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Assessment of Dye Adsorption by *Luffa Cylindrica* fibers Using Experimental Design Methodology

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Abstract— Response surface methodology (RSM) was applied to optimize the methylene blue adsorption onto *Luffa Cylindrica* fibers. The individual effects, as well as the interactions between variables such as pH and initial concentration dye were studied. From a Pareto chart, it appears that the most significant effect is clearly that of the maximum dye concentration. Such effect can be graphically verified through response surfaces and contour line plots. The optimum concentrations of dye, and pH were found to be 97.25 mg/dm^3 and pH 4.17 respectively, for maximum MB adsorption (83.44 mg/g). A quadratic model was obtained for dye adsorption through this design. The experimental values were in good agreement with predicted values and the model was highly significant, the correlation coefficient being 0.9906. Increased adsorption was observed with increase in dye initial concentration at lower pH. Interaction between MB concentration and pH was negligible. The optimization of dye concentration is independent of pH.

Adsorption kinetics to optimal conditions determinated by RSM was investigated.

Keywords— Adsorption, *Luffa Cylindrica*, Methylene blue, Response surface methodology.

I. Introduction

PRINCIPALLY, textile industry discharge to natural water sources colored effluents with pigments and dyes that are toxic and have carcinogenic and mutagenic effects [1].

Treatment of the textile dye containing effluent is difficult and ineffective with conventional biological processes because many synthetic dyes are very stable to light, temperature and resistant to microbial attack. Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation, sonochemical degradation, micellar enhanced ultrafiltration, cation exchange membranes, electrochemical degradation, adsorption/precipitation processes, integrated chemical–biological degradation, integrated iron(III) photoassisted-biological treatment, solar photo-Fenton and biological processes, Fenton-biological treatment scheme and adsorption on activated carbon.

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Unfortunately, these methods of effluent treatment have high operating costs and limited applicability. As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater [2].

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [3]. The accumulation and concentration of dyes from aqueous solutions by the use of biological materials is termed bioadsorption. Bioadsorption is a novel approach, competitive, effective and cheap.

Luffa cylindrica is lignocellulosic material that can be used as bioadsorbent because its fibrous vascular system, allows it removal of water pollutants as dyes. Therefore tough fibers can promise as being processed into industrial products such as filters. In removal processes, it is recommended that the capacities be taken as specific set of conditions rather than as maximum adsorption capacities.

Response surface methodology (RSM) is a collection of useful mathematical and statistical techniques for analyzing the effects of several independent variables. In many processes, the relationship between the response and independent variables is unknown; therefore, the first step in RSM is to approximate the function (response) in terms of analyzing the independent variables. Usually, this process employs a low-order polynomial equation in a predetermined region of the independent variables, which will later be analyzed to locate the optimum values of independent variables for the optimum response [4].

The purpose of the present study was evaluated the methylene blue adsorption on *Luffa Cylindrica*, using RSM to optimize the main parameters affecting process such as the initial concentration of dye (MB) and pH. Kinetics parameters were investigated to determine the ratio of reaction time versus adsorbed amounts under optimized conditions certained by RSM.

II.. Materials and methods

A. Materials

The Luffa fibers were washed with water to remove the adhering dirt. Lately, they were dried in an oven at 70 ◦C for 7 h. They were obtained from local shop. After drying, they were cut for reducing dimensions to 2–3 mm. Fibers were pretreated in order to increase hydrophilicity by NaOH boiling solution 0.1 M during 20 min. Fibers were washed with deionized water until whole sodium hydroxide was removed. After washing, they were dried in oven at 70°C for 6 h. Chloride acid (Carlo Erba), sodium hydroxide (Sigma, 99%), methylene blue (Merck) were used in the experiments.

B. Methods

In all experiments, 80 mg of dried luffa fibers were immersed in 100 cm^3 MB solutions according to experimental conditions. For building a response surface plot, it is necessary to consider a full-composite experimental design which consists of a 2^k factorial design with central and star points, where *k* corresponds to the number of selected variables or main effects [5]. In this case, the chosen response variable was the MB adsorbed on fibers and the levels of the main effects were established from the obtained results in previous works [1,6,7]. The main effects and their levels used for this experimental design were set as follows: A, initial concentration of MB, 25 – 85 mg/dm^3; B, initial pH, 5 – 9. The concentrations of the solution samples were measured using a Spectroquant Pharo 300 Merck UV–Vis visible spectrophotometer. The amount of MB adsorbed onto Luffa fibers after shaking for 5 h. was estimated from mass balance according to Eq. (1):

$$q_e = (C_0 - C) \times \frac{V}{M} \tag{1}$$

where C_0 and C correspond to the initial and the final concentration in liquid phase, mg/dm^3; V is volume of the solution, l; and M is mass of the luffa fibers, g.

