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Box-Behnken experimental design for the optimization of methylene blue adsorption onto Aleppo pine cones

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Abstract

Box-Behnken experimental design has been used to study the influence of operational parameters on the adsorption of methylene blue (MB) by a natural and low cost adsorbent, Aleppo pine cone (APC). Our main goal is to optimize the process at a lower cost with maximum efficiency, achieving this through sound testing, identification of influential factors to the process, the evaluation of interactions between these factors, and modeling mathematical result. In the experimental field study the amount of MB adsorbed by APC depending on the pH, the initial concentration of MB, and adsorbent dosage. Therefore, from the obtained results the large variation indicates that a factor at least has an influence on the adsorption efficiency. The coefficients of pH, concentration of the MB, are positive; these parameters (pH and concentration of the MB), thus positively affect the adsorption of MB. For those against the adsorbent dosage are negative, it means that their influence is negative on the adsorption process. Analysis of variance (ANOVA) showed a high coefficient of determination value (R^2=0.96) and satisfactory prediction of the regression model was derived. The highest CR, estimated by multivariate experimental design, was found at the optimal experimental conditions of initial dye concentration of 100 mg/L, adsorbent dosage 0.5 g/L and pH=10. Finally, the results could show that the adsorbent (APC) used is very effective in removing textile dyes.

1. Introduction

The rapid growth in the use of synthetic dyes in the textile industry has led to a significant increase in environmental pollution. Many of these dyes are toxic and therefore, should be removed from wastewater before being discharged into water resources in order to protect the living organisms [1]. Therefore, the purification of colored wastewater has received much attention in recent years [2, 3]. In addition, it should be noted that the presence of organic dyes in water bodies can act against light penetration, thereby hindering photosynthesis [4-6]. Various treatment technologies are employed for the removal of organic dyes from aqueous environments. These are such as coagulation/flocculation [7,8], membrane [9], chemical oxidation [10-13] and biological processes [14-16]. However, these methods have some problems such as plenty waste sludge and high capital cost [17]. Based on the related literature on wastewater treatment, adsorption process can be a promising and efficient method to diminish colored wastewater due to its low cost, insensitivity to toxic substances, simplicity, ease of operation and no sludge formation [18-23]. Various materials such as Activated carbon (AC), natural materials, polysaccharide materials, starch, bioadsorbents and agricultural wastes have been used for the removal of dyes from solution [20–25]. In an earlier study, we used a natural adsorbent, abundant and existing in large quantities in the region of Khouribga – Morocco, Aleppo pine cone to remove textile dyes in general and in particular methylene blue. [26] The results of this study were satisfactory and indicate the great potential of Aleppo pine cone for removal of methylene blue in aqueous solution, a low processing cost and ecological adsorbent.

To further probe the effect of various operational parameters, including the initial dye concentration, the adsorbent dosage, and the pH of the solution, on the adsorption of MB via the adsorption technique, response surface methodology (RSM) based on experimental design method (EDM) was employed. RSM was selected as an effective statistical and mathematical approach in order to recognize the efficiency of an experimental system [27, 28]. Various parameters were simultaneously appraised using RSM with a minimum number of experiments. Therefore, a study conducted by RSM can reduce the cost, decrease process variability and need less time in comparison to the conventional one-factor-at-a-time statistical strategy [29-32].

The objective of this work is to assess at first, from a statistical analysis of experimental results obtained in our previous study [26], the effects of three independent variables (pH, concentration, adsorbent dosage) on the adsorption MB dye on a biosorbent type Aleppo pine cone. The second step is then to optimize the factors influencing the adsorption using the response surface methodology (RSM). The effects of interactions between independent variables will also be discussed. The treatment of the experimental results will also develop a mathematical model.

1. Material and methods

2.1. Preparation and characterization of the adsorbents

2.1.1. Materials

All chemicals were reagent grade and were used without further treatment. Methylene blue (MB) was purchased from Sigma–Aldrich (Germany). NaOH was purchased from Merck (Germany), and HNO_3 from Scharlau (Spain). All solutions were prepared using deionizer water.

