ARPN Journal of Engineering and Applied Sciences

OPTIMIZATION OF OPERATING PARAMETERS BY RESPONSESURFACE METHODOLOGY FOR MALACHITE GREEN DYE REMOVAL USING BIOCHAR PREPARED FROM EGGSHELL

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ABSTRACT

This study focuses on the adsorption of malachite green (MG) dye using eggshell biochar as adsorbent. Agricultural waste of eggshell turned into low cost and eco-friendly biochar adsorbent was studied. Central Composite Design (CCD) was successfully employed for the experimental design and results analysis. The effect of initial concentration (30-70 mg/L), adsorbent dosage (0.5-2.0 g) and contact time (5-20 min) on the percentage of malachite green (MG) dye removal was investigated and optimized using response surface methodology (RSM). From the analysis of variance (ANOVA), the contribution of quadratic model is significant for the response in this study. The results showed that the response of dye removal was significantly affected by the synergistic effect of the linear term of initial concentration, adsorbent dosage and contact time and the quadratic term of initial concentration. The optimum removal efficiency of 92.39% was obtained with the optimal operating conditions of initial concentration of 70 mg/L, adsorbent dosage of 1.99g and contact time of 16.25 minutes, and desirability of 0.998. Good agreement was found between both the experimental results and predicted values and the suitability of the model was confirmed to predict the adsorption process. Eggshell biochar was found to be effective in removing MG dye from aqueous solution.

Keywords: eggshell biochar, adsorption, malachite green, response surface methodology.

INTRODUCTION

Nowadays, water pollution has become one of the most dangerous threats to the environment in today's world. There are various ways of polluting water and the most common way is the discharge of industrial wastewater through spillage into water bodies. Recently, progress in industrialization in different types of industries including textile, leather, paper, printing, dyestuff, plastic and others have been producing a large amount of wastewater with colour into the environment. Textile industries use dyes or pigments in their operational process to produce their products. Approximately 12% of synthetic textile dyes used each year are lost during the manufacture and processing operation and 20% of these dye will be released to the environment as effluents (Rajeshkannan *et al.*, 2010).The wastewater containing synthetic dyes from industries causes pollution to the rivers and consequently harm to humans and other living organisms, especially aquatic life (Belay & Hayelom, 2014). Effluent from the textile industries could enter the water supply, resulting in exposure to the general public through recreational activities and drinking water.Some dyes can cause allergic dermatitis, skin irrigation, and cancer and gene mutation in living organisms (Rajeshkannan *et al.*, 2010).

Malachite green (MG) is an organic compound that is used in various industries as dyestuff, a triarylmethane dye. This compound has no relation with the mineral malachite. It is called malachite green due to the similarity of colour between them. In actual form, malachite green refers to the chloride salt that has the chemical formula of $(C_6H_5C(C_6H_4(CH_3)_2)_2)Cl$. MG is most widely used for colouring among all other dyes of its category. It is extensively used in the textile and fish farming industries as a biocide. MG is a popular cationic dye for materials such as leather, silk, wool, jute, ceramics, cotton, acrylic fibers, and paper (Makeswari& Santhi, 2013). MG and its reduced form, lecomalachite green, may persist in edible fish tissues for an extended period of time (Shedbalkar & Jadhav, 2011).MG also affects the immune and reproductive system in human beings and has toxic effects on aquatic life following acute or chronic exposure. Since this dye poses significant health affects to humans and the aquatic life, it is quite important to establish a colour removal technique which is effective and inexpensive such as the adsorption technique(Sartape *et al.*, 2014).

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, adsorption, ozonation, electrochemical techniques and fungal decolonization (Santhi *et al.*, 2010). However, some of the chemical based methods are found to be the cause of byproduct pollution, expensive and inefficient, especially when treating wastewater with a low concentration of dye. Among these methods, adsorption technique is being considered as one of the most effective and low cost applied techniques for the decolourization of dye from industrial effluents. Besides, adsorption technique is economically favorable and technically easy to separate as the requirement of the control system is minimal (Renge*et al.*, 2012).

An effective alternative method which is biosorption using agricultural waste has been more favorable in recent years. A number of alternative low cost adsorbents materials have been studied for the removal of malachite green from wastewater. They are inexpensive, efficient and practical to be utilized (Putra *et al*., 2014). Low cost adsorbents such asrubber seed coat based activated carbon (Idris *et al.*, 2011), corn cob coke (Anupama & Subbarao, 2014), tamarind seed (Rajeshkannan *et al*., 2011), orange peel (Laxmi, 2013), and lime peel activated carbon (Ahmad *et al.*, 2015) have been studied for MG adsorption. The application of agriculture waste as adsorbent for the removal of MG has many advantages such as available in large quantity, renewable in nature, eco-friendly and low-cost.

Biochar from eggshell is one of the low cost adsorbent and readily available materials in most countries that have the potential for the adsorption of MG from aqueous solution. Eggshells contain a network of protein fibers, associated with crystals of calcium carbonate (96% of the shell weight), calcium phosphate (1%) and magnesium carbonate (1%) and some organic substances and water (Oliveira *et al.*, 2013). The thermal treatment for eggshell in producing biochar would increase the surface pore of the eggshell which is able to increase the adsorption process. The conversion of the eggshell wastes into biochar will reduce waste disposal and also turn these wastes into a value-added product. According to Rohaizar*et al*. (2013), by using the adsorption process with eggshells, it will not produce chemical sludge, hence there is no byproduct pollution and it is more efficient and easy to be carried out compared to other methods.

