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Biosorption of Methyl Red: Parametric Optimization Using Response Surface Methodology

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***Abstract*- The removal of dyes from wastes has been the object of many researches in the past few years because of the potential toxicity of dyes and visibility problems. Conventional tertiary treatment techniques are having technical and/ or economical constrains. In the present investigation the potential use of wheat bran (an agricultural waste) as low cost biosorbent for removal of methyl red from water was studied. For this purpose a three-level three-factor fractional factorial Box-Behnken Design (BBD) of Response Surface Methodology (RSM) which leads to only 15 sets of sorption runs was conducted to study the influence of pH, initial metal ion concentration and temperature and their interactions on dye removal. The pH had negative and temperature and concentration had positive effect on uptake of dye. Very high value of regression coefficient (R-Sq = 99.8%) indicates an excellent evaluation of the experimental data by second-order polynomial regression model. The maximum removal of methyl red (91.5181 mg/g) was predicted using contour and optimization plots and can be achieved at pH 2.0, initial metal ion concentration 300 mg/L and temperature 40 °C.**

***Keywords*— Response Surface Methodology, Box-Behnken Design**

I. Introduction

One of the major causes of environmental pollution are the industrial effluents because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid [1]. The untreated disposal of this colored water into the aquatic environment causes damage to aquatic life as well as human beings by mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons [2,3]. Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation and ozonation [4]. However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams.

Biosorption has emerged as an alternative to traditional methods with advantage of being technically easy, and potential for regeneration and sludge free operation, eco friendly nature, excellent performance, and low cost domestic technique for remediating even heavily metal loaded water [5]. To avoid wastage of time and large experimental runs in the conventional method, Response surface methodology (RSM) is utilized in the sorption process which involves factorial search by examining simultaneous, systematic and efficient variation of important components. It helps to predict a model for the process, identify possible interactions, higher order effects and determine the optimum operational conditions [6,7]. The present investigation was to utilize wheat bran for the removal of methyl red dye from water and to optimize the parameters affecting the sorption for its maximum removal via Box-behnken RSM experimental design.

II. Materials And Methods

A. Batch sorption experiment

Batch experiments were carried out in Erlenmeyer flasks by adding wheat bran (100 mg) in 50 mL of aqueous dye solution of desired initial conditions. Initial pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution. The flasks were gently agitated in an electrically thermostated reciprocating shaker at 200 rpm for a period of 140 mins. The content of flask was separated from biosorbent by centrifuging at 15000 rpm and was analyzed for remaining dye concentration in the sample using UV-Vis spectrophotometer (Shimadzu, Japan, Model AA6300). The amount of dye sorbed per unit mass of the biosorbent (q_t in mg/g) was evaluated by using following equations;

$$q_t = (C_i - C_t) \times V / W \qquad (1)$$

where, C_i and C_t are the dye concentrations in mg/L initially and at a given time t, respectively; V is the volume of the dye solutions in mL; W is the weight of biosorbent in mg.

B. Response surface methodological approach

The sorption of dye was evaluated and optimized by three-level three-factor Box-Behnken Design (BBD) [8] using MINITAB® 15 software. The influence of three factors, pH (2, 4 and 6), initial dye ion concentration (100, 200 and 300 mg/L) and temperature (20, 30 and 40 °C) coded as – (low), 0 (central point or middle) and + (high) were employed, coupled to each other and varied simultaneously to cover the combination of variables in the box behnken design, on the removal of dye using wheat bran has been investigated. Uptake (mg/g) of dye was taken as response of the system. The number of experiments (N) required for the development of BBD can be calculated from equation N = 2k(k−1) +Co (k is number of factors and Co is the number of central points). Thus for a three factor design, consisting of 3 central points, a total of 15 experimental runs are required [9].

Data of dye removal using wheat bran was subjected to a second-order multiple regression analysis to explain the behaviour of the system using the least squares regression methodology to obtain the parameter estimators of the mathematical model:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j + \varepsilon \qquad (2)$$

where, Y = response, β0 is the constant, βi the slope or linear effect of the input factor Xi, βii is the quadratic effect of input factor Xi, βij the linear by linear interaction effect between the input factor Xi and ε is the residual term.

III. Results And Discussion

A. *Optimization of biosorption process using RSM approach*

The experimental design matrix obtained after running on Minitab® 15 software Box-Behnken design on the experimental data along with experimental and predicted responses (mg/g) is given in Table I.

TABLE I BOX-BEHNKEN DESIGN MATRIX OF THREE VARIABLES (UNCODED AND CODED VALUES) ALONG WITH EXPERIMENTAL AND PREDICTED RESPONSE (UPTAKE) (MG/G)

Run Order	pH	Concentration (mg/L)	Temperature (°C)	Experimental (mg/g)	Predicted (mg/g)
1	2 (-)	300 (+)	30 (0)	82.135	81.9474
2	6 (+)	300 (+)	30 (0)	13.020	10.9664
3	2 (-)	100 (-)	30 (0)	43.600	45.6538
4	6 (+)	100 (-)	30 (0)	8.500	8.6878
5	2 (-)	200 (0)	40 (+)	79.210	78.7906
6	6 (+)	200 (0)	40 (+)	15.350	16.7971
7	2 (-)	200 (0)	20 (-)	59.940	58.4931
8	6 (+)	200 (0)	20 (-)	12.120	12.5396
9	4 (0)	300 (+)	40 (+)	39.560	40.1669
10	4 (0)	100 (-)	40 (+)	22.680	21.0458
11	4 (0)	300 (+)	20 (-)	26.420	28.0544
12	4 (0)	100 (-)	20 (-)	9.210	8.6033
13	4 (0)	200 (0)	30 (0)	30.300	30.3001
14	4 (0)	200 (0)	30 (0)	30.300	30.3001
15	4 (0)	200 (0)	30 (0)	30.300	30.3001

1) *Interpretation of the regression analysis*:

The response surface regression results thus obtained from BBD namely the T and the P-values along with the constant and coefficients (estimated using coded values) are given in Table II.