2.1.2. Preparation of adsorbent (APC)

The collected *Aleppo Pine Cones (APC),* collected from the region of Khouribga in Morocco, was repeatedly washed with distilled water to remove dirt particles and then was air-dried. The dried plants (stems) was then cut into small pieces, powdered to particles of small sizes using a domestic mixer (APC) and then sieved in particles sizes lower than 125µm.

2.2. Adsorption experiments

The adsorption tests were carried out in a discontinuous reactor at room temperature in 100 ml flask containing the adsorbent material and the dye solution. The effect of the adsorbent dosage (R=m/V), where m is the adsorbent mass and V is the volume of solution dye), the initial pH and the initial concentration of the dye on adsorption (C_0) were studied separately.

The mixture was constantly stirred for a period of time fixed by kinetic tests and then. The equilibrium concentration (C_e) was determined by a UV–visible spectrophotometer (TOMOS V-1100 UV/Vis Spectrophotometer). The amount of dye adsorbed per unit mass of adsorbent, or adsorption capacity, was calculated as:

$$q_{t,e} = \frac{(C_0 - C_{t,e})V}{m} \qquad \text{(Eq.1)}$$

Where $q_{t,e}$ was the amount of dye adsorbed per gram of adsorbents (mg/g) at time and at equilibrium, C_0 and $C_{t,e}$ is the initial and equilibrium concentrations (g/L) of MB in solution, V is the volume of the solution (L), and m was the weight of the adsorbent (g). To determine the effect of experimental parameters onto adsorption process, this method was also applied at different concentrations, pHs and temperatures of MB solutions.

2.3 Design of experiments

Factorial experimental design was used to optimize the preparation conditions and methylene bleu removal efficiency. RSM designs allow us to estimate interaction and even quadratic effects, and hence give us the idea of the (local) shape of the response surface under investigation. Box-Behnken design is having the maximum efficiency for an RSM problem involving three factors (pH(X_1), initial concentration (X_2) and adsorbent dosage (X_3)) and three levels (high, middle and low). Thus, the number of runs required is less compared to a central composite design. The other parameters (temperature, agitation, nature, and adsorbent volume of solution) are attached to each experiment. As regards the measured responses, we retained the amount adsorbed by removal of the dye (expressed in mg / g) after 120 min. Process parameters for the study had three levels as given in Table 1. The levels were fixed based on the preliminary experiment-trials, discussion with cutting tool manufacturers and also the available literatures.

Table 1: Process factors and their levels.

Factors	Levels of Box-Behnken		
	Low (−1)	Middle (0)	High (+1)
pH (X_1)	4	7	10
Concentration (mg/L) (X_2)	50	100	150
Adsorbent dosage (g/L) (X_3)	0.5	1	1.5

In the optimization process, the response can be related to chosen variables by linear or quadratic models. A quadratic model is given in Eq. (2) [34, 35];

$$\mathbf{Y=Qe(MB) = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X^2_1 + b_{22}X^2_2 + b_{33}X^2_3} \quad \textbf{(Eq.2)}$$

Where *Y* is the response, b_0 is the constant, $b_i$is the linear coefficient, b_{ii} represents the quadratic coefficient, b_{ij} is the interaction coefficient, X_i is the coded variable level and *i or j* is the number of independent variables.

3. Results and discussion

3.1. Experimental results

The proposed Box-Behnken design requires 17 runs for modeling a response surface. Design expert software was used to design the experiment and randomize the runs. Randomization ensures that the conditions in one run neither depend on the conditions of the previous runs nor predict the conditions in the subsequent runs. Randomization is essential for drawing conclusions from the experiment, in correct, unambiguous and defensible manner. Details of the experimental runs with the set of input parameters that were conducted are given in Table 2. Most importantly, parameters corresponding to the central point (0,0,0) are repeated five times to establish that the experimental data is within the normal dispersion,and repeatability is ensured.

