is less than 0.2 which is a reasonable agreement between the two values and this is another argument to indicate the validity of the model. Also, the model can be used to navigate the design space when the noise ratio was greater than 4; in our case, the ratio (Adq Precision) of 53.06 indicates an adequate signal. The value of determination coefficient R^2 for the response R1is found to be 0.99 (Table 5) which signifies that the generated model is in agreement with the experimental results, and this means that the selected model could be explain 99% of the

variability and the rest of 1% from the total variability will be not explained by the generated model. The p-value is less than 0.05 indicate the significance of the model. The same observations are registered for R2.

Table 5: Fit statistics for R1 (BR dye removal)

Std. Dev.	0,8798	**R^2**	0,9905
Mean	37,24	**Adjusted R^2**	0,9811
C.V. %	2,36	**Predicted R^2**	0,9456
p-value	<0.0001	**Adeq Precision**	35,2067

Table 6: Fit statistics for R2 (BR dye removal)

Std. Dev.	0,8544	**R^2**	0,9860
Mean	37,24	**Adjusted R^2**	0,9822
C.V. %	2,29	**Predicted R^2**	0,9583
p-value	<0.0001	**Adeq Precision**	53,0674

In order to predict significant parameters, Tables 7 and 8 give the effects of each parameter on the response (R1 and R2). The Variance Inflation Factor (VIF) values are 1 which means the factors are orthogonal. The application of BBD design gives the following mathematical model which links the independent factors (B= pH, C=C and D=m) and the removal capacity qe (R1 or R2). The two models fitted on the second-order polynomial equation with the interaction between independent factors. From the listed estimate coefficient in Tables 7 and 8, the mathematical formulas are:

Table 7: Coefficients in Terms of Coded Factors for R1

Factor	Coefficient Estimate	Standard Error	VIF
Intercept	37,98	0,3935	
A-time	0,3682	0,2540	1,0000
B-pH	1,70	0,2540	1,0000
C-C	9,43	0,2540	1,0000
D-Mass	-0,0967	0,2540	1,0000
AB	-0,4734	0,4399	1,0000
AC	0,0864	0,4399	1,0000
AD	0,0010	0,4399	1,0000
BC	1,05	0,4399	1,0000
BD	0,8271	0,4399	1,0000
CD	0,0511	0,4399	1,0000
A^2	-0,3583	0,3454	1,08
B^2	-1,67	0,3454	1,08
C^2	-0,1791	0,3454	1,08
D^2	0,4173	0,3454	1,08

Table 8: Coefficients in Terms of Coded Factors for R2

Factor	Coefficient Estimate	Standard Error	VIF
Intercept	0,7265	0,0380	
B-pH	-0,7217	0,0452	1,0000
C-C	0,1317	0,0452	1,0000
D-Mass	-0,1079	0,0452	1,0000
BC	-0,2312	0,0783	1,0000
B^2	0,6857	0,0591	1,0000

$$R1 = 37.93 + 1.7B + 9.43C - 0.0967D + 1.05\,BC + 0.08271\,BD - 1.67\,B^2 \quad (13)$$

$$R2 = 0.7265 - 0.7217B + 0.1317C - 0.1079D - 0.2312BC + 0{,}6857B^2 \quad (14)$$

The two mathematical formulas eq (13) and (14) in terms of coded factors given by BBD design can be used to make predictions about the response (R1and R2) for given levels of each factor. From the eq (13), it can be seen there are two independent factors with a positive effect on MB dye removal capacity (B= pH and C = C) and one negative effect for the weight sorbent (D=m). The most important effect is recorded for the initial dye concentration (+9.43). That means, the removal dye capacity increases rapidly when the initial dye concentration increases. And from the eq (14), there are two independent factors with negative effect (B=pH and D=m) and one factor with positive effect (C=C) on the response R2. The absence of factor time in both formulations of the two dyes' responses means that time had an insignificant effect on the response because the adsorption process of the two dyes is fast. However, interactions AB, BD, CD, and AD did not exhibit any significant effect in any dyes response. Fig. 14 shows a contour plot of the relationship between contact time and initial dye concentration C for MB dye (response R1). The color degradation indicates the variation in adsorption capacity as a function of time and C. When the C (initial dye concentration) increases from 40 to 50mg/L (from 0 to 1) the adsorption capacity is greater than 37 mg/g for a time greater than 10 min. The same conclusions for the same design (BBD design) when an Azo-dye batch adsorption by activated carbon-commercial grade (ACC) was studied [37] are registered. Fig. 15 represents the contour plot of the second dye (BR) of the relationship between the pH (B) solution and initial dye concentration (C), the obtained results clearly show that the favorite medium for dye removal is an acidic medium. Also from the contour plot, the results show that the maximum removal dye capacity was observed when a C decreased to 50mg/L and pH solution is 2.

