Sorption of methylene blue by luffa cylindrical, optimization and modeling using the response surface methodology

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Abstract

Luffa cylindrical fibers were used to remove the cationic dye methylene blue (MB) from aqueous solutions. Screening factors which can affect the sorption has been discussed previously. In this study, a response surface methodology (RSM) based on three-level three-factorial Box–Behnken design was used. The effects of three variables, such as the ratio(R) mass of adsorbent/initial concentration of dye, pH_0 and size of particles on the adsorption capacity for MB were examined. The optimum conditions (R : 527.27, pH_0 : 6 and very fine particle size) for achieving an elimination of 90.04%, were determined by the results of statistical analysis.

Keywords: *Adsorption, Box–Behnken, Luffa Cylindrical fibers, Methylene Blue (MB), RSM.*

I. Introduction

Industrial development causes serious environmental pollutions [1]. Among these industries we found the textile one which is the major source of colored effluents production in wastewater [2].This wastewater contains a variety of substances and organic compounds which are toxic for the aquatic organisms and plants [3]. Methylene blue (MB) is the most dye widely used by textile industries to color their products. Therefore, there are a lot of methods to treat this effluent [4-16]. Adsorption process is one of the most used due to their low energy cost which is economical and easy to manufacture [17-19]. More than 185 published papers show that low-cost adsorbents have the capacity to remove the MB [20-26].

In the present article we chose to work with an agricultural solid waste such as a Luffa cylindrical fibers. This biomaterial is used for the disposal of toxic products in aqueous effluents. In fact, different studies used this biomaterial in different ways and their characteristics had been mentioned [27-29].

The aim of this study is to optimize and to model the sorption phenomenon of cationic dye (MB) using fibers of Luffa Cylindrical as an adsorbent. To determine the optimum, a response surface methodology [30-33] had been applied [34-37] using a Box-Behnken design. This design uses three factors with three levels [38-40]. The parameters were the mass ratio adsorbent/initial, the particle size of adsorbent and pH_0. The response was the elimination percentage of dye.

II. Material and methods

Methylene blue (99.9% from Aldrich) was the dye to be removed. Luffa Cylindrical fibers were used without treatment. The physical characteristics of Luffa cylindrica fibers were shown in previous study [41]. The deionized water was used to prepare all aqueous solutions.

Tests were performed in a backer of 250 mL capacity. Temperature was kept constant using a thermostatic bath. The experiments were performed by contacting a certain mass of adsorbent with 100 mL of desired concentration of cationic dye.

The residual concentration of the MB was analyzed by the spectrophotometric method using a visible spectrophotometer (CecoMAM) set at a wave-length of 665 nm, corresponding to a maximum absorbance determined experimentally.

Dye removal, $Y_{exp.}(\%)$, was obtained by equation 1:

$$Y_{exp.}(\%) = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

Where C_0 and C_{eq} are the initial and the equilibrium liquid-phase concentrations of MB (mg L^{-1}) respectively.

III. Results and discussion

A. Experimental domain

The factors selected for this study and their levels are shown in Table 1. For the size of adsorbent the different granulometry is coded by the software in the following way: gross (1), fine (2) and very fine (3).

The domain of the other factors was determined in previous study when we used a screening design [41]. Applying the Plackett-Burman design, it was found that the influence factors in this phenomenon are: the pH_0 of solution, the initial concentration of dye and the weight of adsorbent.

The results of the eliminated percentage of MB ($Y_{exp.}$ and $Y_{theor.}$) are presented in table 2.

Table 1: Experimental domain for factors

Stand. Order	Run Order	R	Size	pH_0	$Y_{exp.}$%	$Y_{theor.}$%
14	1	1100	2	8	87.78	87.78
12	2	1100	3	10	82.71	83.13
1	3	200	1	8	86.97	85.42
9	4	1100	1	6	86.29	85.87
13	5	1100	2	8	87.78	87.78
5	6	200	2	6	86.29	86.26
11	7	1100	1	10	86.96	87.75
6	8	2000	2	6	82.23	83.47
7	9	200	2	10	87.04	86.79
10	10	1100	3	6	91.84	90.04
2	11	2000	1	8	84.97	84.15
4	12	2000	3	8	78.81	80.36
15	13	1100	2	8	87.78	87.78
3	14	200	3	8	84.95	85.77
8	15	2000	2	10	85.88	84.91

Table 2: Experiment results using Box-Behnken matrix

Levels	**R**	**pH_0**	**Size**
Maximum	2000	10	Gross
Middle	1100	8	Fine
Minimum	200	6	Very fine

B. Histogram and line Henry residual values for yield

It can be seen that the histogram follows a bell curve. It is also observed that the values of the histogram are highly symmetrical with wider-looking fitted distribution (Fig.1-left).