For the removal of MB, it could be seen that, the maximum sorption capacities were 113.07 mg/g. This greater capacity was obtained in the conditions of the following operations: pH=10, initial concentration of MB=100mg/l, and the adsorbent dosage =0,5g/L. In fact, the regression analysis was performed to fit the response functions with the experimental data. The values of regression coefficient obtained are presented in Table 2.

This model shows that the adsorbent dosage has a negative effect on the amount adsorbed disposal one hand, when the concentration of the MB believes the amount adsorbed Qe(MB) increases, on the other hand, we also note that the amount adsorbed increases as increasing pH. The positive effect on the elimination of dye (MB) in terms of the interaction effects between methylene blue concentration and the adsorbent dosage can be explained by the adsorbent dosage have much less effect than the concentration of methylene blue is under high concentration conditions. The effect of negative interaction of order 1 between the pH and the adsorbent dosagecan be explained by the pH with much more positive effect as a return, such that increasing the pH did not increase linearly adsorption. Likewise, double interaction effect of concentration, pH and dual interaction of the dual interaction of the adsorbent dosage a negative effect on the amount adsorbed such as a decrease in any of these parameters causes a decrease in the amount adsorbed except decrease in the adsorbent dosage leads to an increase in the amount adsorbed.

Among these parameters, the concentration is the most influence on the amount adsorbed. But to obtain good removal of the dye must increase its pH. The model also shows that the first order of interaction between pH and the adsorbent dosage and the dual interaction of concentration are the most important (Table 3).

Note that in this model certain factors such as the coefficient associated with the dual interaction of pH and adsorbent dosage have very low values. Therefore, we can assume that these terms are not influential. A statistical analysis of model elements will answer this question. Therefore, interaction effects as significant model terms can be used for modeling the experimental system. In terms of coded factors, the models can be described by the following equation (Eq 3):

$$Q = 78.72 + 11.33X_1 + 17.15X_2 – 13.78X_3 + 7.05X_1X_2 -10.26X_1X_3 + 9.96X_2X_3 -8.86X_2^2 \quad \text{(Eq.3)}$$

Table 2*:* Factorial experimental design matrix coded, real values and experimental results of the response (Qe).

Run	Coded values			Experimental value			response Qe(mg/g)
	X1	X2	X3	X1	X2	X3	
1	-1	0	1	4	100	1.5	54.95
2	0	0	0	7	100	1	80.24
3	1	0	1	10	100	1.5	64.3
4	-1	1	0	4	150	1	72.47
5	0	1	1	7	150	1.5	78.29
6	1	0	-1	10	100	0.5	113.07
7	0	-1	1	7	50	1.5	31.15
8	0	0	0	7	100	1	81.33
9	0	0	0	7	100	1	77.11
10	0	0	0	7	100	1	75.75
11	1	-1	0	10	50	1	46.59
12	-1	-1	0	4	50	1	45.23
13	0	0	0	7	100	1	79.15
14	1	1	0	10	150	1	102.04
15	-1	0	-1	4	100	0,5	62.67
16	0	-1	-1	7	50	0,5	77.93
17	0	1	-1	7	150	0,5	85.28

Table 3: Values of model coefficients of the responses.

Main coefficients	Value
b_0	78.72
b_1	11,33
b_2	17.15
b_3	-13.78
b_{12}	7.05
b_{13}	-10.26
b_{23}	9.96
b_{11}	-3.27
b_{22}	-8.86
b_{33}	-1.69

3.2. Analyse of variance

The analysis of variance (ANOVA) was used to determine the significance of the curvature in the responses at a confidence level of 95%. After discarding the insignificant terms, the ANOVA data for the coded quadratic model for the response are reported in Table 4. The effect of a factor is defined as the change in response produced by a change in the level of the factor. This is frequently called the main effect because it refers to the primary factors of interest in the experiment. The ANOVA results showed that the equations adequately represented the actual relationship between each response and the significant variables. The *F*-value implies that the models are significant and values of "Prob >*F*" less than 0.05 indicate that models terms are significant. Especially larger *F*-value with the associated *P* value (smaller than 0.05, confidence intervals) means that the experimental systems can be modelled effectively with less error [36-38].