Yang*et al*. (2014) have reported that the bamboo biochar was successfully proven as an effective low- cost adsorbent for removing metal-complex dye acid black 172 from aqueous solutions. Even at a very high $NaNO_3$ concentration, the adsorption capacity of biochar for this dye appeared to be less affected by ionic strength. The effectiveness and mechanisms of dye adsorption on a straw-based biochar have been studied by Qiu *et al*. (2009). They reported that the high surface area and proper microporous structure of biochar made it an effective adsorbent for both cationic and anionic dyes. Biochar can be readily prepared along with its cost-effectiveness which may be an excellent substitute for activated carbon in dye water treatment.

Optimization study using response surface methodology (RSM) is an experimental design that aims to reduce the cost of expensive analysis. RSM is a collection of statistical and useful mathematical techniques for developing, improving and optimizing process. Recently, RSM has been applied to optimize and evaluate interactive effects of independent factors in numerous chemical and biochemical process.RSM is also used to evaluate the relative significance of several process parameters in the presence of complex interactions. The main objective of RSM is to determine the optimum operational conditions of the process or a region that satisfies the operating specification. Besides that, RSM is considered as an efficient, cost effective method to model and optimize bioprocess as it enables researcher to identify interactions between different study parameters with few possible experiments (Jain*et al.*, 2011).

RSM is one of the most popular used methods in experimental design for the study of biosorption literature for heavy metal removal and dye removal (Ngoh*et al.*, 2015; Ghorbani & Kamari, 2016; Sadhukhan *et al*., 2016). This methodology is widely applied in industries such as the food industry, chemical and biological processes, for the aim of either producing high quality products or operating the process in a more economical way and ensuring the process in a more stable and reliable way (Sudamalla*et al.*, 2012).

The present study is aimed at removing MG dye from wastewater using eggshell biochar as adsorbent by employing central composite design (CCD) in response surface methodology (RSM) Design Expert software version 7.0. The major investigation in this study includes optimization of the influencing factors (initial concentration, adsorbent dosage and contact time) on the response of removal efficiency of MG. RSM was selected to elucidate the simultaneous effects of operating parameters on the adsorption process. The optimized conditions developed from the model were validated using experimental results and the feasibility of eggshell biochar for the adsorption of MG was obtained.

MATERIALS AND METHODS

Chemicals: MG was purchased from Bendosen. Distilled water was used in the preparation of all solutions. The chemical formula of MG is $C_{23}H_{25}N_2Cl$ with molecular weights of 364.91 g/mol. All chemicals were used without any purification.

Preparation of adsorbent: Eggshells were collected from the Jeli district, Kelantan, Malaysia. The chicken eggshells were then washed a few times with tap water to remove the dirt and egg yolk sticking to the eggshell membrane and then rinsed with distilled water. The eggshells weredried using an ovento remove the water content. The oven temperature used was60^{o}C for 24 hours until the eggshells were completely dried. After that, they were grinded to powder form using a grinder. Then, the eggshell powder was sieved using a sieving machine to obtain a standard particle size (63μm to 150μm) of the eggshell powder. The eggshell powder was heated in a muffle furnace at 600^{o}C for 2 hours. When the eggshell powder was completely turned into a dark grey colour, the biochar powder was collected into an airtight zipper bag and stored in a dry environment before further use.

Preparation of stock solution and calibration curve: The stock solution of 1000 mg/L MG dye was prepared. Required dilutions were made from the stock solution to prepare solutions in the range of 0.5 – 50 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 study: Batch adsorption studies were carried out using the eggshell biochar to study the effect of initial concentration of MG, adsorbent dosage and contact time on the removal efficiency of MG. In the adsorption studies, there are several fixed variables used to create the appropriate condition for the adsorption of malachite green. Constant parameters that were used in this study are agitation speed (150rpm), pH 7 and volume of MG solution (50mL). The purpose of agitation during adsorption is to increase the kinetic movement of both adsorbate and adsorbent, thus increasing the effective collision between particles which is able to increase the effectiveness of adsorption. In the adsorption kinetic study, the adsorption rate increases significantly with the agitation speed. However, there might occur a destruction of the adsorbent structure during agitation if too high stirring speeds were used (Kusmierek & Swiątkowski, 2015).

For the volume of MG solution, it was depending on the amount of the adsorbent used. When a high volume of MG solution is used, it will contain a large amount of adsorbate to be adsorbed and it might require more adsorbent to remove the adsorbate from the solution in order to have an effective adsorption. In a previous study, the amount of eggshell adsorbent used for methyl orange removal was in range of 0.5g to 2.5g with a 50 mL of methyl orange solution (Belay & Hayelom, 2014). Therefore, 50mL of MG solution for adsorption will be the most appropriate volume in this study with the amount of adsorbent of 0.5g to 2g.

The batch adsorption study was performed in Erlenmeyer flasks containing 50 mL MG solution by shaking the flasks at 150 rpm. The mixture of MG dye and adsorbent was shaken until it attained equilibrium. Samples were withdrawn at the time intervals of 5, 12.5 and 20 minute and filtered through 0.45 µm filters. The residual of MG concentration in the supernatant was then determined using a UV–Visible Spectrophotometer at 617 nm wavelength. The percentage of MG removal was calculated using equation (1):

$$\text{MG Removal, Y (\%)} = \frac{C_i - C_e}{C_i}\, x\, 100 \qquad (1)$$

where Y is the percentage of MG removal (%) and $C_i$and C_e are the initial and equilibrium concentration of MG (mg/L), respectively.

Experimental design using CCD: The experimental design for the adsorption of MG was performed using response surface methodology (RSM). A central composite design (CCD) was employed for determining the optimum operating parameters for MG removal. This method gives an estimation to evaluate the interaction and quadratic effects on the responses. Response surface procedures are not primarily used for the purpose of understanding the mechanism process, but their purpose is to determine the optimum operating conditions or to determine a region for the variables in which certain operations are met. CCD model is an ideal design tool for sequential experimentation and allows testing the lack of fit when an adequate number of experimental values are available (Mune, 2008).

