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Scale-up of a dye adsorption process using chemically modified rice husk: optimization using response surface methodology

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ABSTRACT

This article extends our previous study on malachite green (MG) adsorption using chemically modified rice husk at shake flask level, by investigating the scale up of the dye adsorption process to a laboratory level stirred batch reactor. Response surface methodology (RSM) was employed to investigate the effect of different operating conditions on the uptake of MG. A two level three factor (2^3) full factorial central composite design (CCD) with the help of Design Expert Version 7.1.6 (Stat Ease, USA) was used for the optimization of the adsorption process and to evaluate the effects and interactions of process variables: initial solution pH (4.0–10.0), initial dye concentration (100–500 mg/l), and adsorbent dose (10–50 g/l). Multiple response optimization was applied to the experimental data to discover the optimal conditions for a set of response, simultaneously, by using a desirability function. The optimum conditions for MG adsorption were found to be 8.30, 500 mg/l and 29.31 g/l respectively, for initial solution pH, initial dye concentration and adsorbent dose. Under these conditions, the removal efficiency was found to be 90.83%.

Keywords: Adsorption; Rice husk; Malachite green; Stirred batch reactor; Central composite design; Response surface methodology

1. Introduction

The contamination of water bodies by synthetic dye stuffs is considered to be a global environmental problem in recent years. It is well recognized that their existence in aquatic ecosystem is accountable for causing several damages to the environment and can have adverse effects on many forms of life [1].

Malachite green (MG) is one of the most widely used dye for coloring purposes. It is extensively used in textile industries for dyeing nylon, wool, silk, leather, and cotton [2]. It is also used as a food coloring agent, food additive, and a medical disinfectant and anthelminthic [3]. It also finds application as an antifungal agent in the fish farming industry due to its high effectiveness against parasitic treatment, and fungal and bacterial infections in fish and fish eggs. As such, a considerable amount of the used dye enters the natural environment through wastes resulting in colored effluents. The discharge of MG into the aquatic ecosystem has generated much concern due to its reported genotoxic, mutagenic, teratogenic and carcinogenic effects [4]. The dye is highly cytotoxic and carcinogenic to mammalian cells and acts as a liver tumor promoter. It decreases food intake capacity, growth and fertility rates; causes damage to liver, spleen, kidney and heart; inflicts lesions on skin, eyes, lungs and bones [4]. MG is also environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals [4]. It promotes hepatic tumor formation in rodents and also causes

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reproductive abnormalities in rabbits and fish [5]. Discharge of MG into the hydrosphere can even cause environmental degradation as it gives undesirable color to water and reduces sunlight penetration [5]. Therefore, effective treatment of MG bearing effluents prior to discharge into receiving water bodies is of great importance for human health and also for the protection of water resources.

Adsorption using low-cost adsorbents is considered to be the most effective and economic method to treat dye-bearing effluents, offering advantages over conventional treatment processes such as simplicity of design, low initial cost, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions [6–9]. A number of non-conventional low-cost adsorbents, including natural materials, and waste/by-products from agriculture and industry, have been proposed by several workers as effective adsorbents for the removal of dyes from their aqueous solutions [10,11]. Likewise, our previous study suggests that rice husk; a readily available agricultural waste material could be employed as a cost-effective adsorbent in chemically modified form for the removal of hazardous malachite green (MG) from aqueous solutions [12]. To apply this low-cost adsorbent in an industrial process, scale-up studies need to be performed. Therefore, the present work extends our previous investigation on MG adsorption by considering the dye adsorption process in a stirred batch reactor (SBR) for scale-up purposes.

In most of the reported batch adsorption studies, effect of individual parameter on the adsorption process has been investigated maintaining other process parameters such as initial solution pH, adsorbent dose, initial adsorbate concentration, temperature etc constant at unspecified levels [13]. This approach does not depict the combined effect of all the process parameters. Moreover, for scale up studies, this approach is time consuming, requires a number of experiments to determine the optimum levels (which may be unreliable) thereby elevating the overall cost of the process. These limitations can be eliminated by optimizing all the process parameters collectively by statistical experimental design such as response surface methodology (RSM). RSM is a combination of mathematical and statistical techniques used for developing, improving and optimizing the processes and to evaluate the relative significance of several process parameters even in the presence of complex interactions [13,14]. The primary objective of RSM is to determine the optimum operational conditions of the process. RSM offer certain advantages like higher percentage yield, reduced process variability, closer confirmation of output response to nominal and target achievement [14].