Henry's lines are useful for evaluating the normality of a data file, even when the number of observations is rather small. It was observed that the points tend to form a straight line, indicating that the residual values are distributed approximately normally (Fig. 1-right). It is also observed that the ends of the distribution deviate slightly from a straight line.

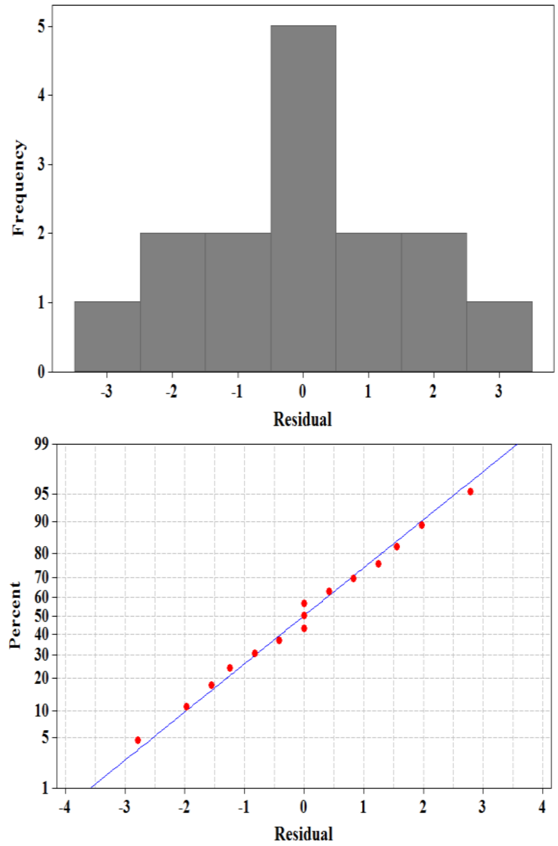


Figure 1: Histogram and line Henry residual values for yield

C. ANOVA

The results of the analysis of variance (ANOVA) are shown in Table 3.

Table 3: Coefficients and P-value of the factors considered by

Termes	Coef	P
Constant	87.7810	0.000
R	-1.6688	**0.125**
size	-0.8605	0.387
pH_0	-0.5082	0.600
R^2	-2.7231	**0.097**
$Size^2$	-1.1339	0.435
pH_0^2	0.3000	0.831
R × Size	-1.0354	0.457
R × pH_0	0.7255	0.596
Size × pH_0	-2.4494	**0.115**

From Table 3, it can be seen that among the factors studied, the most significant factors are the ratio mass of the adsorbent to the initial concentration of the dye (**R**), **R^2** and the interaction effect between the particle size and the initial pH (**Size × pH_0**) with the **α**value of **0.15**.

D. Mathematic model

For uncoded units

$$y_{exp.}(\%) = 71.1917 + 0.00461853 \times R + 14.7383 \times Size + 0.551912 \times pH_0 - 3{,}36186E-06 \times R^2 - 1.13388 \times Size^2 + 0.0750063 \times pH_0^2 - 0.00115045 \times R \times Size + 0.000403029 \times R \times pH_0 - 1.22472 \times Size \times pH_0 \quad (2)$$

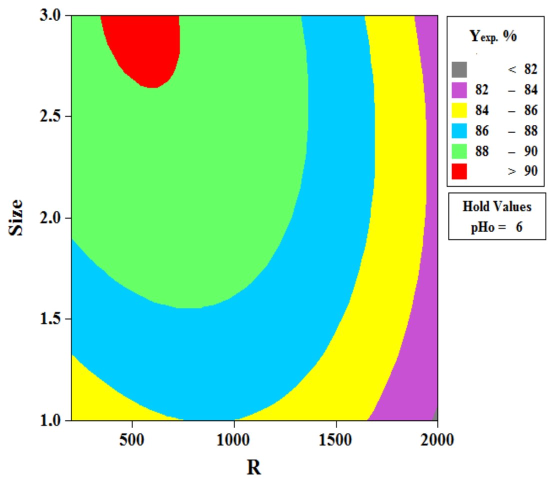
For coded units

$$y\,(\%) = 87.7810 - 1.6688 \times R - 0.8605 \times Size - 0.5082 \times pH_0 - 2.7231 \times R^2 - 1.1339 \times Size^2 + 0.3000 \times pH_0^2 - 1.0354 \times R \times Size + 0.7255 \times R \times pH_0 - 2.4494 \times Size \times pH_0 \quad (3)$$

E. Response surfaces and contours

The software Minitab 16 allowed us to plot the response surfaces and contours for all factors with the chosen response. The best elimination percentages of MB are represented by a red zone in all response contours.

