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Theoretical investigation of the mechanism, chemo- and stereospecifity in Box–Behnken design for the optimization of methylene blue and methyl orange removal from aqueous solution by activated carbon

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Abstract

In this work, experimental design approach was adopted for the optimization of the removal of anionic and cationic model dyes (methylene blue and methyl orange) by activated carbon. A Box–Behnken surface statistical design with three factors and three-level combined with response surface modelling was employed to maximize dyes removal from aqueous solution. Three factors were used; solution pH, dyes concentration and activated carbon ratio to aqueous volume. Experimental results showed that solution pH has a positive effect on the adsorption of MB and a negative effect on the adsorption of MO. MO adsorption was more influenced by dye concentration in solution compared to MB adsorption. On the other side, MB adsorption was more influenced by the mass ratio of activated carbon compared to MO adsorption. The mass ration of activated carbon influence more MB adsorption at low dye concentration. In addition, at low solution pH, MO adsorption depends strongly on its concentration in solution.

Keywords: *Activated carbon; Methylene blue; Methyl orange; Adsorption; Box–Behnken design..*

1. Introduction

With the growth of humanity, science and technology, the demand for water has increased tremendously in agricultural, industrial and domestic sectors, and this resulted in the generation of large amounts of wastewater containing many pollutants. Among the pollutants currently released into the waterways are thousands of tons of organic dyes discharged from textile mills [1]. Wastewaters generated by the textile industries are known to contain considerable amounts of non fixed dyes during application and manufacture. It is esteemed that a total of 10-15 % of the world production of dyes is lost during the dyeing process and is released in textile effluents [2]. This massive influx of untreated organic chemicals into the waterways not only introduces aesthetic concerns, but far more importantly it promotes eutrophication and adversely affects the environmental health [3]. It also represents an increasing environmental danger due to their refractory carcinogenic nature [4]. A wide variety of techniques have been used for dyes removal from wastewaters including coagulation [5], biological degradation [6], photodegradation [7], membrane filtration [8], reverse osmosis [9], adsorption [10], or the synergic treatment of different methods. Among these processes, adsorption is one of the most favorable methods for the removal of dyes due to its effectiveness and its simplicity in using. The principle of adsorption treatment is to trap dyes with a solid adsorbent material. In the literature, several solid materials were used in wastewater treatment processes [11-16]. Because of their extensive porous structure, their high surface area and high adsorption capacity, the activated carbons are the mostly used for treating wastewaters containing soluble molecules [17-19]. The removal of dyes by activated carbon is influenced by many factors including the dyes concentration, mass of activated carbon, solution pH and temperature, among other factors. The optimization of experimental conditions for high removal efficiency cannot successfully done by using factor-by-factor optimization only. For this reason, the application of experimental design methodologies can result in improved removal efficiency with the lesser number of experiments [20]. In addition, Response surface methodology (RSM) is a powerful and widely used mathematical method suitable for modelling and optimizing chemical reactions and or industrial processes [7]. The objective of the optimization is to determine the optimum value of variables from the model obtained via experimental design and analysis. The objective of this research is to investigate the feasibility of activated carbon and their ability for cationic and anionic dyes removal from aqueous solution. Box–Behnken design combined with response surface methodology (RSM) was used to optimize the adsorptive removal of anionic and cationic dyes from aqueous solution by activated carbon. The factors used are solution pH, dye concentration and mass ratio of activated carbon. These factors were chosen based on preliminary investigations in order to minimize non-significant contribution of other factors.

2. Materials and methods

2.1 Materials

The chemicals used in this study were of analytical grade. Commercial activated carbon, methyl orange, sodium hydroxide (NaOH), Sulphuric acid (H_2SO_4) were purchased from Sigma-Aldrich (Germany). Methylene blue was purchased from Panreac (Spain). Solution were prepared in bi-distilled water.

