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Optimization Study of Malachite Green Dye Adsorption by Eggshell Using Response Surface Methodology

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Abstract. Batch adsorption studies for the removal of Malachite green (MG) dye using eggshell was performed. Response Surface Methodology (RSM) was applied to investigate the effect of significant operating parameters on the uptake of the dye molecule. The aim of this study is to determine the potential of eggshell as adsorbent for MG removal and determine the optimum conditions for the adsorption process by using RSM with Central Composite Design (CCD). A 2^3 full factorial CCD was generated using Design Expert. The effects and interactions of different parameters were evaluated which are contact time (20-60 min), pH (4-8) and adsorbent dosage (0.5-2.0 g). A quadratic model was developed correlating the adsorption variables to the response (percentage of MG removal). Analysis of variance (ANOVA) was used to determine the significant factors on experimental design response. The predicted results obtained were found to be in good agreement (R^2 = 0.9388) with the experimental results. The optimum percentage of MG removal was found to be 90.66% with the operating conditions of 40 minutes contact time, pH 6 and 1.25 g of adsorbent dosage. It was suggested that eggshell could be a potential adsorbent in removing MG from aqueous solution.

Introduction

Malachite green (MG) is one of the popular dyes which is used extensively in distilleries for colouring purpose such as dyeing of cotton, silk, paper, leather, manufacturing of paints and printing inks. MG is not only highly toxic to flora and fauna but also has mutagenic and carcinogenic characteristics poses in human. Direct contact with MG either inhalation or ingestion can cause injuries to humans and animals. It can trigger the risk of cancer, which act as liver tumor-enhancing agent and cause severe adverse effect on nervous system, reproductive system, brain, liver and kidney etc. [1].

The discharge of dye wastewater is a big challenge because it is difficult to treat due to its inert properties. Among of existing technologies available for dye removal such as precipitation, coagulation, flocculation, filtration, chemical oxidation, membrane processes, electro dialysis etc., adsorption process was found to be the most effective, low capital cost and economical method for dye-bearing effluent treatment. Compared to other methods, adsorption process has a lot of advantages due to its simplest design, low cost and ease of operation, insensitivity to toxic substances as well as removal of pollutants completely even from dilution solutions [2]. There are various materials have been utilized as adsorbent for dye removal. However, these materials usually are high cost and involved complex preparation conditions as well as limit the practical promotion and application. Hence, with the purpose of achieving environmental sustainability, low-cost adsorbent can be developed from natural materials or waste materials, for instance eggshells, maize cob, rice husk, wheat straw, banana peels, pumpkin seed shell, and coconut husk. Moreover, these kinds of materials are cheap, easily available and low cost [3].

In the present study, eggshell is used as adsorbent due to its calcium carbonate content. Eggshell is the example of domestic waste or agricultural by-product that commonly available from hatcheries, homes, and restaurant or fast-food industries. Eggshell can be divided into calcified shell and shell membranes including inner and outer layer membranes. Basically, eggshell and shell membranes are taken over 10.2% of the whole egg. The composition of the eggshell is approximately consists of 94% calcium carbonate, 1 % magnesium carbonate and 1 % calcium phosphorous and 4% organic material. Meanwhile, the shell membrane comprises of protein, fat, moisture and ash with 69.2, 2.7, 1.5, and 27.2%, respectively [4]. Therefore, this present study aimed to evaluate MG removal potential of eggshell under various operating conditions such as contact time, pH and adsorbent dosage. The parameters for the optimum MG removal are optimized using Central Composite Design (CCD).

Materials and Methods

Preparation of Eggshell as Adsorbent. Eggshells were collected from Jeli district, Kelantan, Malaysia. The chicken eggshells were then washed a few times with the tap water to remove the dirt and egg yolk that stick to the eggshell membrane and then rinsed with distilled water. The eggshells were dried using oven to remove the water content. The temperature used was 60°C for 24 hours until the eggshells were completely dried. After that, it was grinded into powder form. Then, the eggshell powder was sieved using sieving machine to obtain a standard particle size (63 μm to 150 μm) of the eggshell powder. The eggshell powder was collected into airtight zipper bag and stored before further use.

Batch Adsorption Studies. A stock solution of 1000 mg/L MG dye was prepared. Required dilutions were made from stock solution to prepare solutions in the range of 0.5 – 10 mg/L for the calibration curve. The absorbance reading for each concentration of MG solution was determined using UV-Vis spectrophotometer (Thermo Scientific, Gynesis 20) at 617 nm wavelength. Batch adsorption studies were carried out using the eggshell to study the effect of contact time, pH and adsorbent dosage on the removal efficiency of MG. In the adsorption studies, there are several fixed variables used to create the appropriate condition for adsorption of malachite green. Constant parameters that were used in this study are agitation speed (150 rpm), room temperature, 50 mg/L of initial MG concentration and volume of MG solution (50 mL). The residual of MG concentration in the supernatant was determined using UV–Visible Spectrophotometer at 617 nm wavelength. The percentage of MG removal was calculated using Eq. 1. The data was then inserted in Design Expert software for analysis.

$$\text{Percentage of MG removal, Y (\%)} = \left(\frac{C_o - C_f}{C_o} \times 100\%\right) \quad (1)$$

where, C_o is initial concentration and C_f is final concentration of MG solution.