In this study, three independent variables were investigated for the removal of MG: A, initial concentration (mg/L), B, adsorbent dosage (g) and C, contact time (min). These variables have been considered as the factors that may influence or potentially affect the adsorption response function. The ranges and levels of the variables were investigated. A complete design matrix of the experiments was employed as shown in Table-1 based on the ranges and the levels given.

Table-1. Experimental design parameters with coded factor.

Factor	Name	Units	Actual factors			Coded factors		
			Low	Middle	High	Low	Middle	High
A	Initial Concentration	mg/L	30	50	70	-1	0	+1
B	Adsorbent Dosage	g	0.5	1.25	2	-1	0	+1
C	Contact Time	min	5	12.5	20	-1	0	+1

As presented, the experimental design involved three parameters (A, B and C), each at three levels, coded -1, 0 and +1, respectively. Percentage of MG removal (Y) was considered as the dependent factor (response). The behavior of the adsorption process is explained by the following empirical second-order polynomial model (equation 2):

$$y = \beta_o + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1\le i\le j}^{k} \beta_{ij} x_i x_j + \epsilon \qquad (2)$$

where y is the predicted response (percentage of dye removal), β_o is the constant coefficient, β_i *is* the linear coefficients,β_{ii} is the quadratic coefficients, $\beta_{ij}$is the interaction coefficients and x_i, $x_j$are the coded values of the variables.

A total of 20 experimental runs were carried out according to the experimental design using CCD obtained from the Design Expert software as presented in Table-2. The response and the corresponding parameters were modeled and optimized using analysis of variance (ANOVA), which was used to identify significant variables. The individual and interactive effects on the MG removal process had also been studied. Based on the coefficient of R^2 and ANOVA, the reliability of the fitted model was justified.

VOL. 12, NO. 11, JUNE 2017 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

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RESULTS AND DISCUSSIONS

Model fitting and statistical analysis: Design Expert Software version 7.0.0 (STAT-EASE Inc., Minneapolis, US) was used to analyze the experimental data.

Development of regression model equation of MG removal: In this study, the experimental design used was response surface methodology (RSM) by employing central composite design with 3 factors of input variables.The three variables studied were: initial concentration (A), adsorbent dosage (B) and contact time (C) with the response; MG removal, Y (%). These variables were chosen based on the literature and results obtained from the preliminary studies.

Table-2. CCD design and its observed and predicted values.

Run	Coded factor			MG removal (%)	
	A	B	C	Experimental	Predicted
1	-1	-1	-1	65.86	66.92
2	+1	-1	-1	74.16	73.66
3	-1	+1	-1	77.32	78.28
4	+1	+1	-1	82.31	82.56
5	-1	-1	+1	77.39	77.06
6	+1	-1	+1	81.54	80.50
7	-1	+1	+1	89.90	90.32
8	+1	+1	+1	92.45	91.31
9	-1	0	0	86.70	84.59
10	+1	0	0	86.01	88.45
11	0	-1	0	75.04	75.85
12	0	+1	0	87.41	86.93
13	0	0	-1	76.14	74.38
14	0	0	+1	81.75	83.83
15	0	0	0	84.13	83.47
16	0	0	0	84.40	83.47
17	0	0	0	84.30	83.47
18	0	0	0	83.66	83.47
19	0	0	0	81.21	83.47
20	0	0	0	83.78	83.47

By referring to Table-2, the maximum percentage of MG removal was 92.45% with operating conditions of 70mg/L initial concentration, 2g adsorbent dosage and 20min of contact time. All of the parameter conditions are in the high level code. This may indicate that the higher level of parameter is more effective in the adsorption process. According to Laxmi (2013), the adsorption capacity of orange peel at equilibrium increased with the increase in initial concentration of malachite green and Haddadian *et al*. (2013) also proved that increasing the concentration of methyl orange dye from 12.5 to 250mg/L, increased the biosorption capacity from 2.984 to 21.051mg/g using dragon fruit foliage as adsorbent. Previous results revealed that at high concentration of dye, there is a high driving force for mass transfer that can overcome the mass transfer resistance of the molecules between the aqueous solution and solid phase. Also, the active sites of adsorbent are surrounded by higher number of dye molecules which leads to a more efficient adsorption. The minimum percentage of MG removal was 65.86% with the conditions of 30mg/L initial concentration, 0.5g adsorbent dosage and 5 min of contact time. All of the factor conditions are in the low level code. This can be concluded that the amount of each factor is least effective toward the adsorption of MG.

The model was selected based on the highest order polynomials where the additional terms were significant. Based on the data for MG removal in Table-2, a 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 1.76. Correlation coefficient,

 ISSN 1819-6608

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R^2 value was important for validation of the model developed. In this study, the R^2 for quadratic model is 0.9563. In a statistical study, the closer the R^2 value to 1, the better the model will be, as this will give the predicted value which is closer to the actual values for the response and the model is suitable to correlate with the experimental data (Salman, 2014; Ahmad *et al.*, 2015). The R^2 of 0.9563 was considered relatively high and this indicates that 95.63% 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 the percentage of MG removal.

RSM generates an empirical model expressed by a second-order polynomial equation in terms of coded factors which reflect the interaction and significance of variables toward response. The coefficient with one factor stands for the effect of the particular factor only, whereas the coefficients with two factors, and also with second-order term correspond to the interaction between the two factors and quadratic effect, respectively (Ahmad *et al.*, 2015). The final empirical formula models for the response in terms of coded factors are represented by equation 3.

$$Removal\ of\ MG, Y\ (\%) = +83.47 + 1.93\text{A} + 5.54\text{B} + 4.72\text{C} - 0.61\text{AB} - 0.82\text{AC} + 0.48\text{BC} + 3.05\text{A}^2 - 2.08\text{B}^2 - 4.36\text{C}^2 \qquad (3)$$

By referring to Equation 3, the term coded factors can be used to make prediction about the response for the given levels of each parameter. So, the coded equation is useful for identifying the relative impact of the parameter by comparing the coefficients (Ogueke *et al.*, 2015). In a coded equation, a positive sign in front of the terms indicates synergistic effect, whereas a negative sign indicates antagonistic effect (Salman, 2014). The factors A, B, C, BC and A^2 show positive coefficients which indicates that the increase of respective parameters will increase the effect of response. Meanwhile, increasing the factors AB, AC, B^2 and C^2 will give a negative effect to the response.