2.2. Experimental design

The Box–Behnken design was used to optimize the number of experiments to be carried out to evaluate the possible interactions between studied parameters and their effects on the adsorption of dyes. A three-level three factorial Box–Behnken experimental design with 17 experiments was applied. The factor levels were coded as −1 (low), 0 (central point) and 1 (high). According to preliminary experiments carried out to identify the appropriate parameters and to determine the experimental domain, Solution pH (X_1), Dye concentration (X_2) and activated carbon ratio (X_3) were chosen as the most affecting parameters. Table 1 shows the Box–Behnken design levels for each. The Design Expert

8.0.7.1 Trial software was used for generating the statistical experimental design and analysing the observed data. A manual regression method was used to fit the second-order polynomial equation (Eq.1) to the experimental data and to recognize the relevant model terms. Considering all the linear terms, square terms and by linear interaction items, the quadratic response model can be described as:

$$Y= \beta_0 + \Sigma\ \beta_i X_i + \Sigma\beta_{ii} X_{i2} + \Sigma\beta_i X_i^2 + \ \Sigma_i\Sigma_j\beta_{ij}X_iX_j + e_i \qquad (1)$$

where Y is the responses of interest (adsorption capacity of MB, q_e(MB), and adsorption capacity of MO, q_e(MO). βo is the constant, βi the slope or linear effect of the input factor xi, βij the linear by linear interaction effect between the input factor xi and xj, βii is the quadratic effect of input factor xi.

2.3. Adsorption experiments

Stock solutions of synthetic dyes at a concentration of 200 mg/L were prepared by dissolving desired weight of each dye in distilled water and subsequent solution were prepared by dilution. Sorption experiments were done in a series of beakers containing 100 mL of the dye solution at different initial concentrations (X_2= 50, 125 and 200 mg/L) and the corresponding mass of activated carbon (X3= 0.1, 0.3 and 0.5). The pH of the solutions was adjusted to (X_1= 4, 7 and 10) for methylene blue or (X_1= 2, 6 and 10) of methyl orange using NaOH or H_2SO_4 (1M) solutions. The mixtures were stirred at 300 rpm for 2 h at the ambient temperature. The measure of solution pH was done using a sensION+ PH31 pH meter. After sorption experiments, samples were centrifuged at 3400 rpm for 10 min and residual dye concentrations were determined using a TOMOS UV-Vis spectrophotometer. The adsorption capacity of the dyes at equilibrium was defined as the amount of adsorbate per gram of adsorbent (in mg/g) and was calculated using following equation:

$$qe = \frac{(C_0 - Ce)}{R} \qquad (2)$$

where q_e is the adsorbed quantity (mg/g), C_0 is the initial dye concentration (mg/L), C is the residual dye concentration (mg/L), and R is the mass of activated carbon per litre of aqueous solution (g/L).

Table 1. Process factors and their levels

Factors	Levels					
	MB			MO		
	−1	0	+1	−1	0	+1
X_1: Solution pH	4	7	10	2	6	10
X_2: Dye concentration (mg/L)	50	125	200	50	125	200
X_3: Activated carbon ratio (g/L)	0.1	0.3	0.5	0.1	0.3	0.5

3. Results and Discussions

3.1. Experimental results

Table 2 shows the preparation conditions and experimental results for the studied responses; Adsorption of methylene blue (q_e(MB)) and adsorption of methyl orange (q_e(MO)). Values of adsorption capacities varied between 100.8 and 485.8 mg/g for methylene blue and between 95.5 and 612.2 mg/g for methyl orange. Both the highest values of 485.8 and 612.2 mg/g were obtained for the activated carbon ratio of 0.1 g/L but at basic medium for methylene blue and acidic medium for methyl orange. This result is in agreement with the change in surface charge of activated carbon and the protonation of the functional groups of dyes molecules with the change in solution pH. In acidic medium, the activated carbon acquires a positive charge by protonation with facilitate the interaction with anionic dye (methyl orange). In basic medium, there is a net negative charge on the cell surface of activated carbon. Consequently, the

adsorbent-adsorbate interactions for the cationic dye (methylene blue) become progressively significant for larger pH values. The regression analysis was performed to fit response functions with the experimental data. Values of the main effect of individual variables and their interaction effects obtained are presented in Table 3.

Table 2. Factorial experimental design matrix coded, real values and experimental results of the two responses.

Run	Coded values			Actual values				q_e (mg/g)	
	X_1	X_2	X_3	Solution pH		Dye concentration (mg/L)	Activated carbon ratio (g/L)	MB	MO
				MB	MO				
1	1	-1	0	10	10	50	0.3	164.1	158.6
2	0	0	0	7	6	125	0.3	302.3	228.6
3	0	1	-1	7	6	200	0.1	303.0	211.5
4	0	0	0	7	6	125	0.3	314.5	242.5
5	1	1	0	10	10	200	0.3	330.5	239.7
6	1	0	-1	10	10	125	0.1	485.8	256.2
7	-1	1	0	4	2	200	0.3	312.9	474.4
8	-1	0	-1	4	2	125	0.1	341.4	612.2
9	0	0	0	7	6	125	0.3	304.6	222.5
10	0	0	0	7	6	125	0.3	293.7	225.7
11	0	-1	1	7	6	50	0.5	100.8	95.5
12	0	0	0	7	6	125	0.3	315.2	238.2
13	0	1	1	7	6	200	0.5	285.2	252.6
14	-1	0	1	4	2	125	0.5	229.9	254.0
15	1	0	1	10	10	125	0.5	236.2	274.4
16	-1	-1	0	4	2	50	0.3	160.8	160.8
17	0	-1	-1	7	6	50	0.1	337.3	337.3

Table 3. Values of model coefficients of the two responses.