Therefore, the aim of the present work was to conduct MG adsorption onto chemically modified rice husk in a SBR for scale-up purpose and to investigate the combined effect of various process parameters like initial dye concentration, pH of the solution and adsorbent dose on MG removal using central composite design in response surface methodology (RSM).

2. Experimental

2.1. Preparation of adsorbate solutions

Malachite green used in this study was of commercial quality (CI 42000, FW: 365, MF: $C_{23}H_{25}N_2Cl$, λ_{max}: 618 nm) and was used without further purification. Stock solution (1000 mg/l) was prepared by dissolving accurately weighed quantity of the dye in double-distilled water. Experimental dye solution of different concentrations was prepared by diluting the stock solution with suitable volume of double-distilled water. The initial solution pH was adjusted using 0.1 (N) HCl and 0.1 (N) NaOH solutions.

2.2. Preparation of adsorbent

Rice husk used in this study was obtained from a rice mill in Durgapur, West Bengal, India. The adsorbent was prepared by following the procedure given in paper [12]. The characterization of the adsorbent has been reported elsewhere [15].

2.3. Experimental setup

All experiments were conducted in 5 l capacity indigenously designed rectangular glass reactor having 28.4, 17.9 and 11.2 cm length, width and depth respectively. Temperature fluctuations in the reactor were within ± 1K. The reactor was closed by a detachable glass cap with different openings that enabled the introduction of the adsorbent. The reactor was equipped with a paddle agitator.

2.4. Optimization of adsorption process by response surface methodology

The optimization of MG uptake was carried out by three chosen independent process variables including pH of the solution, initial dye concentration and adsorbent dose. The ranges and levels of variables investigated in the research are given in Table 1. The percent removal of MG was taken as response of the system. The quadratic equation model for predicting the optimal point was expressed according to Eq. (1):

Table 1
Experimental range and levels of independent process variables

Independent variable	Range and levels (coded)				
	−α	−1	0	+1	+α
pH (A)	1.95	4.00	7.00	10.00	12.05
Initial dye conc., mg/l (B)	36.36	100.00	300.00	500.00	636.36
Adsorbent dose, g/l (C)	3.64	10.00	30.00	50.00	63.64

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1} \sum_{j=1+1} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where Y response (dependent variable); β_0 constant coefficient; β_i, β_{ii}, β_{ij} coefficients for the linear, quadratic and interaction effect; x_i, x_j factors (independent variables); ε error.

Three factors were studied and their low and high levels are given in Table 1. Percentage removal of MG was studied with a standard RSM design called the central composite design (CCD). Twenty experiments were conducted in duplicate according to the scheme mentioned in Table 2. Design Expert Version 7.1.6 (Stat Ease, USA) was used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The variability in dependent variables was explained by the multiple coefficient of determination, R^2 and the model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range.

2.5. Adsorption studies

Adsorption experiments were carried out in 5 l SBR by adding a desired quantity of chemically modified rice husk in 3.5 l of aqueous dye solution of desired initial concentration and pH. The reactor was operated in batch mode at 303 K and continuously stirred at 200 rpm for predetermined time (180 min). All experiments were performed as per the design expert software. The residual amount of dye in the reactor was investigated using UV/VIS spectrophotometer (Model Hitachi – 2800). The response or percent removal (%) of MG was calculated using the following equation:

$$R(\%) = \frac{C_i - C_0}{C_i} \times 100 \quad (2)$$

Table 2
Central composite design for three independent variables used in this study along with the observed response

Run no.	Coded values			Real values			Percent removal (%) of MG
	A	B	C	A	B	C	
1	−1	−1	−1	4.00	100.00	10.00	25.57
2	+1	−1	−1	10.00	100.00	10.00	85.69
3	−1	+1	−1	4.00	500.00	10.00	2.48
4	+1	+1	−1	10.00	500.00	10.00	63.74
5	−1	−1	+1	4.00	100.00	50.00	63.36
6	+1	−1	+1	10.00	100.00	50.00	100
7	−1	+1	+1	4.00	500.00	50.00	49.58
8	+1	+1	+1	10.00	500.00	50.00	94.25
9	−α	0	0	1.95	300.00	30.00	3.56
10	+α	0	0	12.05	300.00	30.00	95.26
11	0	−α	0	7.00	36.36	30.00	100
12	0	+α	0	7.00	636.36	30.00	65.36
13	0	0	−α	7.00	300.00	3.64	29.76
14	0	0	+α	7.00	300.00	63.64	93.69
15	0	0	0	7.00	300.00	30.00	95.46
16	0	0	0	7.00	300.00	30.00	95.47
17	0	0	0	7.00	300.00	30.00	95.46
18	0	0	0	7.00	300.00	30.00	95.47
19	0	0	0	7.00	300.00	30.00	95.46
20	0	0	0	7.00	300.00	30.00	95.46

where is C_i the initial dye concentration (mg/l) and C_0 is the final dye concentration in solution (mg/l).