The results of the analysis of variance are summarized in (Table 5). Table 5 shows that the interaction effects between the pH of the solution and the concentration of methylene blue, between the solution pH and the adsorbent dosage, between the methylene blue concentration and the adsorbent dosage and the dual interaction of the concentration methylene blue were statistically significant in the dye removal (methylene blue) solution, with pValues of 0.0417, 0.0085, 0.0099 and 0.0149, respectively. As against the dual interaction effects of pH and dual interaction of the adsorbent dosage were not statistically significant on the elimination of methylene blue adsorption on biosorbent with pValues of 0.5590 and 0.2745, respectively.

Table 4: Analysis of variance of removal of MB

Source	Sum of squares	Df	Mean square	F value	p-value Prob > F
Model	6329.148	9	703.239	21.891	0.0003
X_1-pH	1027.858	1	1027.858	31.996	0.0008
X_2-Concentration	2352.294	1	2352.294	73.223	< 0.0001
X_3-adsorbent dosage	1519.658	1	1519.658	47.305	0.0002
X_1X_2	198.951	1	198.951	6.193	0.0417
X_1X_3	421.276	1	421.276	13.117	0.0085
X_2X_3	395.811	1	395.811	12.321	0.0099
X_1^2	45.140	1	45.140	1.405	0.2745
X_2^2	330.469	1	330.469	10.288	0.0149
X_3^2	12.086	1	12.086	0,376	0.5590
Residual	224.874	7	32,125		
Lack of Fit	204.154	3	68.051	13.137	0.0154
Pure Error	20.720	4	5.180		
Cor Total	6554.022	16			

3.3. Diagnostic model

A summary of information for the proposed model as diagnostic case statistic actual and predict values for testing the significance of the regression coefficients is presented in Fig.1. The values obtained by the models (*Y* predicted) are compared with those of experimental data (*Y* experimental).

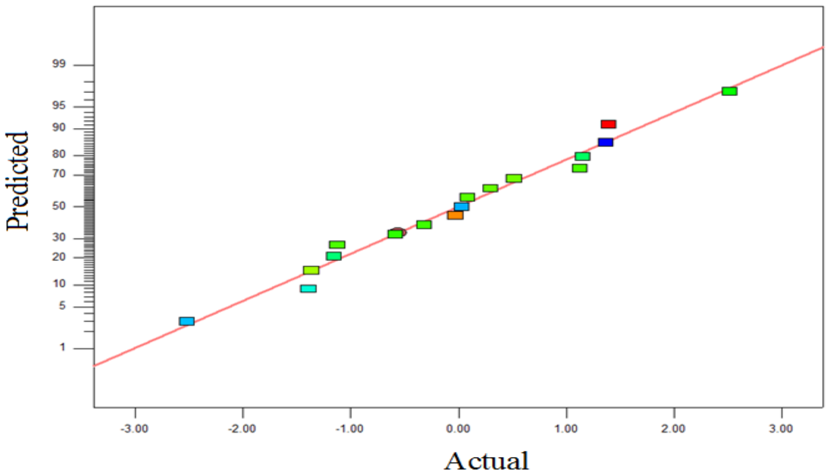

Figure 1: Experimental and predicted response for MB removal

These values for the model are close indicating a correspondence between the mathematical model and the experimental data. The correlations between the theoretical and experimental responses, calculated by the model, are satisfactory. Therefore, the "R^2" are in reasonable agreement with the "R^2 Adj". It can be seen that, more than 95% of the response can be well predicted by the models, indicating that the terms which were considered in the proposed models are significant enough to make acceptable predictions. However, adding more terms improve the model predictions.