Main coefficients	q_e(MB)	q_e(MO)
b_0	+306.1	+231.5
b_1	+37.7	-84.0
b_2	+37.5	+63.9
b_3	-63.6	-44.5
B_{12}	+3.6	-58.2
b_{13}	-34.5	+119.1
b_{23}	+54.7	+49.4
b_{11}	+1.4	+74.0
b_{22}	-65.4	-47.2
b_{33}	+15.9	+18.7

According to the table, the mass ratio of activated carbon presented a negative effect and the dye concentration had a positive effect on the adsorption the both dyes. Whereas, the pH of solution had a negative effect on the adsorption of

methyl orange and a positive effect on the adsorption of methylene. The analysis of the interaction effects showed significant interactions between solution pH and activated carbon ratio with negative effect (b_{13} = -34.5), and between dye concentration and activated carbon ration with positive effect (b_{23} = +54.7) in the case of the adsorption of methylene blue. For the adsorption of methyl orange, the most significant interaction was the interaction between solution pH and activated carbon ration with a positive effect (b_{13} = +119), followed by the interaction between solution pH and du concentration with a negative affect (b_{12} = -58.2).

3.2. Analysis of variance (ANOVA)

The analysis of variance (ANOVA) was used to determine the significance of the curvature in the responses at a confidence level of 95%. 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 a main effect because it refers to the primary factors of interest in the experiment. The model and model terms are considered to be significant only when the values of (Prob > F) are less than 0.05 and terms with Fisher's statistical test F-test. The ANOVA assessed the significance fitting of the quadratic model for the two responses with results indicated in Tables 4-5. ANOVA results showed that equations adequately represented the actual relationship between each response and significant variables.

Table 4. Analysis of variance for MB adsorption

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob> F
Model	1.429E+5	9	15880.80	12.31	0.0001*
X_1	36.64	1	36.64	0.028	0.0011*
X_2	48153.91	1	48153.91	37.32	0.0011*
X_3	75246.78	1	75246.78	58.31	0.0001*
X_1X_2	1084.71	1	1084.71	0.84	0.4729
X_1X_3	10622.39	1	10622.39	8.23	0.0016*
X_2X_3	5953.67	1	5953.67	4.61	0.0003*
X_1^2	1303.29	1	1303.29	1.01	0.7667
X_2^2	274.28	1	274.28	0.21	0.0001*
X_3^2	112.37	1	112.37	0.087	0.0225*
Residue	9032.94	7	1290.42		
Lack of Fit	8383.40	3	2794.47	17.21	0.0095
Pure Error	649.54				
Cor Total	1.520E+5	4	162.39		

$R^2 = 0.997$; $R_{adj}^2 = 0.9844$

From the ANOVA analysis, all the three factors contribute significantly in the adsorption yield. For both dyes, the dye concentration in solution has a positive effect on the adsorption yield, contrariwise; the mass ration of activated carbon has a negative effect. According to the correlation coefficients, MO adsorption was more influenced by dye concentration in solution compared to MB adsorption. On the other side, MB adsorption was more influenced by the mass ratio of activated carbon compared to MO adsorption. The ANOVA analysis also indicated that solution pH has a positive effect on the adsorption of MB and a negative effect on the adsorption of MO. This result was because MB is a cationic dye and MO is an anionic dye. At acidic pH, the presence of excess H+ ions competed the adsorption of cationic dye, while, at higher pH values, more negatively charged surface sites are available, which facilitates the adsorption of the dye [21]. The opposite behaviour can be observed in the case of the anionic dye MO.

The analysis of the linear-by-linear interactions indicates that, the interaction between solution pH and mass ratio of activated carbon (X_1X_3) and the interaction between dye concentration and mass ration of activated carbon (X_2X_3) were the most significant interactions for MB Adsorption. For MO adsorption, the most significant interactions were obtained between solution pH and mass ratio of activated carbon (X_1X_3) and between solution pH and dye concentration (X_1X_2).

