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Modelling and Optimization of Dye Removal Process Using Hybrid Response Surface Methodology and Genetic Algorithm Approach

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Abstract

In the present study, an efficiently, economically, and eco-friendly green carbon biosorbent derived from the plant bio waste, *Acacia Arabica* fruit, was used to treat aqueous solutions containing a basic dye, Methylene Blue (MB). The effect of various process parameters such as temperature, pH of solution, initial dye concentration and biosorbent dosage on dye removal was studied by using experimental runs designed by Central Composite Design. The optimization studies were carried out by changing the temperature in the range of 293-323 K, pH between (6-11), initial dye concentration between (25-150 mg/l), and adsorbent dosage between (0.05-0.25g). Regression and ANOVA data was analysed to know the interaction effect of dye on the biosorbent. A hybrid RSM-GA based technique was successfully developed to model, simulate, and optimize the biosorption process. The performance of the RSM-GA method was found to be very impressive. Results proved that the prepared green carbon biosorbent was highly efficient and economical for Methylene Blue removal from aqueous solutions.

Keywords: Biosorption, Methylene blue, Acacia Arabica, Central composite design, Response surface Methodology, Genetic algorithm

Introduction

In recent times, most of the industries are applying dyes to their products to make them more attractable and valuable. Therefore, the global usage of dyes has been increasing tremendously and in turn caused discharge of large amounts of dyes into industrial effluents. Industries such as textile, paper, printing, food processing etc. are releasing various kinds of synthetic dyes directly into the environment. Due to its inherent characteristic nature, dyes if present in water bodies give abnormal brightness and make water anaesthetic. Dyes present in wastewater are carcinogenic and mutagenic to humans and other living things. Several studies highlighted the adverse effects of dyes such as skin irritation, eye blindness, dermatitis, nausea, respiratory problems, cancer etc [1]. Hence, removal of dyes from effluent water is of great concern. The complete removal of dyes from wastewater effluents is highly difficult since most of the dyes are stable to light, oxidation, heat and biologically non-degradable [2]. The conventional methods such as coagulation, flocculation, and membrane separation processes are not suitable for dye removal because of their complex nature and ability to survive in different process conditions. Moreover, these methods are expensive and produce large amounts of sludge [3-6].

Among various methods of dye removal, adsorption found to be very effective. Activated carbon is extensively used as adsorbent in most of the adsorption processes, however its high cost and difficulty in regeneration makes its usage restricted in most of the developing countries [7,8]. This drawback has prompted the researchers to develop an adsorbent from waste sources, mainly industrial or agricultural wastes. A number of adsorbents prepared from different waste materials have been studied for dye removal from aqueous solutions. However, most of them found to be not feasible to use in large scale because of economic and or technological considerations [8-13]. Thus, still there is a need to develop an efficient and low cost biosorbents for dye removal processes. Therefore, in this study, the potential and effectiveness of plant waste collected from *Acacia Arabica* fruits were examined as an alternative to the current expensive Activated Carbon for MB dye removal.

Modelling and simulation of biosorption process is very difficult as mechanism involved in biosorption processes is highly complex and it involves the interaction of more number of process variables in a non-linear way. The conventional classical methods do not describe the interaction effects of all the factors involved in biosorption process. In addition, this method is time consuming and requires large number of experimental runs to determine optimum levels. Response Surface Methodology (RSM) is used to develop, improve, and optimize different processes. RSM gives complete interaction effects of all the parameters influencing the process [14-16]. Hence, in this study, RSM was used to design the experimental runs to get more accurate model than traditional one factor method. The optimisation of the dye removal process was done by a novel hybridization of RSM and Genetic Algorithm (GA) method.

Materials and Methods

All the chemicals and Methylene Blue dye used in this study were procured from Coastal Enterprises, Visakhapatnam. Methylene blue dye was used directly without any further purification in this study. The glassware was thoroughly washed with de-ionized water prior to its use. All dye solutions used in this study were prepared freshly with de-ionized water and used immediately. The stock dye solution was prepared by dissolving accurately weighed amount of Methylene blue dye in deionised water in 500 ml volumetric flask. It was then diluted to the required concentrations of dye (25 mg/L-150 mg/L) by mixing with appropriate volumes of deionised water.

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Preparation of biosorbent

The *Acacia Arabica* fruit (AAS) used in this study was collected from the nearby forest of Visakhapatnam Steel Plant, Andhra Pradesh, India. The collected biomass was thoroughly washed with tap water until all the dirt was removed and then it was dried in sunlight for one week. At the end of one week, biomass was cut into small pieces and grounded in a commercial grinder. The finely grounded material was washed with de-ionized water until the entire colour of the material was removed. The resulted wet biomass was dried again in sunlight for three more weeks; and dried product was then screened into different sized particles and stored in air-tight containers kept in desiccators for further use.