Statistical analysis and model fitting: ANOVA is a statistical tool that subdivides the total variation in a set of data into components parts associated with specific sources of variation for the purpose of testing hypotheses on parameters of the model.The significance and adequacy of the model were justified through analysis of variance. In an experimental design, low value of Prob> F less than 0.05 indicates that the result is not random and the term model has a significant effect to the response (Sahu *et al.*, 2010). The ANOVA for the quadratic model of MG removal by eggshell biochar is shown in Table-3. In the ANOVA Table, the sum of squares, degree of freedom (df), mean square, F value and p-value were calculated among each of the parameters and also the interaction of two different parameters.

Table-3. ANOVA analysis for MG removal using eggshell biochar.

Term	Sum of Squares	df	Mean Square	F Value	p-value Prob> F	Remarks
Model	677.47	9	75.27	24.32	< 0.0001	significant
A-Initial Concentration	37.25	1	37.25	12.03	0.0060	significant
B-Adsorbent Dosage	306.92	1	306.92	99.15	< 0.0001	significant
C-Contact Time	223.16	1	223.16	72.09	< 0.0001	significant
AB	3.01	1	3.01	0.97	0.3471	not significant
AC	5.43	1	5.43	1.75	0.2149	not significant
BC	1.81	1	1.81	0.59	0.4616	not significant
A^2	25.55	1	25.55	8.25	0.0166	significant
B^2	11.92	1	11.92	3.85	0.0781	not significant
C^2	52.32	1	52.32	16.90	0.0021	significant
Residual	30.95	10	3.10			
Lack of Fit	23.80	5	4.76	3.33	0.1066	not significant
Pure Error	7.16	5	1.43			
Cor Total	708.43	19				

The p-values are used to check the significance of each coefficient, which in turn might indicate the pattern of the interactions between the variables (Mourabet *et al.*, 2012). From the table, the F value of 24.32 and the value "Prob> F" of 0.0001 implies that the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. As shown in the Design Expert software, values of "Prob> F" less than 0.05 indicate that

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the model terms are significant. In this case A, B, C, A^2, C^2 are significant model terms.

The "Lack of Fit Test" compares the residual error to the pure error from replicated design points (Mourabet *et al*., 2012). The lack of fit F value of 3.33 implies that the lack of fit is not relatively significant to the pure error. There is only a 10.66% chance that a lack of fit of F value this large could occur due to noise. Non-significant lack of fit is desired in the design; therefore the response was fitted well to the model. Model equation has been used to visualize the effect of experimental factors on response, as in the adsorption factors effect studied with various interactions of factors. Actual values are experimental data for the experimental run in this study, and the predicted values are generated from the CCD model by using approximating functions.

Data were also analyzed to check the normality of the residuals. A normal probability plot of these residuals is shown in Figure-1. The data points on this plot lie reasonably close to a straight line, meaning that the residuals were small. Figure-2 shows the relationship between the actual and predicted values of response for the adsorption of malachite green onto eggshell biochar. It can be seen in Figure-2 that the developed model is adequate because the residuals for the prediction for the responses are less than 3% and the residuals tend to be close to the diagonal line. The figure proves that the predicted response from the empirical model is in good agreement with the actual values based on the R^2 value of 0.9542.

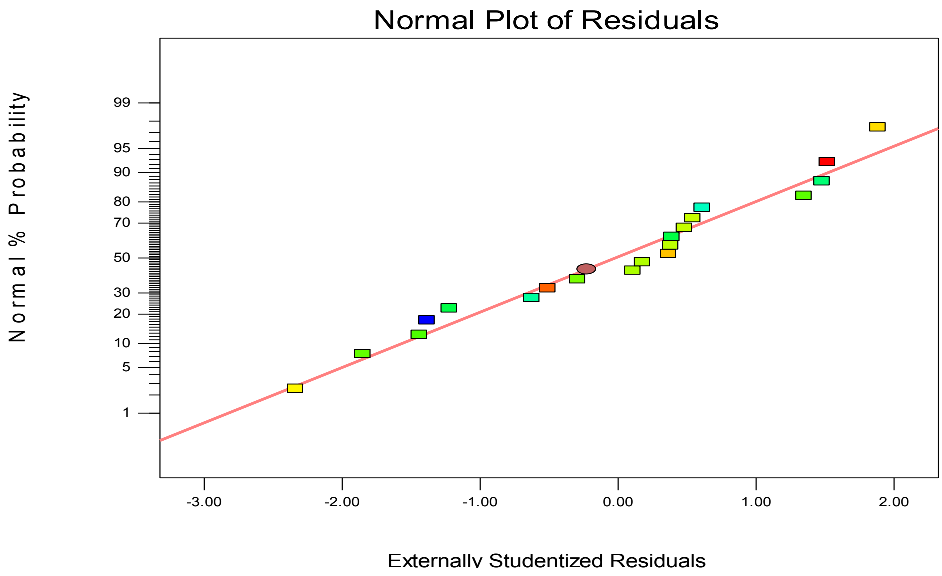

Figure-1. Plot of normal percentage probability versus residual error.