Experimental design and response surface methodology (RSM). A central composite design (CCD) was employed for determining the optimum operating parameters for MG removal. The goals for the variables were optimized within the studied range to investigate the combined effect of three independent variables, which are contact time, pH and adsorbent dosage on removal of Malachite green (MG). For contact time, the range was set at range of 20 minutes to 60 minutes. For pH, the range was set at the ranges of 4 to 8 whereas the adsorbent dosage was set at the range of 0.5 g to 2.0 g. In this study, three independent variables were investigated for the removal of MG, A, contact time (min), B, pH and C, adsorbent dosage (g). These variables have been considered as the factors that may influencing or potentially affect the adsorption response function. The ranges and levels of the variables were investigated. The factors levels with the corresponding real values are shown in Table 1. Statistical analysis was carried out to check the significant effect for the parameters. Analysis of the results involved the effect of parameters on both responses using 3D response surface graph and contour plot.

Table 1. Experimental design parameters with coded factor

Code	Variable	Unit	Actual Factors			Coded Factors		
			Low	Middle	High	Low	Middle	High
A	Contact Time	min	20	40	60	-1	0	+1
B	pH	-	4	6	8	-1	0	+1
C	Adsorbent Dosage	g	0.5	1.25	2.0	-1	0	+1

Results and Discussion

A total of 20 experimental runs were performed according to the experimental design using CCD obtained from Design Expert software is presented in Table 2. The response and the corresponding parameters have been modeled and optimized using analysis of variance (ANOVA), which has been used to identify significant variables. It was observed that the maximum percentage for removal of MG dye is 90.66% with the operating conditions of pH 6, 1.25 g of adsorbent dosage and contact time of 40 minutes. The lowest percentage for the removal of MG was determined at 63.73% with the operating parameters of pH 8, 0.5 g and 20 minutes.

Table 2. CCD design and its observed and predicted values

Run	Coded factor			MG removal (%)	
	A	B	C	Experimental	Predicted
1	0	0	0	87.48	86.85
2	0	0	0	83.84	86.85
3	0	0	0	86.38	86.85
4	0	+1	0	80.49	77.18
5	+1	-1	-1	71.73	70.27
6	0	0	0	90.66	86.85
7	-1	0	0	82.18	82.89
8	+1	+1	-1	67.04	66.94
9	-1	-1	-1	64.53	62.43
10	+1	+1	+1	79.72	81.73
11	+1	-1	+1	74.07	73.95
12	+1	0	0	89.34	89.02
13	-1	+1	+1	75.95	77.32
14	0	0	0	83.95	86.85
15	-1	-1	+1	64.89	64.89
16	0	0	0	89.57	86.85
17	0	0	-1	75.06	78.70
18	-1	+1	-1	63.73	63.75
19	0	-1	0	68.94	72.63
20	0	0	+1	90.57	87.32

Based on the data for MG removal in Table 2, quadratic model was generated by RSM as it is statistically significant for MG dye removal response (Y). The quadratic model is a second-order polynomial model containing linear and two-factor terms. Based on the quadratic model, the standard deviation for response surface quadratic model was 3.19. In this study, the R^2 for quadratic model is

0.9388. In statistical study, the closer the R^2 value to 1, the better the model will be. As this will give predicted value which are closer to the actual values for the response and the model are suitable to correlate with the experimental data [5, 6]. The R^2 of 0.9388 was considered relatively high and indicates that 93.88% of the variability in the response could be explained by the model. Therefore, it shows a good agreement between the experimental and the predicted values for percentage of MG removal.

The final empirical formula models for the response in term of coded factors are represented by Eq. 2. By referring to Eq. 2, the terms of coded factors can be used to make prediction about the response for given levels of each parameter. So, the coded equation is useful for identifying the relative impact of the parameter by comparing the coefficient [7]. In coded equation, a positive sign in front of the terms indicates synergistic effect, whereas a negative sign indicates antagonistic effect [6]. The factor of A, B, C, AC and BC show positive coefficients which indicate increasing of respective parameters will increase effect of response. While increasing the factor of AB, A^2, B^2 and C^2 will give negative effect to the response.

$$Y\ (\%) = 86.85 + 3.06\ A + 2.28\ B + 4.31\ C - 1.16\ AB + 0.31\ AC + 2.78\ BC - 0.90\ A^2 - 11.95\ B^2 - 3.85\ C^2 \quad (2)$$

ANOVA for the quadratic model of MG removal by eggshell is shown in Table 3. In ANOVA table, the sum of squares, degree of freedom (df), mean square, F value and p-value was calculated among each of the parameters and the interaction of two different parameters. In the experimental design, the significance of every source of variation was determined by p-value. If the value of p-value is less than 0.05, it indicates that the result data is not random and the model terms are statistically significant [8]. From the table, the F value of 17.05 and value "Prob > F" of 0.0001 implies the model was significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.05 indicates model terms are significant. In this case A, B, C, BC and B^2 are significant model terms. Non-significant lack of fit is desired in the design; therefore, the response was fit well to the model.