Biosorption experiments

Batch biosorption experiments were carried out by adding known weight of biosorbent in 50 ml of dye solution of known concentration (25-150 mg/L) at desired temperature and pH values. After that, the solution was agitated at 150 rpm in an orbital shaker for the predetermined equilibrium time, then it was centrifuged at 4000 rpm for 15 min and the supernatant was carefully decanted. The dye concentration was measured spectrophotometrically at a maximum wavelength of 665 nm corresponding to Methylene blue. Similar procedure was adopted for conducting all other batch experimental runs by keeping the process variables at the values determined as per experimental design. The percentage of biosorption (% Removal) of dye from the aqueous solution was calculated using the following equation.

$$\%\,Biosorption = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

Where, C_i and C_f are the initial and final concentrations of the Methylene blue in aqueous solution, mg/L. All the experiments were done in triplicate and average values were used for all calculations. The optimization studies were carried out by changing the temperature between 293-323 K, solution pH between 6-11, initial dye concentration between 25-150 mg/L, and biosorbent dosage between 0.05-0.25 g.

Application of GA based RSM for optimization

Presently, application of Genetic Algorithm to the quadratic model of Response Surface Model and Artificial Neural Networks is becoming popular for the optimization of process parameters [17-19]. Genetic Algorithm performs the global search for finding the optimum value, whereas most of the other techniques give local optimum solution [20-22]. In the present study, the objective function f(x*, w) was selected by defining the independent variables vector as $x^* = [x_1^*, x_2^*, x_3^*, x_4^*]$, where x_1, x_2, x_3 and x_4 represents the chromosomes. The model developed from Response Surface Methodology was taken as fitness function of GA for optimization of process variables.

Results and Discussion

The effect of various process parameters such as temperature (x_1),

Experimental Run Number	Temperature, K	pH	Initial Dye Concentration, mg/L	Biosorbent Dosage, g	% Biosorption	
					Experimental	Predicted
1	0	0	-2	0	92.47	92.625
2	1	-1	1	1	86.54	85.324
3	1	1	1	1	87.95	87.212
4	0	0	0	0	88.54	88.540
5	1	-1	1	-1	82.32	82.779
6	0	-2	0	0	84.90	84.880
7	-1	-1	1	-1	84.25	83.968
8	-1	1	-1	-1	90.43	89.748
9	1	1	-1	-1	86.78	87.064
10	1	-1	-1	-1	85.84	85.621
11	1	1	1	-1	84.15	84.324
12	-1	-1	-1	-1	87.14	87.577
13	0	0	0	0	88.54	88.540
14	1	-1	-1	1	89.45	89.359
15	2	0	0	0	84.49	85.767
16	0	0	0	2	90.13	90.694
17	0	0	0	0	88.54	88.540
18	0	0	0	0	88.54	88.540
19	0	0	0	0	88.54	88.540
20	-1	1	-1	1	94.65	94.390
21	1	1	-1	1	91.85	91.144
22	0	0	0	-2	83.58	83.505
23	-1	-1	1	1	87.46	87.075
24	-1	1	1	-1	86.25	86.240
25	0	0	2	0	84.85	85.084
26	-2	0	0	0	89.79	90.202
27	0	0	0	0	88.54	88.540
28	-1	-1	-1	1	92.24	91.878
29	0	2	0	0	89.43	88.939
30	-1	1	1	1	89.86	89.691
31	0	0	0	0	88.54	88.540

Table 1: Experimental design matrix along with % Biosorption of Methylene blue dye.

solution pH (x_2), initial dye concentration (x_3) and biosorbent dosage (x_4) on biosorption of Methylene blue dye was studied by using full factorial rotatable Central Composite Design (CCD). A CCD with 31 experiments, which includes 16 cube point runs, 7 centre point runs and 8 axial point runs, was used for the optimization of process parameters for removal of Methylene blue dye from wastewater solution. Range of variables used in this design was determined based on preliminary experiments done (not shown here). The levels of all independent process variables representing the different experimental conditions in coded form and results obtained are shown in Table 1.