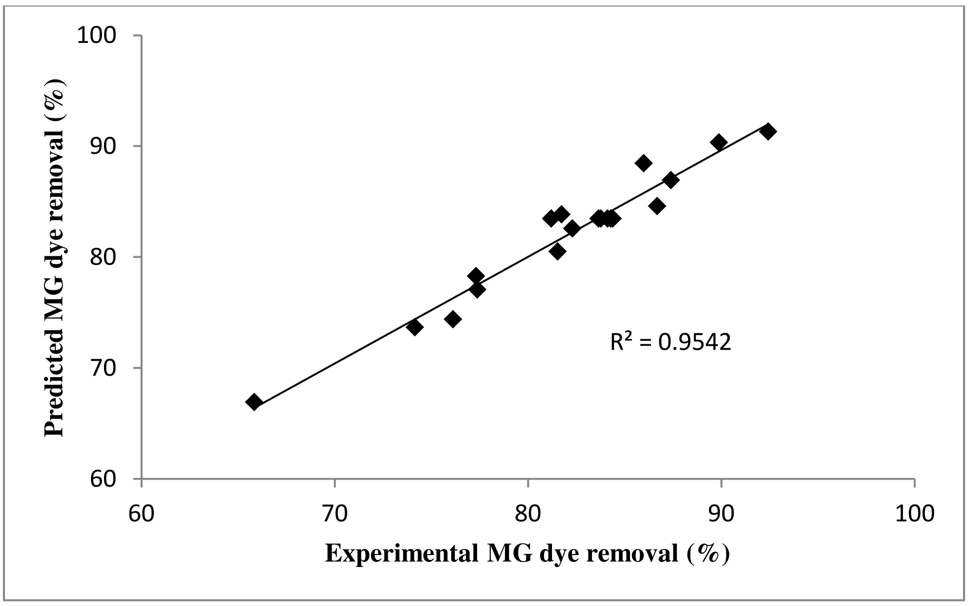

Figure-2. Predicted versus experimental MG dye removal using eggshell biochar.

Optimization of operating parameters

Effect of initial concentration: Increase of the dye concentration consequently increases the number of adsorbate ion in solution. In order to adsorb these increased ions in the solution, more number of active sites is necessary. When the adsorbent dosage is fixed, the number of active site remains constant, thus it will have deficiency in attaching adsorbate ion that will result in a decreased percentage of adsorption. However, when the active sites of adsorbent are surrounded by higher number of dye molecules, it definitely leads to a more efficient adsorption. The adsorption percentage of biochar at equilibrium increases with the increase in initial dye concentration. This trend could be attributed to the fact that for a high concentration of dye, there is a high driving force for mass transfer between aqueous and solid phases (Bazrafshan *et al*., 2014). A similar trend of study was explained by Rajesh Kannan *et al*.(2011). Besides, increasing the initial dye concentration increases the number of dye particle, and this would increase the number of collisions between dye ions and the surface area of the biochar which enhances the adsorption process (Krika & Benlahbib, 2015).

Figure-3 shows the three dimensional (3D) response surface and contour plot of the combined effect of initial concentration (mg/L), contact time (min) and removal of MG at actual factors, keeping the adsorbent dosage at 2g. Initial concentration of the solution of high concentration is preferable. According to the 3D surface graph in Figure-3, for the removal of MG, Y (%) achieves 90% and above at the initial concentration of 70 mg/L. This might be caused by the high driving force in the high initial concentration (Bazrafshan *et al*., 2014). There is some decline for the removal of MG at the concentration of 50 mg/L compared to 30 mg/L initial concentration. This trend might be explained whereby the effect of driving force at 50 mg/L is less than the effect of the particle collision theory at 30 mg/L, causing the less effective adsorption percentage. From the contour plot, at 30 mg/L initial concentration, the adsorption percentage achieves 90% and above at the time range of 15 min to 20 min at a constant adsorbent dosage of 2g. At 50 mg/L, the removal of MG is not as effective compared to 30 mg/L and 70 mg/L. The maximum removal of MG does not achieve 90% at this concentration. The most effective adsorption concentration is 70 mg/L, and the contour plot shows that the removal of MG achieves92% at the contact time of about 16 min. Hence, this point was the optimum condition for the initial concentration as it contributed the highest adsorption percentage.