For the quadratic effect contribution, the mass ration was the influencing on MB adsorption and solution pH was the most influencing on MO adsorption.

$$q_e(MB) = 306.1 + 37.7\ X_1 + 37.5\ X_2 - 63.6\ X_3 - 34.5\ X_1X_3 + 54.7\ X_2X_3 - 65.4\ X_2^2 + 15.9\ X_3^2 \quad (3)$$

$$q_e(MO) = 231.2 - 84.0\ X_1 + 63.9\ X_2 - 44.5\ X_3 - 58.2\ X_1X_2 + 119.1\ X_1X_3 + 74.0\ X_1^2 \quad (4)$$

Table 5. Analysis of variance for MO adsorption

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob> F
Model	2.177E+5	9	24192.51	10.04	0.0030
X_1	56436.24	1	56436.24	23.42	0.0019*
X_2	32689.97	1	32689.97	13.56	0.0078*
X_3	15818.87	1	15818.87	6.56	0.0374*
X_1X_2	13548.96	1	13548.96	5.62	0.0495
X_1X_3	56727.33	1	56727.33	23.54	0.0019
X_2X_3	9782.20	1	9782.20	4.06	0.0838
X_1^2	23075.23	1	23075.23	9.57	0.0175
X_2^2	9396.48	1	9396.48	3.90	0.0889
X_3^2	1467.97	1	1467.97	0.61	0.4607
residue	16871.15	7	2410.16		
Lack of Fit	16580.97	3	5526.99	76.19	0.0006
Pure Error	290.17	4	72.54		
Cor Total	2.346E+5	16			

$R^2 = 0.928$; $R_{adj}^2 = 0.9144$

3.3. Diagnostic model

Statistical actual and predicted values for testing significant effects of regression coefficients for the proposed models are presented in Fig.1. Values obtained by the model (Y predicted) are compared with those of experimental data (Y experimental). It can be seen in the figure, that most of data points were well distributed near to the straight line, which suggested an excellent relationship between experimental and predicted values of the responses [22]. Therefore, the "R^2" were in reasonable agreement with the "R_{Adj}^2". Furthermore, "R^2" were greater than"R_{Adj}^2". It can be seen that, more than 95% of these responses can be well predicted by these models, indicating that terms which were considered in proposed models were significant enough to make acceptable predictions [23]. The Model F-value of the MB and MO adsorption were 12.31 and 10.04, respectively, implies that models are significant. There was only a 0.3% chance for MB adsorption and 7.0% chance for the MO adsorption that the large Model F-Value could due to noise. Indeed, the high value of F-ratio confirms the significance of the proposed models.

3.4. Response surfac e analysis

The 3D response surface plot obtained from statistical processes for different combinations are depicted in Fig.2 and Fig.3. For MB adsorption, the most significant interactions were dye concentration/ mass ratio of activated carbon and

dye concentration/ solution pH. For MO adsorption, the significant interactions were solution pH/mass ratio of activated carbon and solution pH/ dye concentration. Fig.2a shows that the MB adsorption increased with increasing dye concentration and decreasing mass ration of activated carbon. The figure also indicates that, the mass ration of activated carbon influence more MB adsorption at low dye concentration. On the other side, the dye concentration less influenced dye removal at low mass ratio of activated carbon. From Fig.2b, it is clear that solution pH positively influences the MB removal either at low and high dye concentration in solution. A maximal value of MB adsorption was observed at high dye centration and high solution pH.

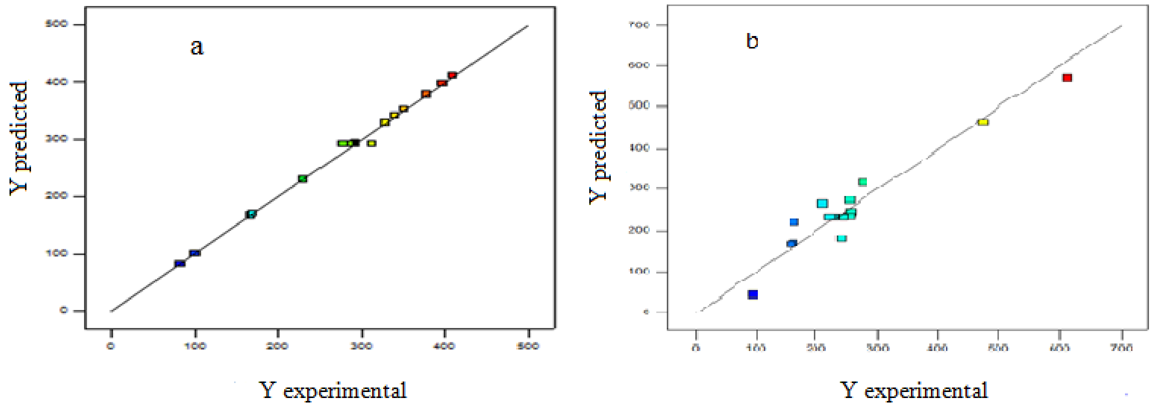

Figure 1. Predicted values vs. actual values for MB (a) and MO (b) adsorption.