The main effects of each of the parameter on Methylene blue dye biosorption by keeping other variables at their middle values are shown in Figure 1. From the Figure 1 it is evident that percentage of dye removal was decreased with increasing temperature. This trend indicates the exothermic nature of the Methylene blue biosorption on AAS powder. The effect of solution pH is extremely important when the biosorbent is capable of ionizing at a given pH. The plot of percentage biosorption of Methylene blue dye versus pH reveals that the basic conditions are favourable for Methylene blue dye removal process. Percentage biosorption of Methylene blue was increased with solution pH up to 8 and after that further increase of pH does not affect the sorption significantly. Solution pH influences both the biosorbent surface and dye chemistry in water. High values of percentage biosorption at increased solution pH values infers that at high pH values, the interaction between Methylene blue ions and biosorbent surface was high due to high attraction forces between opposite charges. Low values of percentage biosorption at low solution pH may be due to repulsive forces between similarly charged ions.

Initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous solution and biosorbent surface. Lower values of percentage of biosorption at high concentrations may be due to the saturation of the sorbed sites on the biosorbent. Biosorption dosage determines the capacity of an biosorbent at the given initial concentration of dye. Increased biosorbent amount increased the percentage removal of dye, however beyond 0.2 g the increase in dye biosorption was drastically attenuated, and finally the curve approached plateau. The reason for higher dye removal with increased amount of adsorbent may be attributed to increased available active sites. However, biosorbent amount above 0.2 g did not show appreciable change, this was due to the increase of unsaturated active biosorption sites. This increase of unsaturated sites was due to the decrease of available active sites per unit of dye molecules.

Response Surface Methodology was used to develop a mathematic model to represent all the correlations among various process parameters and percentage of biosorption of dye. Based on the experimental results obtained, the following second order quadratic equation was developed to model the interaction effects of all parameters involved in the current biosorption process.

$$Y=-174.905+1.522x_1+10.959x_2-0.304x_3+199.704x_4-0.002x_1^2-0.261x_2^2+0.000x_3^2-144.042x_4^2--0.019x_1.x_2+0.001x_1.x_3-0.375x_1.x_4+0.001x_2.x_3+1.370x_2.x_4-0.191x_3.x_4 \quad (2)$$

The predicted values of percentage removal of Methylene blue dye using the above equation 2 are given along with experimental data in Table 2. The efficiency of model in predicting the dye removal behaviour was evaluated by regression coefficients, standard error, t-values, *p*-values, correlation coefficient (R) and the determination coefficient, R^2 (Table 2). The value of determination coefficient (R^2=0.989) indicates that the response model can explain more than 98% of the total variations. The proposed model suggests that the solution pH and biosorbent dosage had a very strong effect followed by initial dye concentration and temperature. The developed model was further tested for its adequacy using ANOVA (Table 3). *P*-value of regression model equation from ANOVA implies that the developed mathematical model fitted well to the experimental data. From the ANOVA values, it is evident that linear and quadratic effects were highly significant compared to interaction effects. The graphical representations of the regression equation -2 were shown by the 3D response surface graphs in Figures 2-7.

The RSM-GA based optimization process was initialized with 20 randomly selected chromosomes. The fitness of each chromosome was evaluated by objective function. Selection, recombination, mutation and cross over operators are performed on the best chromosomes of

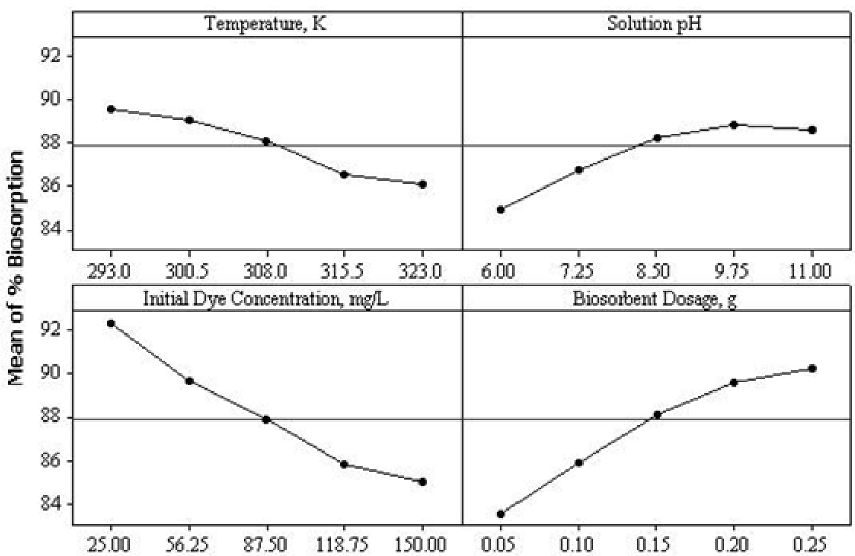

Figure 1: Main Effects Plot of % Removal of Dye.