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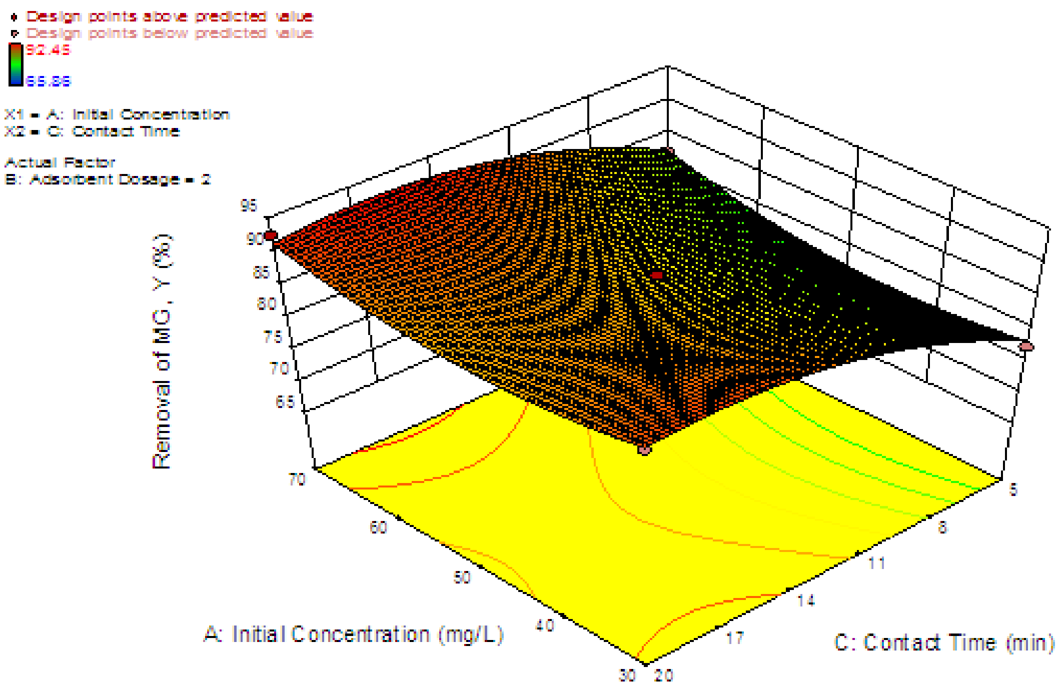
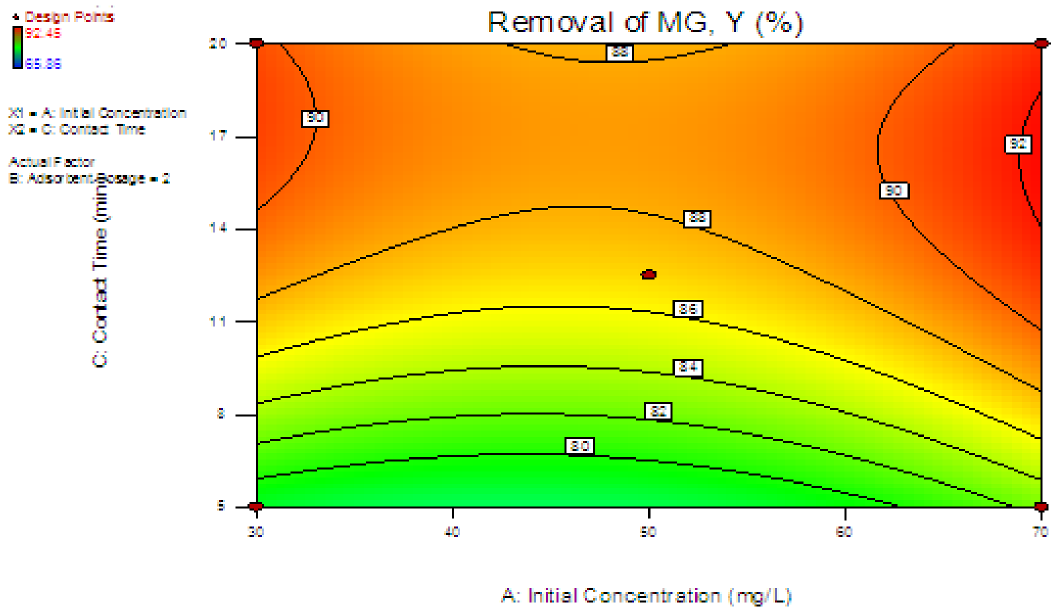


(a)



(b)

Figure-3. (a) Response surface plot and (b) contour plot of combined effects of initial concentration(mg/L) and contact time (min) on removal of MG, Y (%).

Effects of adsorbent dosage: The effects of biochar adsorbent dosage on the percentage removal of MG dye for different dosages were studied. The percentage of removal of dye will increase with the increase in the adsorbent dosage up to the adsorbate limiting point, but after, that there is no significant increase in the removal. This is due to the fact that increasing adsorbent dosage would increase the surface area of the adsorption sites (Sharma, 2013). Increasing the adsorption capacity will be limited when it achieves the saturation point in which there is no more dye particle to be adsorbed. However, the aggregation of adsorbent particles at higher dosage will lead to the decrease in the surface area and an increase in the diffusion path length (Belay & Hayelom, 2014). In this study, the aggregation factor of adsorbent particles was overcome by the agitation factors.

Figure-4 shows the response surface plot and contour plot of the combined effect of initial concentration (mg/L) and adsorbent dosage (g) on the removal of MG, Y (%) at a constant parameter of contact time (20 min). Traditionally, the analysis of adsorbent dosage has