3. Results and discussion

3.1. Response surface estimation for maximum removal of MG

The results of each experiment performed as per the software are given in Table 2. An empirical relationship between the response and the independent variables has been expressed by the following quadratic model.

$$\begin{aligned}\text{\% Removal of MG} = {} & 95.54 + 26.13\,A + 17.37\,B - 8.99\,C \\ & - 5.01AB + 1.15AC + 3.19BC \\ & - 16.74A^2 - 12.38B^2 - 4.97C^2\end{aligned} \quad (3)$$

The results of second-order response surface model in the form of analysis of variance (ANOVA) are shown in Table 3. The statistical significance of the model equation was evaluated by the *F*-test ANOVA. The significance of each coefficient was determined by *F*-values and *P*-values. It is observed from Table 3, the coefficients for the main and square effects were highly significant ($P < 0.0001$) in comparison with interaction effects. Table 4

Table 3
Regression analysis using the 2^3 factorial central composite design

Model term	Coefficient estimate	Standard error	*F*-value	*P*-value
A	26.13	0.74	1239.05	<0.0001
B	17.37	0.74	547.38	<0.0001
C	–8.99	0.74	146.72	<0.0001
AB	–5.01	0.97	26.68	0.0004
AC	1.15	0.97	1.40	0.2646
BC	3.19	0.97	10.82	0.0082
A^2	–16.74	0.72	536.22	<0.0001
B^2	–12.38	0.72	293.53	<0.0001
C^2	–4.97	0.72	47.38	<0.0001

Table 4
Analysis of variance (ANOVA) for the response surface quadratic model for MG removal

Source	Sum of squares	Degree of freedom (df)	Mean square	*F*-value	Probability >F
Model	20634.53	9	2292.73	304.58	<0.0001
Residual	75.28	10	7.53		
Lack of fit	75.28	5	15.06	1.915	0.1284
Pure error	0.000	5	0.000		
Total	20709.80	19			

R^2 = 0.9864; Adjusted R^2 = 0.9831; Predicted R^2 = 0.9720.

shows ANOVA for the response surface quadratic model. The *F*-value (304.58) with a low probability value (P < 0.0001) demonstrates a high significance for the regression model. The goodness of fit of the model was also checked by the multiple correlation coefficient (R^2). In this case, the value of the multiple correlation coefficient was 0.9864, which revealed that this regression is statistically significant and only 1.36% of the total variations is not explained by the model. The value of predicted multiple correlation coefficient (pred. R^2 = 0.9831) is in reasonable agreement with the value of the adjusted multiple correlation coefficient (adj. R^2 = 0.9720). The non-significant value of lack of fit (more than 0.05) showed that the quadratic model was valid for the present study [16,17].

3.2. Effect of initial solution pH and adsorbent dose

The combined effect of initial solution pH and adsorbent dose on MG removal is shown in the contour plot of Fig. 1. It is observed that percentage dye removal increased with increasing the amount of adsorbent as well as initial solution pH. This means

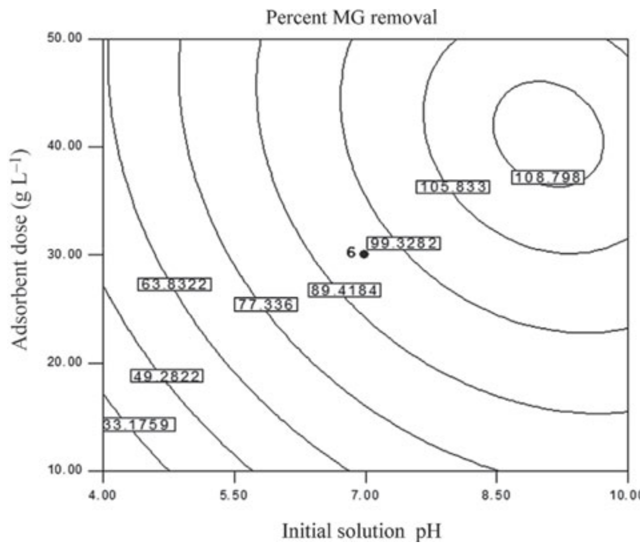

Fig. 1. Contour plot showing effect of pH and adsorbent dose on percent removal of MG.

that higher values of dye removal can be obtained by simultaneous increase in adsorbent dose and initial solution pH. The primary factor explaining this characteristic is that increasing adsorbent dose leads to increased adsorbent surface area and the availability of more sorption sites [2]. From this contour plot, a maximal removal efficiency of 100% was achieved at an initial solution pH of 7.24 and adsorbent dose of 33.39 g/l, while the initial dye concentration was set at the middle value.

