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Comparative study of Central Composite and Box-Behnken design for the optimization of malachite green dye adsorption onto Sal seed activated char

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Abstract

Aim : Malachite green dye is extensively used for coloring purpose, as therapeutic agent and as a biocide in the aquaculture industry. The presence of dye in the industrial effluents is an environmental concern, and therefore its removal is inevitable. Sal seed activated char was utilised for the removal of malachite green dye from aqueous solution through adsorption process. The purpose of the present study was to examine and optimize the effect of adsorbent dose, pH and initial dye concentration on dye adsorption Central Composite Design (CCD) and Box-Behnken Design (BBD).

Methodology : Adsorbent was prepared by pyrolysing raw Sal seeds followed by chemical activation of resultant char using 85 % phosphoric acid. The characterization of activated char was done with SEM, FTIR and XRD. Batch adsorption studies were carried out at different pH, adsorbent doses and initial concentrations of malachite green dye. The experimental data were used as input in the Central Composite Design and Box-Behnken Design.

Results : The adsorption was found to be exothermic and spontaneous in the temperature range studied and followed pseudo second order kinetics. Freundlich isotherm was in good agreement with the experimental data. The percentage removal of malachite green dye increased with pH and adsorbent dose, whereas it decreased with the initial dye concentration. The optimum values obtained for the pH, adsorbate concentration, adsorbent dose and dye removal were 10, 50 mg l⁻¹, 1.2 g l⁻¹ and 96.3% for Box-Behnken Design and 9.89, 12.5 mg l⁻¹, 1.7g l⁻¹, and 100% for Central Composite Design, respectively.

Interpretation : Central Composite Design was found to be better in comparison to Box-Behnken Design for the optimization of malachite green dye adsorption onto Sal seed activated char.

Introduction

Malachite green, a basic dye, is extensively used in silk, wool, cotton, leather, paper and acrylic industries for coloring purpose. Also, it is used as a biocide in the aquaculture industry worldwide and as therapeutic agent to treat parasites, fungal and bacterial infections in fish and fish eggs. It is a toxic compound which causes carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity (Berberidou *et al.*, 2007). Therefore, the removal of malachite green dye from the effluent of these industries is essential before its disposal.

Economic removal of malachite green dye from effluents is a big challenge and a concern for the environment. At present, the methods available for the removal are biological and chemical precipitation. However, these methods are effective when solute concentrations are reasonably high. Among different physicochemical methods, adsorption is considered to be better due to its low cost, high efficiency, design simplicity, simple operation, biodegradability and ability to deal with dyes in concentrated forms (Joshi *et al.*, 2004).

Commercially available activated carbons have been used widely for the removal of dyes from wastewater but its high cost makes the adsorption process expensive (Hameed *et al.*,

2007). Some of the materials used as replacement of activated carbon are: naturally occurring materials like gypsum, activated clay and montmorillonite; biomaterials like *Caulerpa scalpelliformis* (a green algae) (Aravindhan *et al.*, 2007), *Spirodela polyrrhiza* (giant duckweed) (Waranusantigul *et al.*, 2013); industrial waste like sugarcane bagasse (Liew Abdullah *et al.*, 2005), bagasse fly ash (Rachakornkij *et al.*, 2004), carbon nanotubes (a waste product from petroleum industry) (Shahryari *et al.*, 2010); Agrowaste materials like, mango seed kernel powder, mango leaf powder and *Manilkara zapota* seed powder (Sundararaman *et al.*, 2016), rice bran (Hashemian *et al.*, 2008), *Acacia nilotica* leaves (Prasad and Santhi, 2012); Activated carbons derived from agricultural waste, *Piper nigrum* (Arulmathi and Elangovan, 2016), barley straw (Husseien *et al.*, 2007), coconut shell (Gimba *et al.*, 2001), *Delonix regia* plant litters (Daniel *et al.*, 2015) and cassava peel (Rachakornkij *et al.*, 2004). The search is still continuing for low-cost adsorbents having similar adsorptive properties.