3.4. Diagnostic model

The analysis of residuals, difference between the predicted and experimental responses, is another important diagnostic tool for judging adequacy of the fitted model for predicting the response. Figure 2 shows the residual values for each experiment. It shows that the residue does not exceed the amount adsorbed, which is of the order of magnitude of the variety of experimental results due to handling. This residue is evenly distributed in space. The model was accepted. Moreover, this illustrates that this model describes the phenomenon under study.

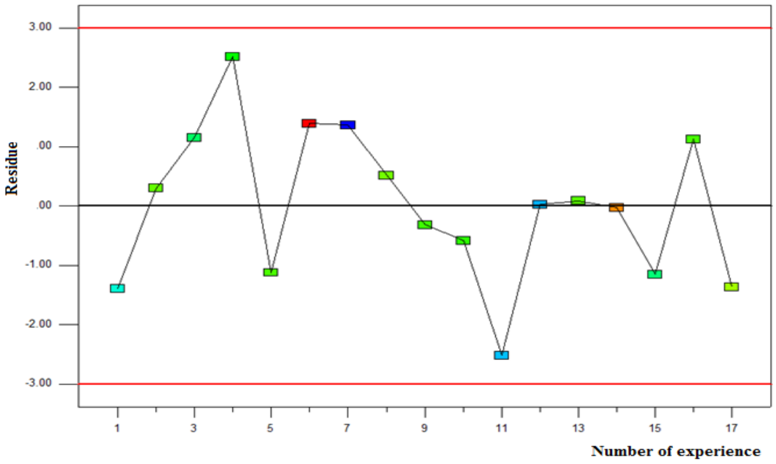

Figure 2: Analysis of residual for the response

3.5. Response surface analysis

The graphical representation of the response surface of the adsorbed amount of MB relative to the three factors studied (pH, initial concentration of MB and adsorbent dosage) was used to achieve a better understanding of interactions between variables and determine the optimum level of each variable to a maximum amount of adsorption. Thus the graphic operation mathematical model for describing the evolution of responses by plotting curves of response surfaces (3D) the following:

3.5.1. Interaction between the concentration of methylene blue and the pH

The interaction between is 150mg / L, the concentration has an influence since the amount Adsorbed pass from 48 to 113.07 mg/g when the pass time ofthe concentration of methylene blue and the pH is shown in Figure 3.

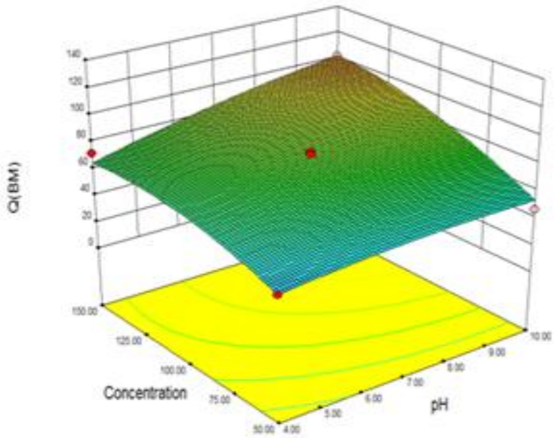

Figure 3: Representation surface for the adsorbed amount depending on concentrations (MB) and the pH

Thus, when the concentration of (MB) of 120 min. therefore the decrease in the concentration of (MB) causes an increase of the amount adsorbed and the pH reduction causes an increase of the amount adsorbed, in addition this increase is more significant on the adsorption amount when the concentration of (MB) is minimal with the adsorbent dosage is equal to 0.5mg/L. We can also see that the adsorbent dosage had positive synergistic effects when coupled with the pH and the concentration of methylene blue. Proof of this is in positive terms in equation (previous mathematical model). However, it can also be seen in the equation, the singular effect of the solution pH on amount adsorbed was positive. This means an increase in the singular variable pH has a significant effect on the overall amount adsorbed. In combination as a pair, however, the pH of the variables of the solution and concentration were statistically significant in terms of Pvalue.