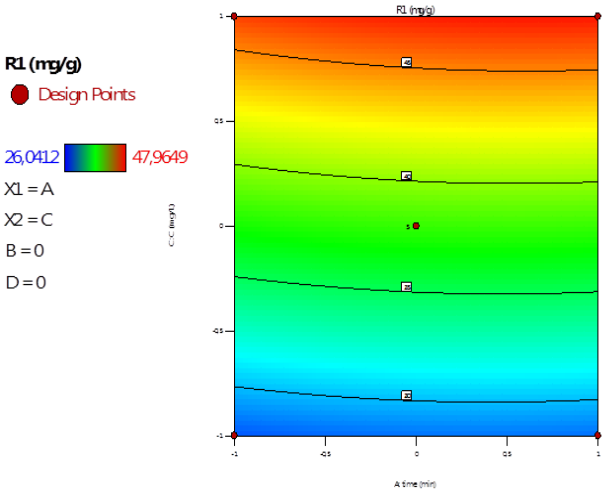

Fig. 14: Contour plot of MB dye removal by BBD

The chosen design gives the possibility to determine the effect of three parameters on the response and draw the formula generated by BBD in 3D (Fig. 16 and 17). It is clear to conclude that the response values R1 and R2 for the two dyes are independent of the chosen time interval (fast adsorption), and the response R1 increased rapidly by the increase in initial concentration for MB (Fig. 16), where R2 decreased by the increase in Solution pH for BR (Fig. 17). The adsorption capacity of MB dye increases from 26.04 mg/g to 47.69mg/g when initial dye concentration increases from -1 to +1 (or from 30 mg/L to 50 mg/L) for any value of time between -1 and +1 (or from 10min to 50min). Also from Fig. 17, the adsorption capacity of BR dye decreases from 2.503mg/g to 0.584 mg/g

when pH solution increases from -1 to +1 (or from 2 to 8) for any value of time between -1 and +1.

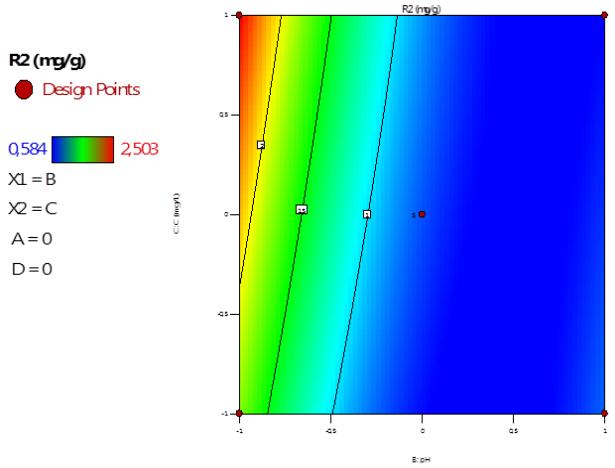

Fig. 15: Contour plot of BR dye removal by BBD

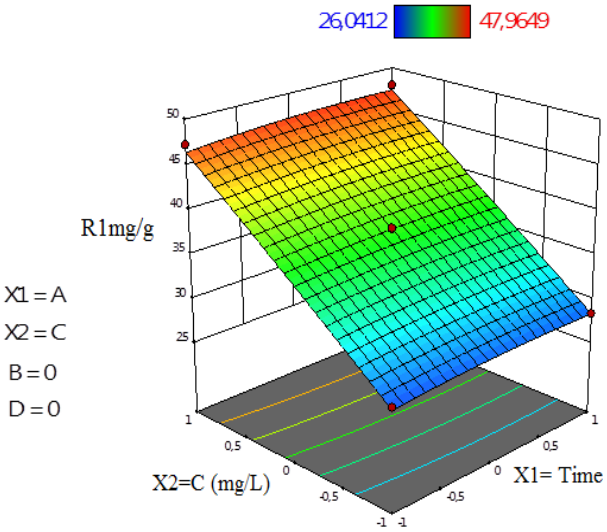

Fig. 16: 3D presentation of response surface model of MB dye adsorption capacity (R1)

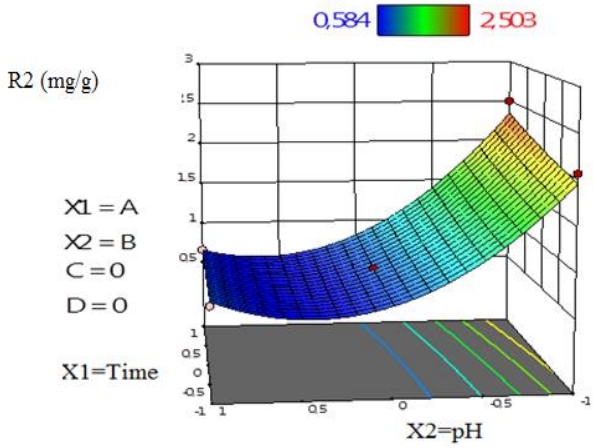

Fig. 17: 3D presentation of response surface model of BR dye adsorption capacity (R2)

4 Conclusion

This study investigated the MB and BR dyes adsorption by Grape Marc (GM) waste adsorbent. A kinetic study revealed that the mechanism follows the pseudo-second-order for the two dyes and that the two transfer modes participate in the adsorption mechanism. To expand the number of studied parameters and minimize the realized experiments, the experiment design is recommended. Application of this methodology allowed statistical determination of adsorption parameters over the entire adsorption surface with minimum experiment. The BBD design chosen in this study provided us with two empirical relationships between four operating parameters with a determination coefficient close to 1 (R^2 = 0.99 and R^2 = 0.98 for MB and BR dye respectively). This means that the empiric relation for MB dye covers 99% of the link between the four independent parameters (time, pH, C, and m) and the dependent one (the response R1 or adsorption capacity) and 98% between the parameters and the response R2 for BR dye. The main conclusions that can be drawn from this statistic part are the negative effect of weight adsorbent on the amount of adsorption for the two dyes MB and BR by Grape Marc (GM). The p-value of this model was less than 0.05, indicating that the model is very significant. Thus these results obtained in this study show that the Spent Grape Marc biosorbent is effective for the elimination of textile dyes.

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Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically about authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

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