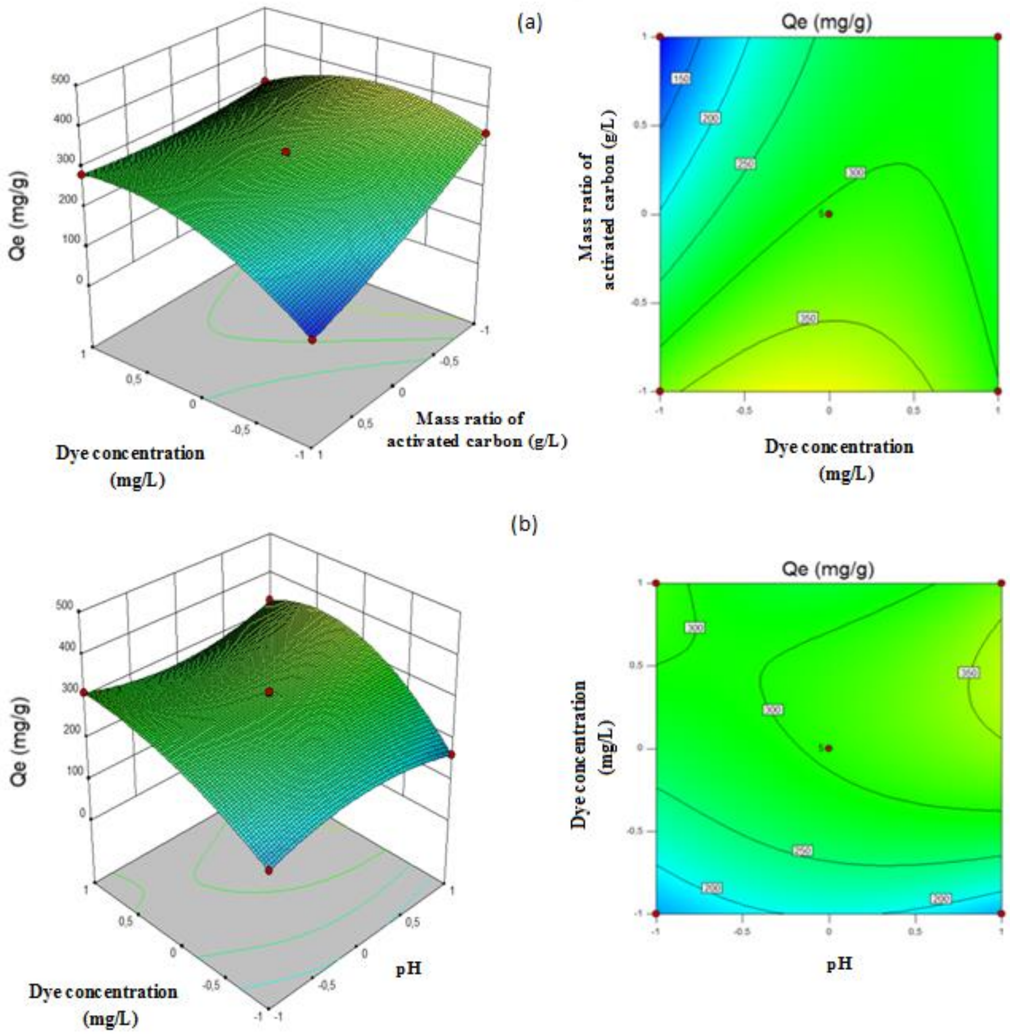

Figure 2. Surface response and contour plots for MB adsorption

According to Fig.3, the MO adsorption is extremely sensible to solution pH. From Fig.3a, we can see that a strong interaction between solution pH and mass ratio of activated carbon. At high solution pH, the MO adsorption increase with the increase of mass ration of activated carbon. On the other hand, reverse behaviour was observed at low solution pH. The maximum MO adsorption was observed at solution pH of 2 and mass ration of activated carbon of 0.1 g/L. Fig.3b indicates that, at low solution pH, MO adsorption depends strongly on its concentration in solution. Also, at high dye concentration, the effect of solution pH is more significant. The highest adsorption capacity of MO was obtained at high dye concentration and low solution pH.