Term	Coef	SE Coef	T	P
Constant	-174.905	131.807	-1.327	0.203
x_1	1.522	0.832	1.829	0.086
x_2	10.959	3.426	3.198	0.006
x_3	-0.304	0.135	-2.244	0.039
x_4	199.704	84.560	2.362	0.031
x_1^2	-0.002	0.001	-1.843	0.084
x_2^2	-0.261	0.048	-5.409	0.000
x_3^2	0.000	0.000	1.044	0.312
x_4^2	-144.042	30.142	-4.779	0.000
$x_1.x_2$	-0.019	0.011	-1.805	0.090
$x_1.x_3$	0.001	0.000	1.905	0.075
$x_1.x_4$	-0.375	0.269	-1.396	0.182
$x_2.x_3$	0.001	0.003	0.254	0.802
$x_2.x_4$	1.370	1.612	0.850	0.408
$x_3.x_4$	-0.191	0.064	-2.959	0.009

Table 2: Response Surface Regression for removal of Methylene blue dye.

Source	DF	Seq SS	Adj MS	F	P
Regression	14	228.529	16.32350	100.53	0.000
Linear	4	217.032	0.92928	5.72	0.005
Square	4	8.512	2.12803	13.11	0.000
Interaction	6	2.985	0.49743	3.06	0.034
Residual Error	16	2.598	0.16238		
Lack-of-Fit	10	2.598	0.25981		
Pure Error	6	0.000	0.00000		
Total	30	231.127			

S = 0.4030, R-Sq = 98.9%, R-Sq (adj) = 97.9%

Table 3: Analysis of Variance for Removal of Methylene blue dye.

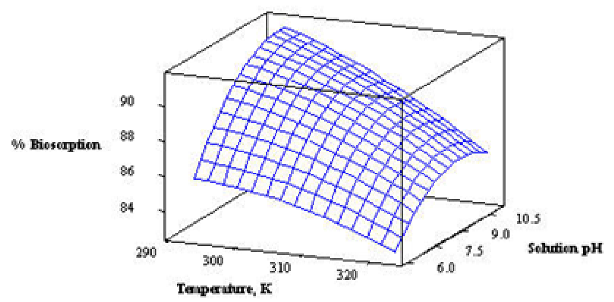

Figure 2: Response Surface Plot of Solution pH Vs temperature.

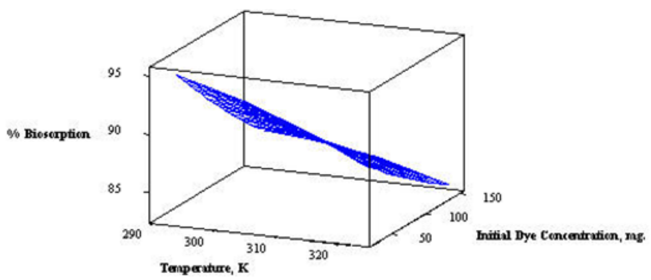

Figure 3: Response Surface Plot of temperature Vs initial dye concentration.

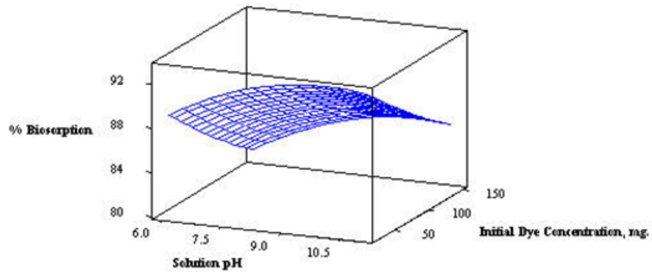

Figure 4: Response Surface Plot of initial dye concentration Vs Solution pH.

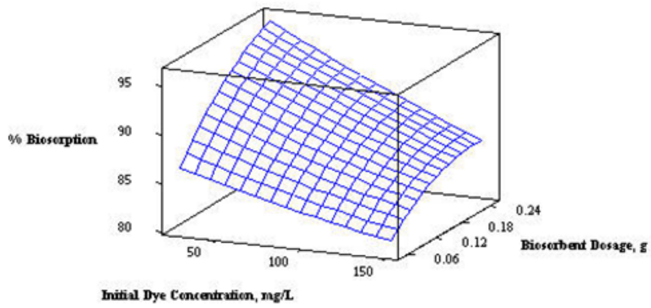

Figure 5: Response Surface Plot of biosorbent dosage Vs initial dye concentration.