VOL. 12, NO. 11, JUNE 2017 ISSN 1819-6608
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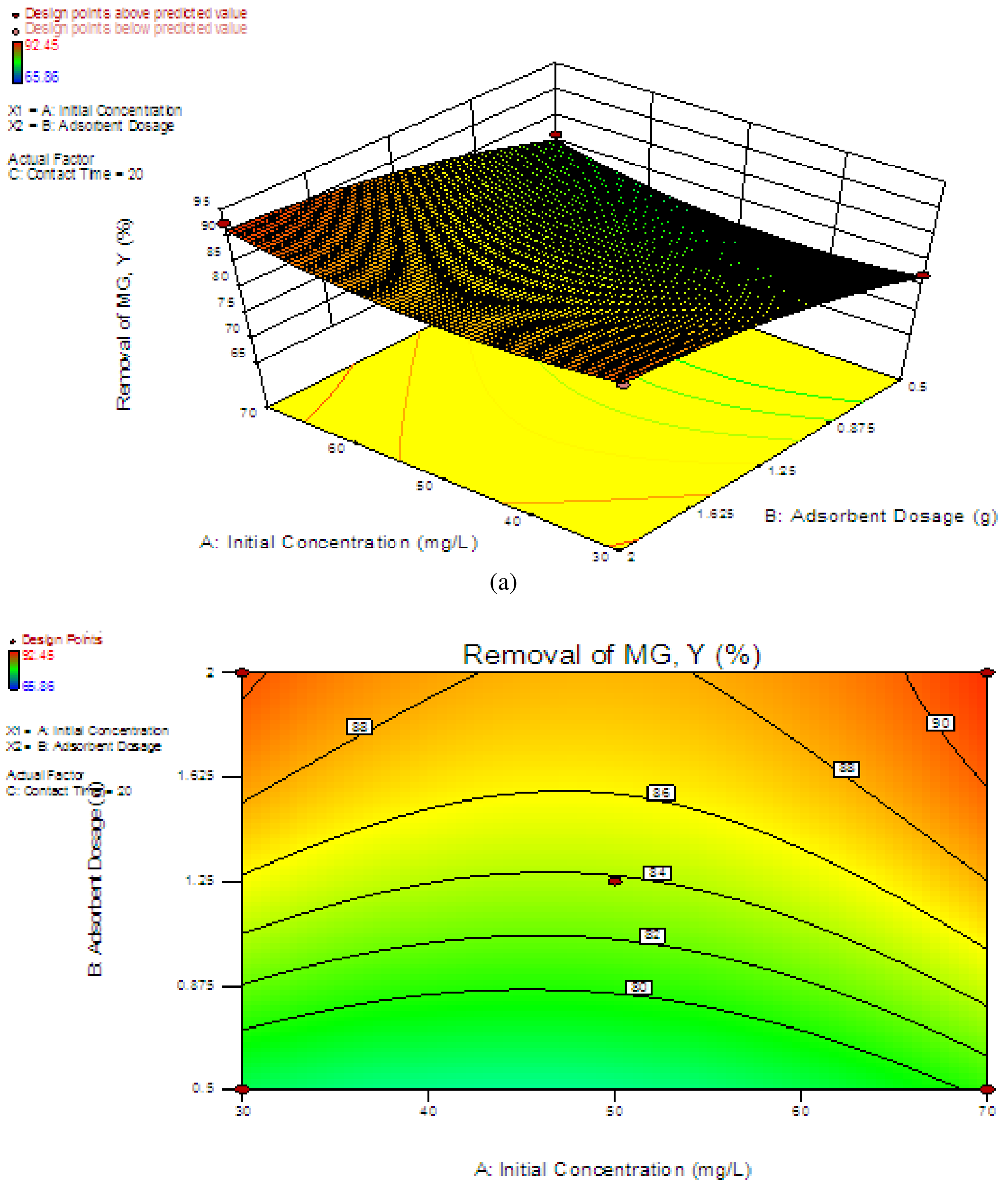
limitations to give information about the effect of variable study on tow parameters only (Vishwanth Sabde, 2013). In the 3D surface graph, increasing the adsorbent dosage will have a better removal of MG. The changing colour from green to red indicates the increase of removal percentage as the nearer the colour is to red, the higher the removal will be. A similar trend had been explained by Bazrafshan *et al.* (2014) and Krika & Benlahbib (2015) in which increasing the dosage can attribute to the increases in surface area and a greater number of attachable sites available for interaction with the dye molecules. From the contour plot in Figure-4 (b), it shows that at 30 mg/L, the adsorption percentage up to 90% is at an adsorbent dosage of 2g. It is much more effective compared to the lower adsorbent dosage at 0.5g, where the adsorption percentage is below 80%.



(a)

(b)

Figure-4. (a) Response surface plot and (b) contour plot of combined effects of initial concentration (mg/L) and adsorbent dosage (g) on removal of MG, Y (%).

Effect of contact time: Contact time study is an important factor to be studied as an increase in contact time will influence all other parameters. It is a fact that as contact time between the adsorbate and adsorbent increases, the rate of adsorption will decrease but the percentage of MG removal will increase (Laxmi, 2014). So, the percentage of MG removal would increase with increase of contact time. This is because there is more time for the adsorbate and adsorbent to collide and effectively bind together. But, the percentage might be constant

VOL. 12, NO. 11, JUNE 2017 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

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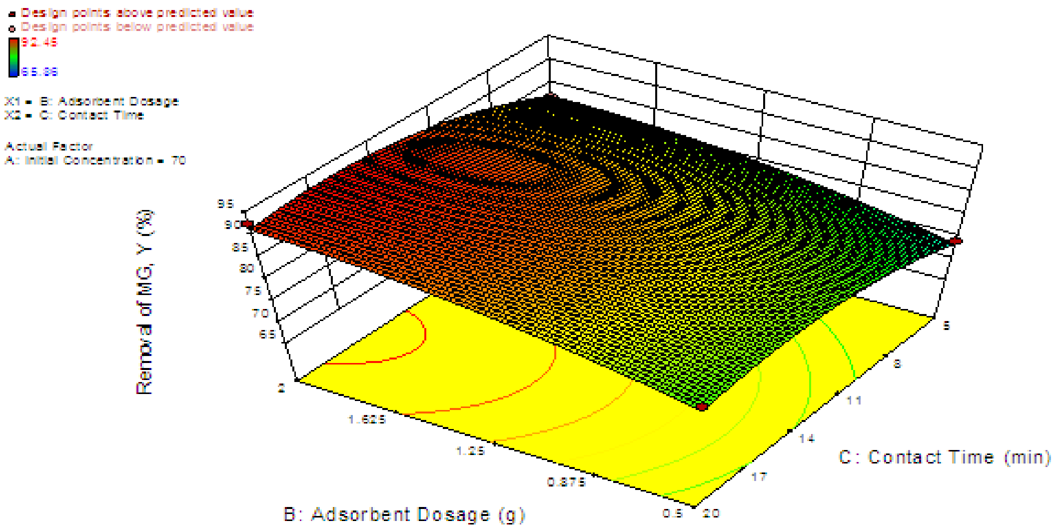
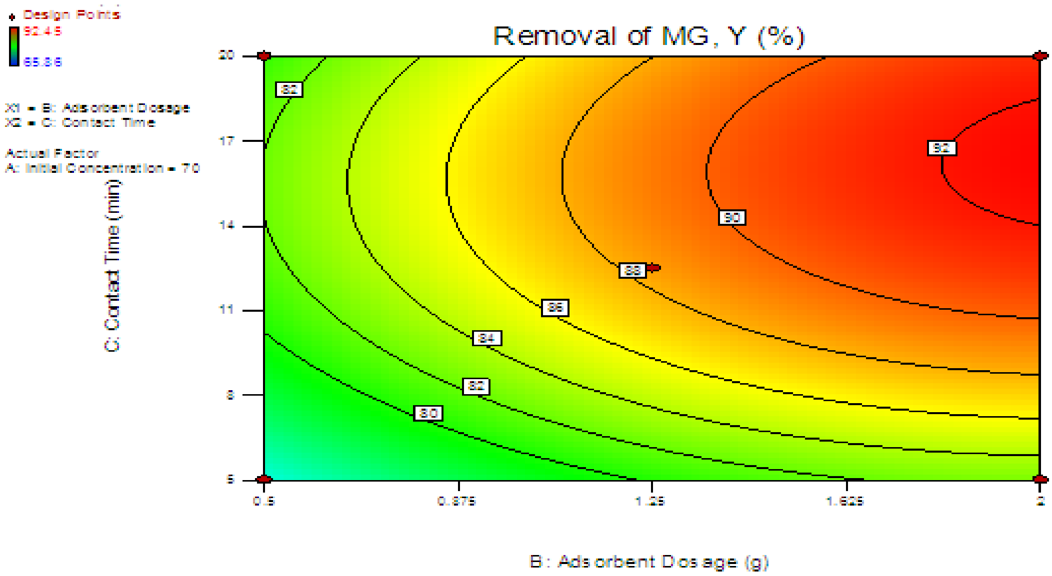
during adsorption to achieve equilibrium time which the saturation of the active sites do not permit further adsorption to occur (Leechart *et al.*, 2009). The saturation is where all the active sites of the adsorbent are fully attached by the dye particles. A similar trend is observed in a previous study conducted by Sharma in 2013.