3.3. Effect of initial solution pH and initial dye concentration

The effect of different levels of initial solution pH and MG dye concentration on chemically modified rice husk can be predicted from the contour plot as shown in Fig. 2. It is evident from Fig. 2 that both the independent variables had a strong influence on the dye sorption process. From this contour plot, a maximal removal efficiency of 100% was achieved at initial pH of 7.25 and initial dye concentration of 246.88 mg/l, while the other variable was set at the middle value. Solution pH affects the chemistry of the dye molecules, the activity of functional groups on the adsorbent surface as well as competition of dye molecules with hydrogen ions for the binding sites [18,19]. The functional groups on the rice husk surface are protonated at pH values lower than 4.0, and thereby restrict the approach of positively charged dye cations to the surface of the adsorbent. In the pH range of 4.0–7.0, these groups are negatively charged and the sorption process of MG then proceeds because of electrostatic attraction between the negatively

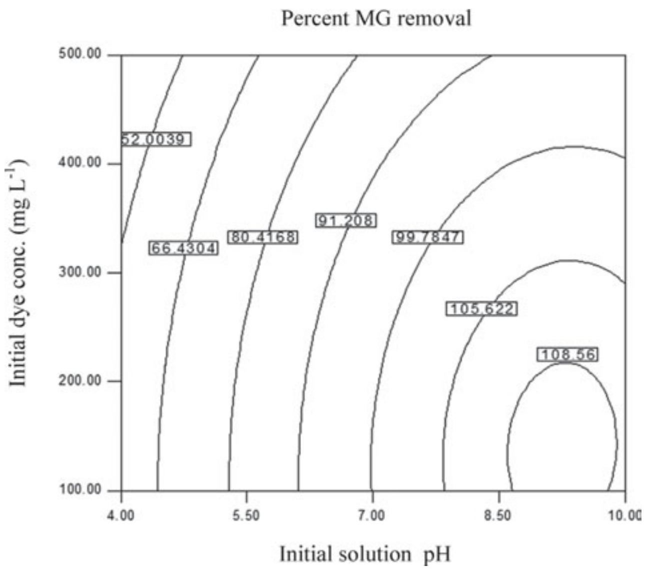

Fig. 2. Contour plot showing effect of pH and initial dye concentration on percent removal of MG.

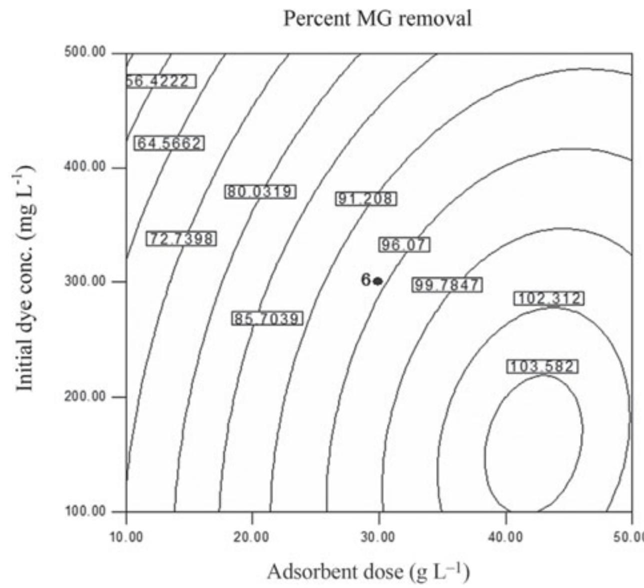

Fig. 3. Contour plot showing effect of adsorbent dose and initial dye concentration on the percent removal of MG.

charged adsorbent surface and the positively charged dye cations. The number of dye cations adsorbed at higher concentrations is more than that removed from less concentrated solutions. Higher dye concentrations enhance the mass transfer driving force and increase the dye cations adsorbed per unit weight of adsorbent at equilibrium.