TABLE II ESTIMATED REGRESSION COEFFICIENTS (USING CODED UNITS) FOR EXPERIMENTAL UPTAKE (MG/G)

Term	Coef	SE Coef	T	P
Constant	30.3000	1.1291	26.835	0.000
pH	-26.9869	0.6914	-39.030	0.000
Concentration (mg/L)	9.6431	0.6914	13.946	0.000
Temperature (°C)	6.1387	0.6914	8.878	0.000
pH*pH	11.8506	1.0178	11.644	0.000
Conc. (mg/L)*Conc. (mg/L)	-5.3369	1.0178	-5.244	0.003
Temp. (°C)*Temp. (°C)	-0.4956	1.0178	-0.487	0.647
pH*Conc. (mg/L)	-8.5038	0.9778	-8.696	0.000
pH*Temp. (°C)	-4.0100	0.9778	-4.101	0.009
Conc. (mg/L)*Temp. (°C)	-0.0825	0.9778	-0.084	0.936

The value of constant was significant and independent of factors, shows that average uptake of dye on wheat bran was 30.30 mg/g. The effect of all the linear, square and interaction terms of pH, concentration and temperature ($P < 0.05$) except for the quadratic term of temperature (P = 0.647) and interaction term of concentration and temperature (P = 0.936) was found to be highly significant on the removal of dye. Very high value of parameter estimate, for pH and relatively high values of coefficients of quadratic term of pH, concentration and interaction term of pH and concentration shows a high level of significance indicating the importance of these variables in the biosorption process. A positive sign of the coefficient represents a synergistic effect, while a negative sign indicates an antagonistic effect. The variable pH had a negative significant relationship with the biosorption process, while the quadratic terms of initial metal ion concentration and interaction terms of pH and concentration and pH and temperature are significant but less affecting the process. The variables initial metal ion concentration, temperature and quadratic term of pH have positive and significant effect. A model is proposed based on the regression coefficients (Table 4) for the biosorption of methyl red dye.

Y = 30.300 -26.9869*pH + 9.6431*conc. + 6.1387*temp. + 11.8506*pH2 -5.3369*conc.2 -0.4956*temp.2 - 8.5038*pH*conc. -4.0100*pH*temp. -0.0825*conc.*temp. (3)

where, Y is the response variable, predicted amount of dye adsorbed (mg/g). The low value of standard deviation (1.956) between the measured and predicted results which shows that the equation adequately represents actual relationship between the response and significant variables. High values of R^2 (99.8%) and R^2(adjusted) (99.3%) indicates a high dependence and correlation between the observed and the predicted values of response.

2) *Interpretation of Contour Plots*:

The contour plots (Fig. 1) shows the optimum uptake was achieved at pH of 2.0, initial metal ion concentration of 300 mg/L and temperature of 40 °C.

The results were also found to be in accordance with the experimental values.

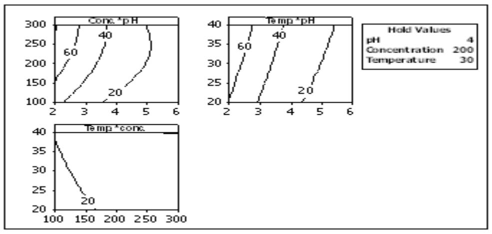

Fig. 1. Contour plots showing the interaction of parameters with uptake

3) Interpretation of Process Optimization Curve: The global solution (optimum condition), which is defined as the best combination of factor settings for achieving the optimum response, was found to be pH (2.0), initial metal ion concentration (300 mg/L) and temperature (40 °C) for a predicted response of 91.5181 mg/g with a desirability score of 0.99426 (Fig. 2).

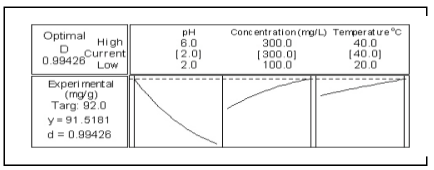

Fig. 2. Process Optimization curve for a target value of 92.0 mg/g

IV. Conclusion

Agricultural waste 'wheat bran' was found very potential for the removal of methyl red dye from aqueous solution. Box-Behnken RSM design was employed successfully to develop a mathematical model for the prediction of dye removal geometry from aqueous solution using wheat bran. The R-Sq value for the predicted model was found to be 99.8% that means there is a high correlation between the experimental and predicted values. The uptake of dye was found to be very sensitive to initial pH of solution, and was found to decrease with an increase in pH. However, there was a positive effect of initial metal ion concentration and temperature on the uptake. With the help of the contour and the optimization plots the predicted maximum removal of dye (91.5181 mg/g) was found to be achieved at pH (2.0), initial metal ion concentration (300 mg/L) and temperature (40 °C).

The predicted model can be used for the better removal of methyl red from aqueous streams by limited number of experiments.

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