The response surface plot and contour plot of combined effect of adsorbent dosage (g), contact time (min), and removal of MG at constant parameter of initial concentration at 70 mg/L is illustrated in Figure-5. The 3D surface graph shows that the removal of MG will increase when increasing the contact time together with the adsorbent dosage. The red colour area in 3D graph is accumulated at the area with a high contact time and adsorbent dosage. The adsorption percentage is slightly decreased after the optimum time which may be due to the weak physical adsorption of adsorbent (Ngadi *et al.*, 2013). According to the contour plot, it clearly shows that at a contact time of 16 min, the removal of MG is up to 92%, which is considered the highest percentage of removal.



(a)



(b)

Figure-5. (a) Response surface plot and (b) contour plot of combined effects of adsorbent dosage (g) and contact time (min) on removal of MG, Y (%).

Numerical optimization: The objective of the experimental design was to find the optimum operating parameters for maximizing the adsorption of MG from aqueous solution. By using numerical optimization, the desirable value for each input factor and response is selected. The possible input for optimizations that can be selected included: in range, maximum, minimum, target to and equal to as to establish an optimized output value for a given set of conditions. In this study, the input variables were given in range values, whereas the response was designed to achieve a maximum. The optimization goals were combined into the overall desirability function. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The goal will seek begins at a random starting point and proceeds up the steepest slope to a maximum. There may be two or more maximums because of the curvature in the response surfaces and their combination into the desirability functions (Mourabet*et al*., 2012).

Figure-6 shows a ramp desirability that was generated via numerical optimization. The best local maximum was found to be at the initial concentration of 70 mg/L, adsorbent dosage of 1.99g, contact time of 16.25 min, removal of MG of 92.39% and desirability at 0.998. The applicability of the model towards response is indicated by the model's desirability approaching unity. The process has the acceptable efficiency at that operating condition as the desirability is 0.998.

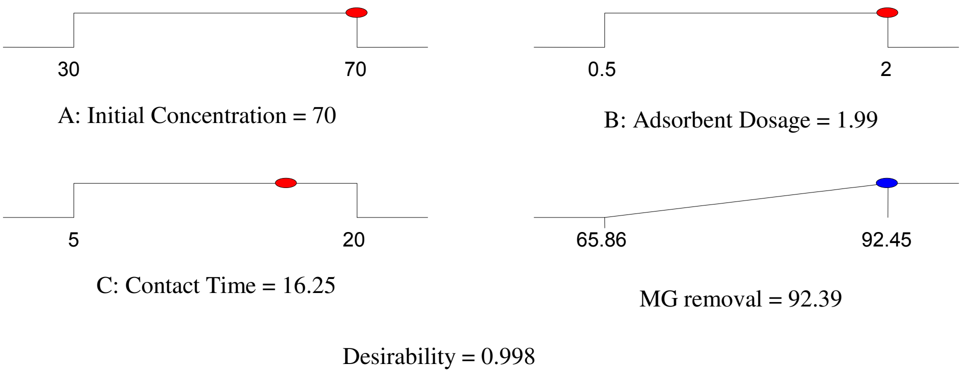


Figure-6. Desirability ramp for numerical optimization of four goals, namely initial concentration of MG, adsorbent dosage, contact time and MG removal.

CONCLUSIONS

The response surface modelling was successfully combined with central composite design (CCD) to determine the effects of process parameters, such as initial MG concentration, adsorbent dosage and contact time on the removal of MG. The results revealed that a second-order polynomial regression model was capable of accurately predict the experimental data with $R^2$of 0.9563. It was shown that the initial MG concentration and contact time had significant effects on MG adsorption through ANOVA. The optimum conditions for the removal of MG using eggshell biochar were determined at the initial concentration of 70 mg/L, adsorbent dosage of 1.99g and contact time of 16.25 min. At these optimum conditions, the percentage of MG removal was up to 92.39% with a desirability of 0.988.This present study has shown that RSM with employing CCD has provided a reliable and accurate methodology in optimizing the adsorption process for the removal of MG from aqueous solution.

ACKNOWLEDGEMENTS

Financial support in the form of grants from the Ministry of Higher Education via the Research Acculturation Grant Scheme (RAGS), R/RAGS/A07.00/01155A/001/2015/000196 is gratefully acknowledged.

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