The coefficients of the linear and quadratic effects of the mathematical model obtained from the statistical analysis were estimated using a multilinear regression analysis of minimal squares. The equations used for describing quantitatively the dye adsorption and the response surface plots were analyzed and interpreted with the Statgraphics® 5.1 software Trial Version.

The kinetics of the adsorption was researched by performing batch experiment at ambient temperature (288 K) to optimal conditions of MB initial concentration and pH (97.42 mg/dm^3, 4.17 respectively) and fixed amount of Luffa fiber (80 mg).

III. Results and discussion

A. Experimental design of MB absorption by Luffa Cylindrica

The results of the experimental runs are listed in Table I. and the mathematical model obtained from these data is described by Eq. (2).

$$MB\ Adsorbed = 8.87 + 1.56 \times A - 4.39 \times B - 0.005 \times A^2 - 0.03 \times A \times B + 0.41 \times B^2 \tag{2}$$

The individual effects of various parameters as well as their interactions can be discussed from the Pareto chart illustrated by Fig. 1, the Pareto chart being an option of Statgraphics Plus

TABLE I
Experimental Results of MB Absorption by *Luffa Cylindrica*

Variables		Observed value mg/g	Predicted value mg/g
A: [MB], *mg/dm³*	B: pH		
25.0	5.0	29.36	28.75
97.42	7.0	72.51	75.02
85.0	5.0	79.09	75.66
25.0	9.0	28.55	30.94
55.0	7.0	54.04	54.78
55.0	7.0	55.53	54.78
55.0	4.17	56.65	59.29
85.0	9.0	70.45	70.02
55.0	9.81	58.46	56.85
12.57	7.0	15.69	14.21

5.1 for Windows. The length of each bar is proportional to the absolute value of its associated regression coefficient or estimated effect.

The effects of all parameters, interactions as well as quadratic terms, are standardized (each effect is divided by its standard error). The order in which the bars are displayed corresponds to the order of the size of the effect. The chart includes a vertical line that corresponds to the 95% limit indicating statistical significance. An effect is, therefore, significant if its corresponding bar crosses this vertical line [8].

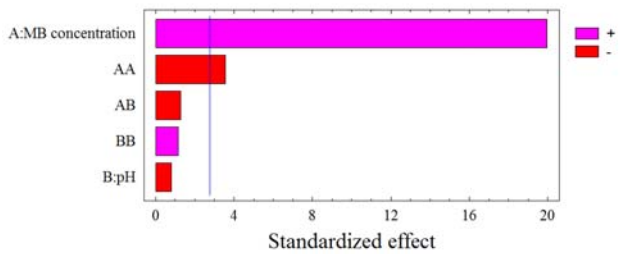

Fig. 1 Pareto chart of standardized effects for MB adsorption

From Fig. 1, the most significant parameter is clearly the MB initial concentration (A). Its quadratic effect (AA) indicates that this variable is outstanding during the process and its behavior presents a maximum that changes slope for its quadratic behavior in some moment. The simple effect of acidity (B), its quadratic effect (BB) and the interaction MB concentration–pH appear actually low and are not significant.

Fig. 2 illustrates that there is not interaction between effects pH–MB concentration. When the MB concentration increases from 25.0 to 85.0 mg/dm^3, the change in the amount of adsorbed MB does not differ with the level of pH. A maximum value in adsorbed MB is observed not only at the higher level of pH but also at the lower one and, the gap between both curves is not large enough to conclude a significant interaction effect between variables. The low interactive effect between pH and MB initial concentration is obvious.

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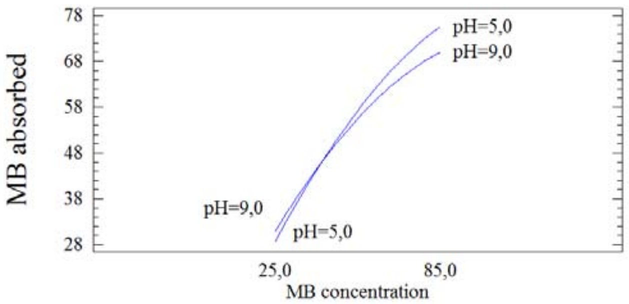

Fig. 2 Interaction plot for MB adsorption.