Sal seed (*Shorea robusta*), a tree-borne oilseeds, can be a potential source of biomass for production of char to be utilized as adsorbent. The estimated production of Sal seed in India is 15 lakh tonnes (Singh *et al.*, 2014). The char obtained from these seeds through pyrolysis process has high porous structure enabling in high surface area for adsorption. Surface morphology

Fig.1: FTIR spectra of Sal seed activated char before adsorption of malachite green dye

of the char can further be changed through activation by chemical reagents like ZnCl_2 , H_3PO_4 , KOH , and Na_2CO_3 . Activation with ZnCl_2 and H_3PO_4 results in large surface area in the temperature range of 500°C to 600°C , while for activation with KOH and Na_2CO_3 the temperature requirement is above 800°C (Hayashi *et al.*, 2000).

The limitations of requirement of large number of experiments to optimize the process parameters can be eliminated by using a statistical experimental design like response surface methodology, where all the affecting parameters can vary simultaneously. The present work attempted to optimize and compare the adsorption process parameters like pH, adsorbate concentration, and adsorbent dose using Central composite and Box-Behnken designs of response surface methodology. The adsorbent for removal of malachite green dye was activated char obtained through pyrolysis of Sal seed followed by chemical activation.

Materials and Methods

Preparation of adsorbent: Sal seeds were washed thoroughly with de-ionized water to remove adhering foreign particles from the surface and dried in hot air oven at temperature of $50\text{--}60^\circ\text{C}$ for about 6 hrs. The seeds were then ground and sieved to a size of 510 micron. Sal seed powder was carbonized in a reactor at 600°C for 2 hrs. The resultant char was mixed with 85% H_3PO_4 in the weight ratio of 1:1.5 and kept in hot air oven at 110°C for 9 hrs. The Sal seed activated char (SSAC), thus obtained, was washed thoroughly to remove acid content, dried and stored in an air tight container.

Characterization of char: The surface morphology of SSAC was studied by means of Scanning Electron Microscope (SEM, ZEISS EVO Series). For the interpretation of functional groups present in SSAC, Fourier transform infrared spectroscopy (FTIR, Bruker Germany; KBr pellets, 500 to 3500 cm^{-1} , 16 scans) was performed. X-ray diffraction (XRD, PANalytical; Cu K α radiation) were carried out to visualize the pore structure.

Batch adsorption experiments: A stock solution of malachite green dye, 4-[[4-(dimethylamino) phenyl](phenyl) methylidene]-N, N-dimethylcyclohexa-2,5-dien-1-iminium chloride, was prepared by dissolving 1 g of dye in 1000 ml of Millipore ultrapure water and further diluted to get solution of different concentrations (50 to 160 mg l^{-1}) as per requirement. The pH of the solution was measured using pH meter (Eutech Scientific Instruments) and adjusted using 0.1N HCl or 0.1N NaOH . The experiments were carried out in 250 ml Borosil flasks. The flasks with reaction mixture were kept in an orbital shaker at a speed of $150\pm 5\text{ rpm}$ to reach an equilibrium. The concentration of malachite green in the solution was determined from the calibration curve prepared by measuring the absorbance of different known concentrations of MG solutions at $\lambda_{\text{max}} = 617\text{ nm}$ using a UV-vis spectrophotometer

(Shimadzu, Kyoto, Japan). The amount of dye adsorbed by adsorbent was also calculated.

The interaction between adsorbate and adsorbent was studied using different isotherms such as Langmuir and Freundlich isotherms. Adsorption kinetics is important since it gives the solute uptake rate, which determines the residence time required for completion of adsorption process; hence it was analyzed using pseudo-first order and pseudo-second order models.

Box-Behnken Design and Central Composite Design of experiments: The independent input variables that affect the removal of malachite green were analyzed using Box-Behnken and Central composite Designs with a total runs of 15 and 20. Minitab 16.1 statistical software was used to run the experiments. BBD adopts a three level ($-1, 0, +1$) design, whereas CCD adopts five level ($-\alpha, -1, 0, +1, +\alpha$) designs. Table 1 shows the experimental range for each factor used. The obtained results were analyzed applying coefficient of determination (R^2), analysis of variance (ANOVA), residual plot, response surface contour plots and experimental vs predicted plot.