From the fig.2 and 3, yields greater than 90% were obtained when the pH_0 is 6 (minimum level), R between 300-700 and a maximum level for the size of adsorbent (very fine). This is confirmed by the sloping convex surfaces.



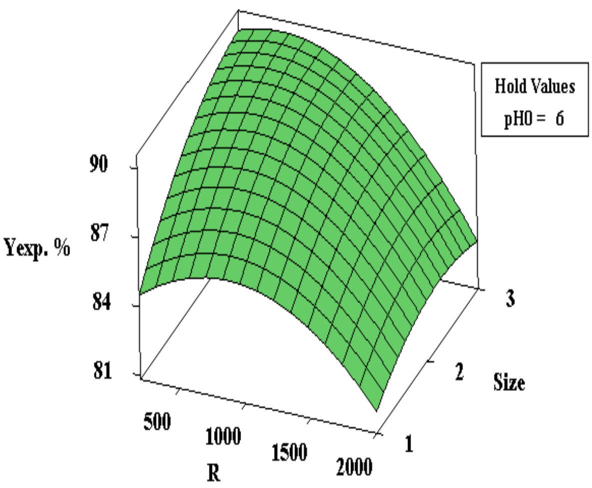
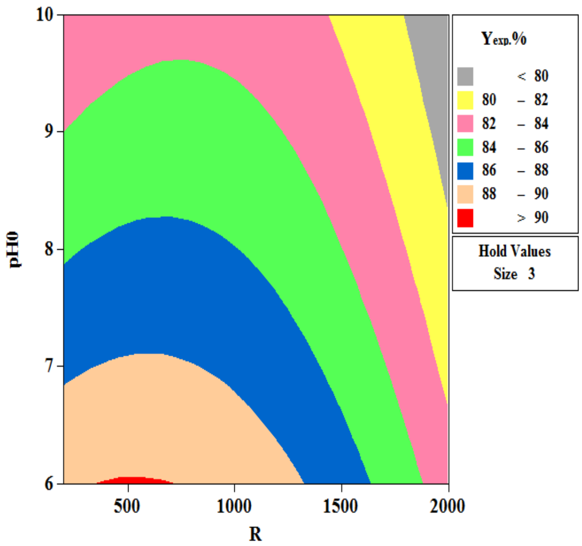


Figure 2: Contour surface and response surface of $Y_{exp.}$ according to R and Size at pH_0 6

With a middle level of ratio R (fig.4), the best percentages of elimination of MB **(Yexp> 89%)** are in two regions: at pH_0 10 with a gross particle size and at pH_0 equal to 6 with a very fine granulometry. And this was reinforced by the shape of the response surface [42].

Indeed, the removal of a high concentration of MB was favored at neutral pH of solution and a very fine granulometry where the contact surface is large [43].



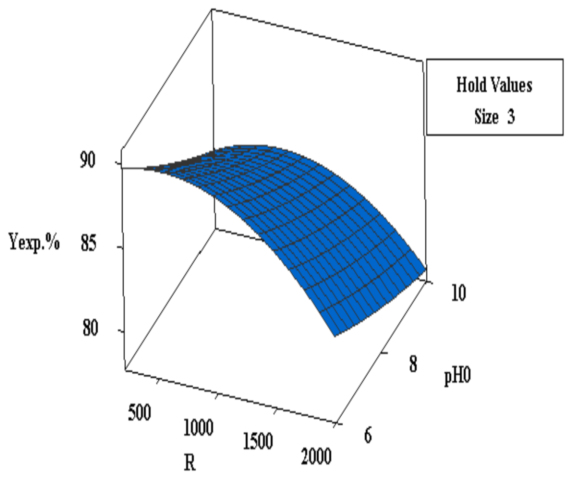
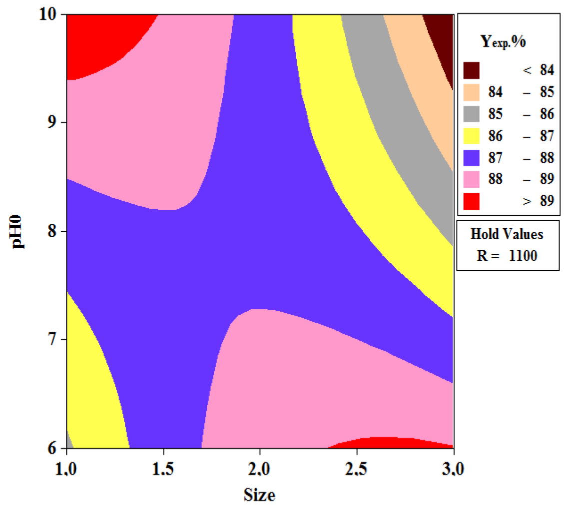