The results of analysis of variance (ANOVA) are shown in Table II which indicates that the predictability of the model is at 95% confidence interval. The predicted response fitted well with those of the experimentally obtained response. Further the computed F value to A factor (397.88) is much greater than that of the tabular $F_{0.05,1,4}$ value (7.71) suggesting that the MB concentration is highly significant. A P value less than 0.01 indicated that the factor is statistically significant. The factor also revealed statistically insignificant lack of fit, as is evident from the lower computed F value.

TABLE II
ANOVA RESULTS FOR THE QUADRATIC EQUATION OF STATGRAPHICS 5.1 FOR MB ABSORPTION BY *LUFFA CYLINDRICA*

Source	Degree of freedom	Sum of squares	Mean square	*F*–ratio	*P* value
A	1	3697.38	3697.38	397.88	0.000
B	1	5.93	5.93	0.64	0.469
AA	1	118.14	118.14	12.71	0.023
AB	1	15.33	15.33	1.65	0.268
BB	1	12.35	12.35	1.33	0.313
Total error	4	37.17	9.29		
Total (corr.)	9	3955.78			

R^2: 0.9906; adj R^2: 0.9788

Fig. 3 shows the incidence of the main effects on the MB adsorption. The most incident effect was the MB concentration. This behavior is according to analysis from Pareto Chart.

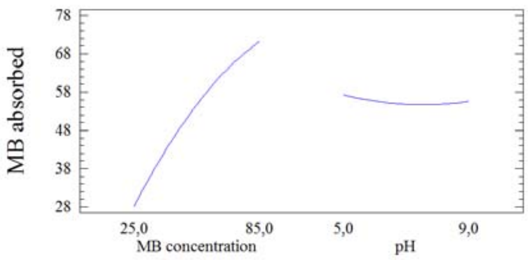

Fig. 3 Main effects plot for MB adsorption by *Luffa Cylindrica*

The various effects of the operating variables can be graphically observed from the response surfaces and the contour plots of the target variable, MB adsorbed. Fig. 4 shows the response surface of MB adsorption onto *Luffa Cylindrica* fibers as a function of two independent variables, (MB concentration and pH). The shape of the response surface, similar to plane and few distorted, is an indication of the low interactive effects between variables. Therefore, Fig. 4 shows little interaction between pH and MB initial concentration.

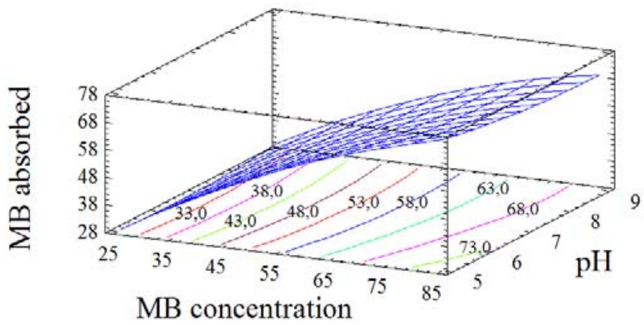

Fig. 4 Estimated response surface for MB adsorption.

Generally, it is important to assess the fitted model to ensure that it gives sufficient approximation of the results obtained in the experimental conditions. A check of the normality assumption can be made by constructing a normal probability plot of the residuals as given in Fig. 5. The normality assumption is satisfied if the residuals plot approximated along a straight line.

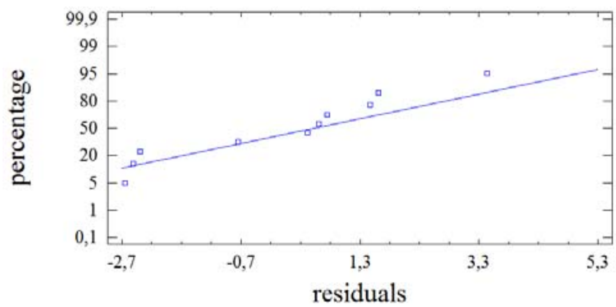

Fig. 5 Normal probability plot for residuals.

The coefficient of multiple regression, R^2, is another statistical parameter to access the fit of a model. In the present model, R^2 was 0.9906, which indicates the fitness of the model. For further validation of the model, adjusted R^2 was used for confirming the model adequacy. The adjusted R^2 was calculated to be 0.9788, which indicates a good model for using in the field conditions.

Examination of the residuals should be an automatic part of any analysis of variance. If model is adequate, the residuals should be structureless; that is, they should contain no obvious patterns [5]. The polynomial function leads to a satisfactory prediction of MB adsorption onto *Luffa Cylindrica* described in Eq. 2 can be illustrated by Fig. 6.