3.5.1. Interaction between the pH and the adsorbent dosage

The interaction between the adsorbent dosage and the pH is illustrated in Figure 4. This one shows that if we keep the maximum level of pH and the minimum level of the adsorbent dosage, the adsorbed amount reached 118 mg/g of a hand. And on the other hand, when the minimum guard pH level and the maximum level of the adsorbent dosage, the adsorbed amount is minimal 62 mg/g with the MB the concentration is 150mg/L. We can also see that the concentration of methylene blue had positive synergistic effects when coupled with pH and adsorbent dosage.

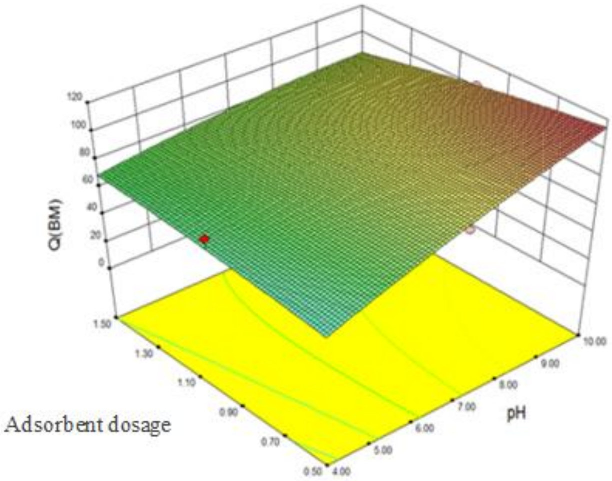

Figure 4: Representation surface of the adsorbed amount depending on the pH and the adsorbent dosage

3.5.3. Interaction between the adsorbent dosage and the concentration of methylene blue

The interaction between the adsorbent dosage and the concentration is shown in Figure 5. This one shows that if we keep the maximum level of concentration of methylene blue and the minimum level of the adsorbent dosage, the adsorbed amount reached 118 mg/g with pH is 10. We can see that the pH had negative effects when coupled with the concentration and the adsorbent dosage. And in response is not convex that involve optimal variables are not well defined or interaction between factors is not good.

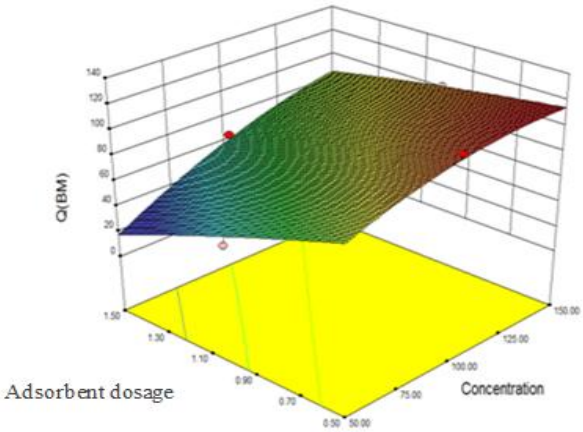

Figure 5: Representation surface of the adsorbed amount depending on the concentration of MB and the adsorbent dosage.

Conclusion

In this study, methodology of experimental design was used to optimize the MB removal ability by APC and to determine the influence of the parameters (pH, dye concentration and adsorbent dosage) on the adsorption of methylene blue by the Aleppo pine cone. The main conclusions that can be drawn from this work are given below, the effect of the adsorbent dosage showed a negative impact on the amount of adsorption of methylene blue (MB) by Aleppo pine cone (APC). However, all the effects are significant on the process of MB phase by adsorption on biosorbent. The model designed for the optimal design has been well fitted the experimental data well, with a coefficient of determination, R^2, of 0.965 and an Adj-R2 of 0.92. The p-value of this model was less than 0.05, which indicates that the model is very significant. Experimental design and response surface methodology were applicated to determine the optimal conditions of MB removal ((X_1 = 10) for the solution pH, (X_2 = 100mg/L) for the concentration of methylene blue, and (X_3 = 0.5 g/L) for the adsorbent dosage). So these results obtained in this study show that the Aleppo pine cone type biosorbent is effective for the removal of textile dyes.

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