Results and Discussion

The FTIR spectrum of SSAC is shown in Fig.1. Several peaks obtained in the spectrum correspond to different functional groups present on the surface of the char which will participate in dye adsorption. Peak at 3448.26 cm^{-1} indicate that the presence of O-H stretching vibrations was due to existence of surface hydroxyl group. Small peaks at 2923.92 cm^{-1} were due to the presence of C-H stretch bonds of alkanes and alkyls (Daniel *et al.*, 2015). Peaks at 1576.8 cm^{-1} and 1020.26 cm^{-1} indicate the presence of N-H bonds of primary amines and C-N stretch bonds of aliphatic amines, respectively. Peak at 520.5 cm^{-1} indicates the presence of C-Br stretch bonds of alkyl halides. The most important changes brought in activated char by the addition of phosphoric acid are the development of C-H vibrations, possibly due to the loss of oxygen at the surface of carbon material (Yakout and El-Deen, 2016). From the SEM images shown in Fig. 2, complete change in surface texture can easily be observed. The activated char exhibited porous structure before the adsorption but the smoother micrograph obtained after the adsorption clearly indicates that the pores were occupied by malachite green dye molecules. The XRD plot shown in Fig. 3, confirms the amorphous nature of the activated char. Absence of sharp peaks indicates that no inorganic material was present in the sample. Similar observations were reported by Daniel *et al.*, (2015), while characterization and removal of methylene blue with *Delonix regia* plant litters activated carbon encapsulated nano metal oxide.

Optimization using RSM : For the optimisation of process conditions, the response surface methodology (RSM) was used by selecting three important factors that affect the adsorption

20µm EHT = 15.00kv Singal A = SE1 Date : 10 Jun 2016
WD = 10.0mm Mag = 500 x Time : 16:18:37 ZEISS

(a)

20µm EHT = 10.00kv Singal A = SE1 Date : 15 Jun 2016
WD = 17.0mm Mag = 500 x Time : 14:58:03 ZEISS

(b)

Fig. 2 : SEM images of Sal seed activated char (a) before adsorption and (b) after adsorption of malachite green dye

Fig. 3 : X-ray diffraction pattern of Sal seed activated char before adsorption of malachite green dye

Fig. 4 : Plot of the experimental vs predicted percentage removal of malachite green dye for Box-Behnken Design by Minitab 16.1 statistical software

Fig. 5 : Plot of the experimental vs predicted percentage removal of malachite green dye for Central Composite Design by Minitab 16.1 statistical software

process viz. , pH (A), initial dye concentration (B) and adsorbent dose (C) as independent variables, whereas the removal of malachite green dye was chosen as the output response (Y).

Experiments were performed for different combination of parameters in order to study the combined effects of the factors A, B and C. The regression model equations (second order polynomial) for BBD and CCD, relating the removal efficiency and process parameters, were developed using the experimental results (Almasifar, 2015) and the corresponding equations are:

$$Y = 81.71 + 16.81 \times A - 2.35 \times B + 0.14 \times C - 6.44 \times A^2 + 1.54B^2 + 0.45C^2 + 0.31 \times AB - 0.44 \times AC - 0.1 \times BC \text{ Eq. (1)}$$

$$Y = 81.71 + 17.04 \times A - 8.25 \times B + 0.73 \times C - 8.95 \times A^2 + 1.25B^2 + 1.48C^2 + 0.08 \times AB - 0.12 \times AC - 0.02 \times BC \text{ Eq. (2)}$$

The fitness of the model was determined by R^2 and its statistical significance was evaluated by an F-test (Peng *et al.*, 2002). Higher the value of R^2 , better is the model. From the Box-Behnken designs (Table 2), it was observed that all the coefficients for the linear effects and quadratic effects were highly significant (p values < 0.05), except for adsorbent dose (p values > 0.05) which was least significant. The value of p was lower than 0.05, indicating that the model may be considered to be statistically significant. It was observed that interaction effects are insignificant

Table 1 : Experimental factors and levels used for optimization by Box-Behnken Design and Central Composite Design

Factor	Level					
	Coded symbol	$-\alpha$	-1	0	+1	$+\alpha$
pH	A	0.614	3	6.5	10	12.386
Initial dye concentration (mg l ⁻¹)	B	12.501	50	105	160	197.499
Adsorbent dosage (g l ⁻¹)	C	0.927	1.2	1.6	2	2.273

Table 2: Estimated regression coefficient of Box-Behnken Design and Central Composite Design for the removal of malachite green dye by Sal seed activated char