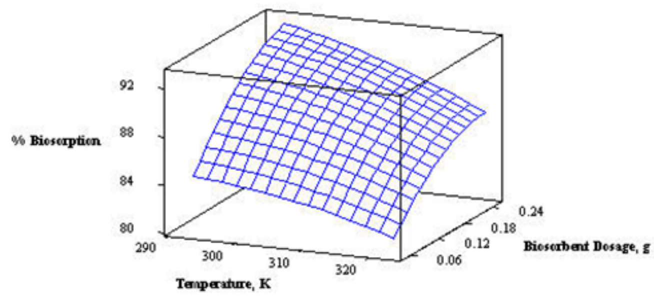

Figure 6: Response Surface Plot of biosorbent dosage Vs temperature.

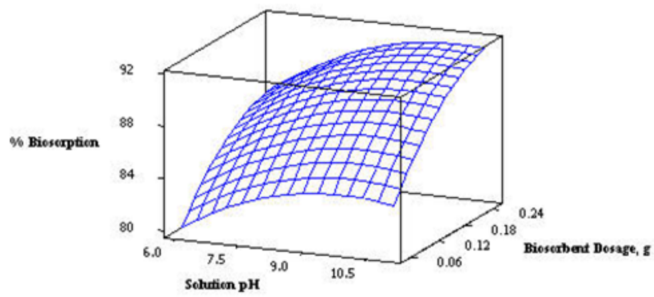

Figure 7: Response Surface Plot of biosorbent dosage Vs Solution pH.

each generation to create new population. This procedure was repeated until an optimized solution was achieved. The simulation of genetic optimization was performed with maximum 100 generations of GA and best fitness plot is shown in Figure 8. Initial population of size 20 was created randomly by choosing constraint dependent creation function. The rank fitness scaling function was used to fit an individual based on raw scores. Stochastic uniform selection function, constraint dependent mutation, and scattered crossover function, were used to lay out a line, adding random number and creation of binary vectors respectively. Forward direction migration with fraction of 0.2 and interval of 20 was

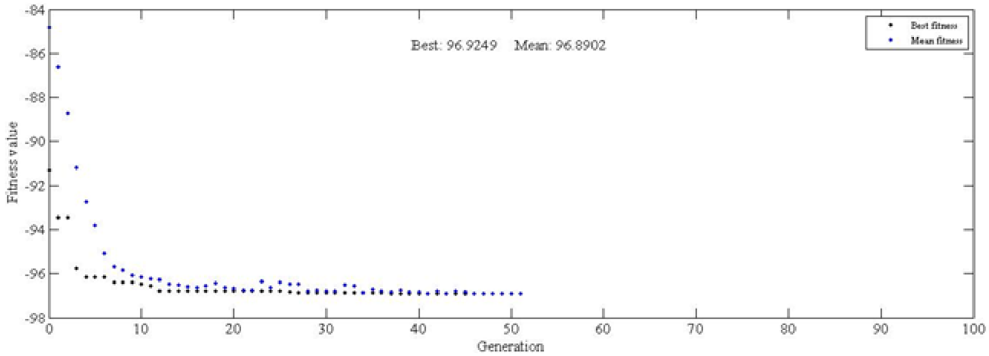

Figure 8: Best fitness plot of RSM-GA optimization.

used for migration towards the last sub population. Optimization of Methylene blue dye removal using Genetic Algorithm was performed to find the local optimum process conditions in a feasible region by incorporating lower and upper bounds for the input variables. RSM based GA optimization has resulted maximum dye removal of 96.9% at a temperature of 300C, solution pH of 9.98, initial Methylene blue concentration of 25 ppm, and AAS amount of 0.2 g. The performance of the RSM-GA method was found to be very impressive. The results indicated that the proposed RSM based GA method has exhibited high percentage of Methylene blue removal values.

Conclusion

A locally obtainable, abundantly available, eco-friendly biosorbent prepared from waste plant biomass, *Acacia Arabica* fruit, has been examined for Methylene Blue removal from aqueous solutions. A highly efficient Response Surface Model was successfully developed to model, and to simulate the Methylene blue dye removal process. The results clearly show that percentage of Methylene blue biosorption was significantly influenced with pH, biosorbent dosage, and initial dye concentration. However, the influence of temperature at 95% confidence level is modest. The results showed that the predicted values well fitted to the experimental values, which was also supported by the relatively high R2 (0.985) value. Optimization experiments reveals that maximum percentage of biosorption of dye of 96.9% was achieved at a temperature of 303 K, pH of 9.98, Initial MB concentration of 25 ppm, and AAS dosage of 0.2 g. The performance of the RSM-GA method was found to be very impressive. The results indicated that the proposed RSM based GA method has exhibited high percentage of biosorption of Methylene blue. From these studies, it may be concluded that green carbon biosorbent prepared is highly efficient and economical for Methylene Blue removal from aqueous solutions.

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