3.4. Effect of adsorbent dose and initial dye concentration

The contour plot of Fig. 3 illustrates the interaction effects of the independent variables (adsorbent dose and initial dye concentration) on the response process. The initial dye concentration showed a little effect while a remarkable effect of adsorbent dose on the removal efficiency of MG is seen in Fig. 3. According to the contour plot of Fig. 3, removal efficiency of MG increased as the adsorbent dose increased. The primary factor explaining this characteristic is that increasing adsorbent dose leads to increased adsorbent surface area and the availability of more sorption sites. According to this figure, the maximal MG removal efficiency of 100% was obtained at an adsorbent dose of 31.07 g/l and initial dye concentration of 274.02 mg/l; at these maximal conditions the initial solution pH was set at the middle value.

3.5. Optimization using the desirability function

In numerical optimization, we chose the desired goal for each factor and response from the menu. The possible goals were: maximize, minimize, target, within range, none (for responses only) and set to an exact value (factors only). A minimum and a maximum level must be provided for each parameter included. A weight can be assigned to each goal to adjust the shape of its particular desirability function. The goals are combined into an overall desirability function. Desirability is an objective function that ranges from zero outside of the limits, to one at the goal. The program seeks to maximize this function. The goal seeking begins at a random starting point and proceeds up the steepest slope to a maximum. There may be two or more maximums because of curvature in the response surfaces and their combination in the desirability function. Starting from several points in the design space improve the chances for finding the 'best' local maximum [19,20]. A multiple response method was applied for optimization of any combination of four goals, namely initial solution pH, initial dye concentration, adsorbent dose and percentage removal of MG. The numerical optimization found a point that maximizes the desirability function. A minimum level of adsorbent dose (10 g/l), maximum level of initial dye concentration (500 mg/l), maximum percentage removal and the level of initial solution pH within the range of 4.0 to 10.0 were set for maximum desirability. The importance of each goal was changed in relation to the other goals. Fig. 4 shows a ramp desirability that was generated from 10 optimum points via numerical optimization. By seeking from 10 starting points in the response surface changes, the best local maximum was found to be at initial solution pH 8.30, initial dye

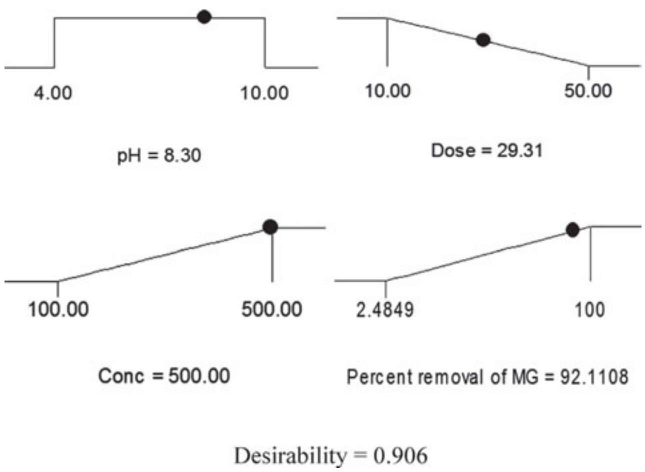

Fig. 4. Desirability ramp for numerical optimization of four goals, namely initial solution pH, initial dye concentration, adsorbent dose and percent removal of MG.

concentration of 500 mg/l, adsorbent dose of 29.31 g/l, MG removal of 92.11% and desirability of 0.906. The equilibrium time, agitation speed and temperature were 180 min, 200 rpm and 303 K, respectively. The obtained value of desirability (0.90) shows that the estimated function may represent the experimental model and desired conditions.

3.6. Confirmation experiments

To support the optimized data given by numerical modeling under optimized conditions, confirmatory experiments were conducted with the parameters as suggested by the model (pH 8.30, adsorbent dose 29.31 g/l, initial dye concentration 500 mg/l, temperature 303 K, equilibrium time 180 min and stirring speed 200 rpm) and the percent removal was found to be 90.83%.

4. Conclusion

The present study was taken with the aim of scale-up of the MG adsorption process onto chemically modified rice husk in a SBR and to investigate the combined effect of various process parameters on MG removal using response surface methodology. The initial solution pH, adsorbent dose and initial dye concentration significantly influenced the dye removal efficiency. Optimization conditions for the maximum removal efficiency of MG were obtained by applying a desirability function in RSM. The level of the three variable, initial solution pH, 8.30; initial dye concentration, 500 mg/l; adsorbent dose, 29.31 g/l, were found to be optimum for maximum MG removal. The corresponding removal efficiency in optimum conditions was found to be 90.83%.

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