Term	BBD				CCD			
	Coefficient	SE coefficient	T	P	Coefficient	SE coefficient	T	P
Constant	81.7100	0.5458	149.716	0.000	81.7089	0.12454	656.082	0.000
A	16.8113	0.3342	50.301	0.000	17.0380	0.08263	206.197	0.000
B	-2.3475	0.3342	-7.024	0.001	-8.2525	0.08263	-99.874	0.000
C	0.1438	0.3342	0.430	0.685	0.7334	0.08263	8.875	0.000
A*A	-6.4375	0.4919	-13.086	0.000	-8.9519	0.08044	-111.29	0.000
B*B	1.5350	0.4919	3.120	0.026	-1.2515	0.08044	-15.559	0.000
C*C	0.4525	0.4919	0.920	0.400	-1.4814	0.08044	-18.416	0.000
A*B	0.3075	0.4726	0.651	0.544	-0.0825	0.10796	-0.764	0.462
A*C	-0.4350	0.4726	-0.920	0.400	0.1175	0.10796	1.088	0.302
B*C	-0.0975	0.4726	-0.206	0.845	-0.0225	0.10796	-0.208	0.839
R² = 99.82% R²(pred) = 97.12% R²(adj) = 99.50% R² = 99.98%					R² (pred) = 99.88% R² (adj) = 99.97%			

A: pH; B: initial dye concentration (mg l⁻¹); C: adsorbent dose(g l⁻¹)**Table 3:** ANOVA of Box-Behnken Design and Central Composite Design analysis for the removal of malachite green dye by Sal seed activated char

Source	BBD				CCD			
	DF	Seq SS	F	Prob>F	DF	Seq SS	F	Prob>F
Regression	9	2477.10	308.01	<0.0001	9	6063.51	7225.29	<0.0001
Linear	3	2305.20	859.91	<0.0001	3	4901.95	17523.52	<0.0001
A	1	2260.95	2530.20	<0.0001	1	3964.51	7683.34	<0.0001
B	1	44.09	49.34	<0.001	1	930.09	31.84	<0.0001
C	1	0.17	0.18	0.685	1	7.34	305.76	<0.0001
Square	3	170.73	63.69	<0.0001	3	1161.39	4151.76	<0.0001
A*A	1	161.61	171.24	<0.0001	1	1112.01	12385.44	<0.0001
B*B	1	8.36	9.74	<0.026	1	17.75	242.09	<0.0001
C*C	1	0.76	0.85	0.400	1	31.62	339.15	<0.0001
Interaction	3	1.17	0.44	0.736	3	0.17	0.60	0.627
A*B	1	0.38	0.42	0.544	1	0.05	0.58	0.462
A*C	1	0.76	0.85	0.400	1	0.11	1.18	0.302
B*C	1	0.04	0.04	0.845	1	0.00	0.04	0.839
Residual Error	5	4.47			10	0.93		
Lack-of-Fit	3	4.47			5	0.93		
Pure Error	2	0.00			5	0.00		
Total	14	2481.57			19	6064.44		

A: pH; B: initial dye concentration (mg l⁻¹); C: adsorbent dose (g l⁻¹)

according to the p value. From the model summary statistics, it can be seen that the predicted R² of 97.12% was in reasonable agreement with the adjusted R² of 99.50% for the quadratic model.

As per the results from Central composite designs (Table 2), the p values for the linear effects and quadratic effects were highly significant. From the model summary statistics, it can be seen that

Fig. 6: Response surface contour plots of malachite green dye removal(%) showing the effect of pH and initial dye concentration by Minitab 16.1 statistical software

Fig. 7 : Response surface contour plots of malachite green dye removal(%) showing the effect of initial dye concentration and adsorbent dose by the Minitab 16.1 statistical software

the predicted R^2 of 99.88% was in reasonable agreement with the adjusted R^2 of 99.97% for the quadratic model. The results indicate that the quadratic model provided an excellent explanation for the relationship between the independent variables and the corresponding response (Liu *et al.*, 2010).

ANOVA was applied to test the statistical significance. Higher the value of F statistics (Table 3), smaller the value of p, the more significant is the corresponding coefficient term (Amini *et al.*, 2008; Kalavathy *et al.*, 2009). P values less than 0.05 indicate that the model is statistically significant (Kim *et al.*, 2003). The ANOVA

Fig. 8 : Response surface contour plots of malachite green dye removal(%) showing the effect of adsorbent dose and pH by Minitab 16.1 statistical software

table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct. For the Central Composite designs model, the F-statistics value for malachite green was 7225.29, which was more than 308.01 for the Box-Behnken designs model, implying that most of the variations in the response could be explained better by the regression equation of Central Composite Designs model and that the model is more significant (Almasifar, 2015).