Figure 3: Contour surface and response surface of $Y_{exp.}$ according to R and pH_0at Size very fine



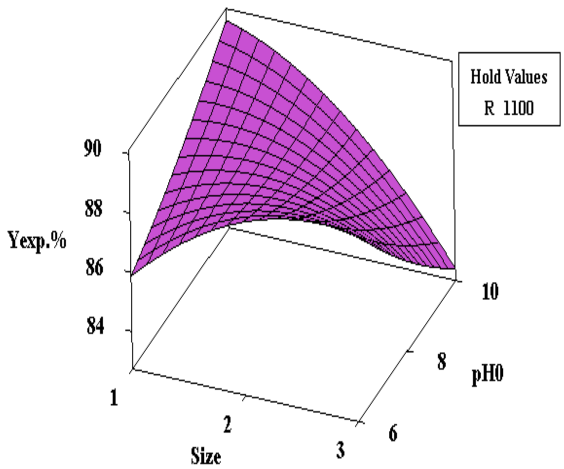


Figure 4: Contour surface and response surface of $Y_{exp.}$ according to Size and pH_0at R 1100

F. Optimization and validation of the model

In the aim to found an optimal point where the response is maximal a constraint was imposed on all factors. As a result of several optimizations the best optimization results are grouped in Table 5.

Table 5: The criteria of optimization

Parameters	FACTORS			$Y_{theor.}$(%)
	R	Size	pH_0	
	527.27	Very fine	**6**	**90.12**

After obtaining the optimum conditions, a verification has been carried out. The same experimental setup was taken as following: the temperature of the bath was 20 °C, the stirring speed was set at 350 rpm, initial concentration of MB of 12 mg/L, a mass of adsorbent of 0.6327 g (for an R ratio of 527.27) where the particle size chosen was very fine and an initial pH of 6. The result of the sorption gives an experimental eliminated percentage of 90.04%.

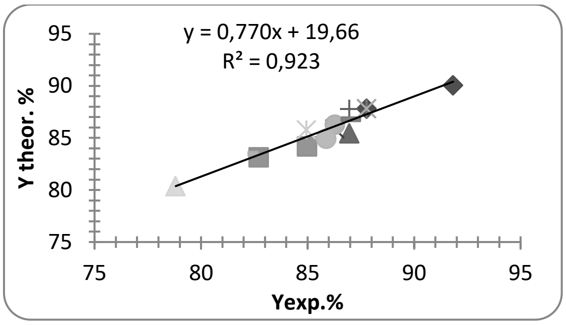


Figure 5: Correlation between theoretical and experimental yield.

To check the model, a comparison between theoretically ($Y_{theor.)}$ and experimentally ($Y_{exp.}$) values was examined. Indeed, from the figure 5 we ought to say that the points are fairly distributed around the regression line with a correlation constant of 0.923. This proves that the mathematical model represents well the sorption phenomenon in this context.

IV. CONCLUSION

This work showed that the optimization of sorption of MB using Luffa cylindrical fibers in batch mode was examined. The Box-Behnken design was used to model and to optimize the phenomenon. It was found that the modeled polynomial of the elimination of MB is function of all the factors studied, their squares and their interactions were given.

The optimum conditions found were verified experimentally. An R = 527.27, a very fine particle size and pH_0 = 6 was obtained for a theoretical response of 90.12% which is close to the experimental value 90.04%. The same optimum conditions are maintained except for the initial pH. The pH_0 was reduced to 5 to give a percentage removed of 90.20% and to 4 to give 88.98% of elimination of MB. This indicates that the number of sorption sites charged negatively, decreased and the number of surface sites charged positively, increased with the decreased in the pH of solution. This result is due to the presence of excess H^+ ions competing with dye cations for the sorption sites of Luffa cylindrical fibers.

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