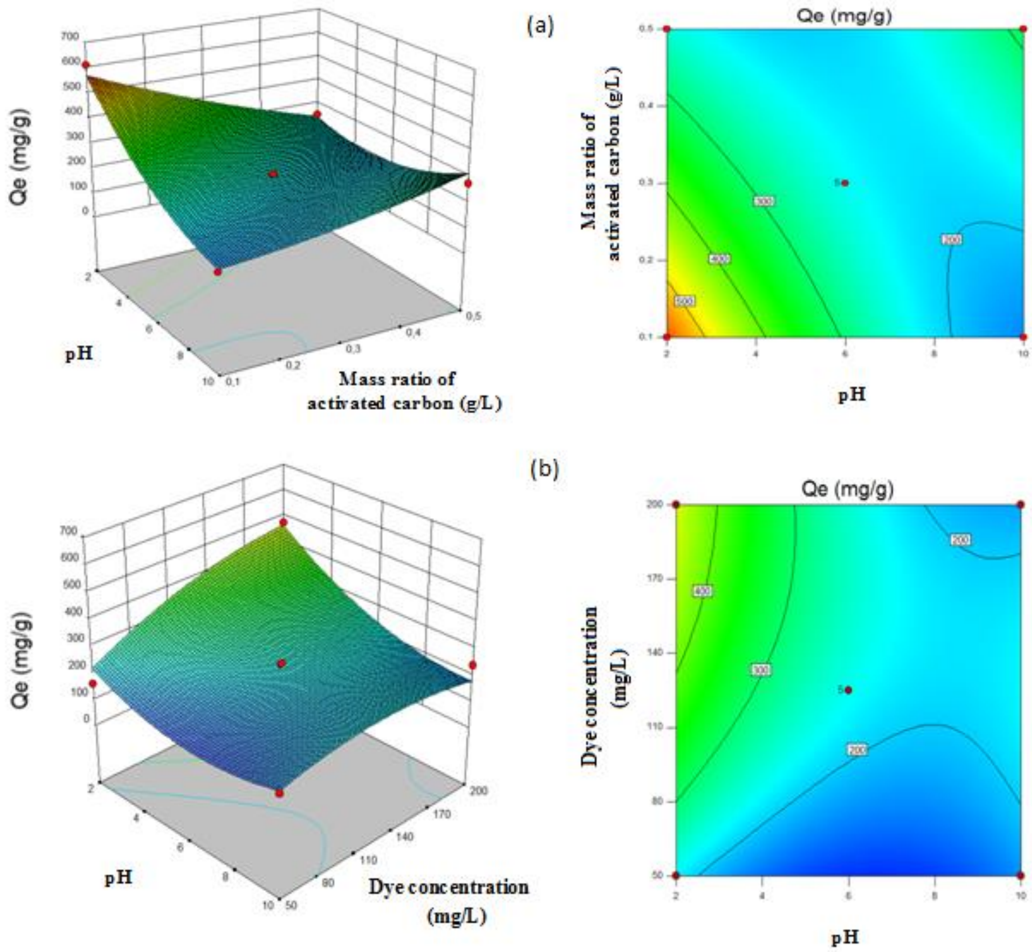

Figure 3. Surface response and contour plots for MO adsorption.

4. Conclusion

This work investigated the optimization of anionic dye (methyl orange) and cationic dye (methylene blue) adsorption by activated carbon. The Box–Behnken design and response surface methodology were applied to determine the best experimental conditions for the greater dyes removal. Three different factors, including solution pH, dye concentration and mass ration of activated carbon are chosen. The obtained results indicated that all the three factors contribute significantly in the adsorption of MB and MO. MB adsorption was more influenced by the mass ratio of activated carbon compared to MO adsorption. On the other side, MO adsorption was more influenced by dye concentration in solution compared to MB adsorption. The analysis of the linear-by-linear interactions indicates that, MB adsorption was more influenced by the interaction between dye concentration and mass ration of activated carbon, compared to MO which was more influenced by the interaction between solution pH and dye concentration. The mass ration of activated carbon influence more MB adsorption at low dye concentration. In addition, at low solution pH, MO adsorption depends strongly on its concentration in solution.

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