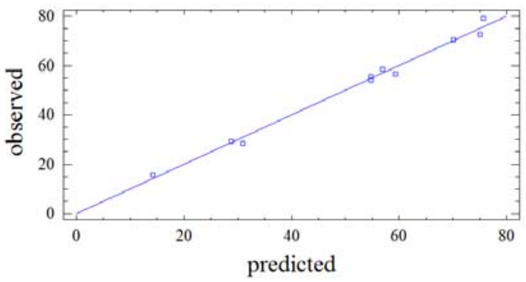

Fig. 6 Comparison between experimental and calculated values of MB adsorption.

As discussed above, the variable MB initial concentration had significant effect, as well as their quadratic interaction so that the results shown on Fig. 4 have a particular importance. Therefore, an optimal set of both, the variables MB initial concentration and pH, can be approximately deduced from the shape of the contour lines on Fig. 4. This optimal set is shown in Table III.

TABLE III
OPTIMIZED RESPONSE FOR MB ABSORPTION ONTO *LUFFA CYLINDRICA*

Factor	Low	High	Optimum
MB concentration	12.57	97.42	97.42
pH	4.17	9.82	4.17

Optimum value 83.44 mg/g

B. Kinetics study

Fig. 7 shows the kinetics of MB adsorption onto *Luffa Cylindrica* fibers corresponding to optimal condition determinated by RSM analysis showed in Table III. This way, MB initial concentration and pH condition used to kinetics studies were 97.42 mg/dm^3 and 4.17 respectively.

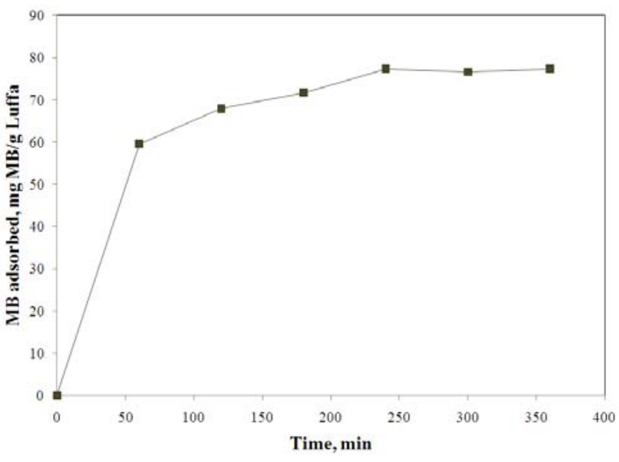

Fig. 7 MB adsorbed by *Luffa Cylindrica* along time to optimal conditions determinate by RSM.

The adsorption isotherms were evaluated by using Langmuir and Freundlich equations [9]. Langmuir isotherm is represented by Eq. 3

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_L q_m}\frac{1}{C} \qquad (3)$$

where
K_L= Langmuir constant (dm^3/mg),
q = MB concentration in fiber (mg/g),
C = MB concentration in solution (mg/dm^3),
q_m= MB concentration when monolayer forms onto fiber (mg/g).

Eq. 4 represents Freundlich's isotherm

$$q = K_f C^n \qquad (4)$$

where
K_f = sorption capacity,
n = sorption intensity.

The Freundlich constants of the isotherms K_f and n were found by drawing log q versus log C (8.369×10^{-4} mg/g, –1.3068). Langmuir constants q_m and K_L were evaluated by plotting 1/q versus 1/C (18.083 mg/g, –0.0259 dm^3/mg, respectively). These values show that the adsorption model constants of MB on luffa fibers can be described by the Langmuir equation since a higher linear regression correlation coefficient, $R2$, of 0.97 was obtained for this model.

IV. CONCLUSIONS

Dye absorption onto Luffa Cylindrica fibers could be optimized by way of an experimental design methodology as a central composite with axial points, allowed on the one hand to classify the effects of each of the parameters, and parameters, on the other hand, to emphasize their interactions and quadratic effects. Moreover, we could determine a statistical model in a polynomial form obviously available in the domain of investigation of the tested parameters. In the present work, this domain appears, nevertheless, a little too restricted. Only MB initial concentration had an effect over response variable but its quadratic effect implies a change slope in some point. Kinetics studies on MB adsorption on *L. cylindrica* fiber revealed that the MB adsorption is a pseudo–first order reaction defined by Langmuir model with linear regression correlation coefficient 0.97.

Luffa fibers promises being a new adsorbent for removing dye from aqueous solution since it is renewable and sustainable and shows adsorption capacity as what were investigated by other researchers in the literature.

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