Table 3. ANOVA analysis for MG removal using eggshell.

Term	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remarks
Model	1557.29	9	173.03	17.05	< 0.0001	significant
A-Contact Time	93.80	1	93.80	9.24	0.0125	significant
B-pH	51.81	1	51.81	5.11	0.0474	significant
C-Adsorbent Dosage	185.79	1	185.79	18.31	0.0016	significant
AB	10.79	1	10.79	1.06	0.3267	not significant
AC	0.75	1	0.75	0.074	0.7914	not significant
BC	61.67	1	61.67	6.08	0.0334	significant
A^2	2.23	1	2.23	0.22	0.6491	not significant
B^2	392.47	1	392.47	38.68	< 0.0001	significant
C^2	40.68	1	40.68	4.01	0.0731	not significant
Lack of Fit	61.59	5	12.32	1.54	0.3226	not significant

Fig. 1 shows three-dimensional (3D) response surface of combined effect of contact time (min), pH and removal of MG at actual factors keeping adsorbent dosage at 1.25 g. The percentage removal of MG was increased slightly with the increasing of contact time from 20 minutes to 60 minutes. The percentage of MG removal was increased with the increase in pH from 4 to 6 and decreased with further increase of pH from 6 to 8. Maximum adsorption is observed at 89.02% in conditions of 60 minutes and pH 6 with constant adsorbent dosage (1.25 g) which also found similar with previous studies [9].

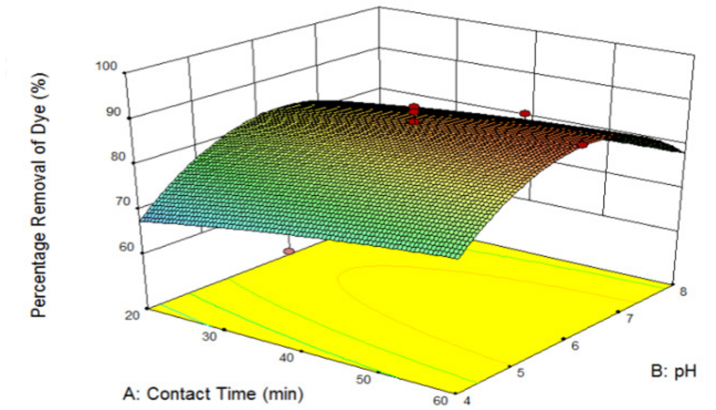

Fig. 1. Response surface plot of combined effect of contact time (min) and pH on the removal of MG

Response surface plot of combined effect of pH, adsorbent dosage (g), and removal of MG at constant parameter of 40 minutes contact time is illustrated in Fig. 2. There is a gradual increase in adsorption of MG dyes with the increase of pH from 4 to 6 and decreased when pH increases to 8. Increase in adsorbent dosage (0.5 g to 1.8 g) has a positive impact on adsorption percentage. Maximum adsorption is noted at 88.30% in conditions of pH 6 and 1.8 g of adsorbent dosage while keeping constant contact time at 40 minutes.

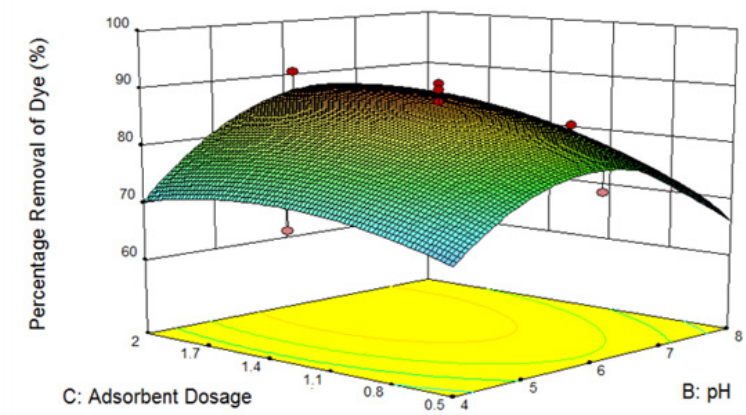

Fig. 2. Response surface plot of combined effect of pH and adsorbent dosage (g) (min) on the removal of MG.

Summary

The response surface modelling was successfully combined with central composite design (CCD) to determine the effect of process parameters, such as contact time, pH and adsorbent dosage on the removal of MG. The results revealed that a second-order polynomial regression model was capable of accurately predicting the experimental data with R^2 of 0.9388. The optimum percentage removal of MG dye was found to be 90.66% with the conditions of contact time in 40 minutes, pH 6 and 1.25 g of adsorbent dosage. This present study has shown that RSM with employing CCD provides a reliable and accurate methodology in optimizing adsorption process for the removal of MG from aqueous solution. Eggshell can be effectively used as an adsorbent for the removal of Malachite green (MG) from aqueous solutions.

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