The data were analyzed to confirm the correlation between the experimental and predicted percentage removal for Box-Behnken Designs and Central Composite Designs (Fig. 4 and 5). The experimental values were the measured response data for the runs designed by Box-Behnken Designs and Central Composite Designs, while the predicted values were obtained by the calculation from the quadratic equation. It can be seen that the data points on the plot were convincingly spread near to the straight line ($R^2 = 0.998$ for BBD and 0.999 for Central Composite Designs), indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis were appropriate. The result also suggests that the preferred quadratic model was suitable in predicting the response variables for the experimental data. Similar observations were reported by Liu *et al.* (2010) while optimizing adsorption process parameters for methylene blue removal by a hydrogel composite.

The contour plots for the percentage removal of malachite green dye is shown in Fig. 6-8. The percentage removal

of malachite green increased with pH in both the cases, but at the same time it decreased with initial dye concentration (Fig. 6 a and b). At higher pH, the percentage removal was more, which might be due to electrostatic attraction between dye molecules and adsorbent. At higher dye concentration, the percentage removal was low as fewer sites were available for adsorption of dye molecule. Besides, the adsorption percentage was found to decrease with increase in the initial dye concentration. This is attributed to the saturation of surface area and active sites of adsorbent (Fig. 7 a and b). Further, the adsorption percentage was found to increase with adsorbent dose as with the increase in the surface area availability of active sites of adsorbent is more. However, after certain amount of adsorbent dose, the removal decelerates, probably due to the agglomeration of adsorbent particles (Fig. 8 a and b). Similar results were reported for heavy metal removal using *Phanerochaete Chrysosporium* (Gopal *et al.*, 2002) and for iodine removal using a novel nanoparticles adsorbent (Almasifar, 2015).

Optimization plots for Box-Behnken designs and Central Composite Designs are shown in Fig. 9 (a) and (b). For complete dye removal, the optimum value calculated from Box Behnken design (Fig 9a and Table 1) are pH 10, initial dye concentration 50 mg l^{-1} and adsorbent dose 1.2 g l^{-1} . Using Central Composite design, the optimum value obtained are pH 9.8891, initial dye concentration $12.5014 \text{ mg l}^{-1}$, and adsorbent dose 1.7155 g l^{-1} (Fig. 9b). In case of Box Behnken design, the predicted percentage removal was 96.3050% with desirability value of 0.99242. However, in case of Central Composite design, it was 100.4190% with desirability value of 1.0000. The optimum values of the factors responsible for the maximum malachite green dye removal

Fig. 9: Optimization plots for the predicted percentage removal of malachite green dye and the desirability value by Minitab 16.1 statistical software for (a) Box-Behnken design (b) Central Composite Design

were in close agreement with the experimental values, confirming that the response surface methodology could be effectively used to optimize the process parameters in complex processes using the statistical design of experiments. (Liu *et al.*, 2010).

Adsorption equilibrium and kinetic studies: The adsorption

equilibrium was analyzed using the Langmuir and Freundlich isotherms. In case of Freundlich isotherm, the values of K_F were found higher and n values were greater than 1, which shows that adsorption was favorable. The values of slope, $1/n$ was found in the range of 0.56 to 0.75 which indicate the highly heterogeneous surface of adsorbent (Daniel *et al.*, 2015).

The kinetics of adsorption was analyzed by pseudo first order and pseudo second order model. The calculated values for pseudo second order model were in good agreement with the experimental values ($R^2 = 0.99$). This indicates the applicability of pseudo second order model to the adsorption of malachite green dye. Similar results were also obtained during the adsorption of methylene blue onto palm oil fibre char (Tan *et al.*, 2007) and Kenaf fibre char (Mahmod *et al.*, 2012).

Thermodynamic studies : The thermodynamic parameters such as standard free energy of adsorption (ΔG°), standard enthalpy of adsorption (ΔH°) and standard entropy of adsorption (ΔS°) were estimated by adsorption isotherm in the studied temperature range (303K-323K). Negative enthalpy revealed that the adsorption process was exothermic in nature. As the adsorption proceeded, randomness at the solid-solution interface decreased, since the value of ΔS was negative. Gibb's free energy showed a negative value, and hence, the adsorption process was spontaneous in the temperature range studied. Similar study of adsorption of malachite green dye onto acid activated low cost carbon has been reported to be spontaneous on the basis of negative values of ΔG° (Hema and Arivoli, 2008).

The adsorption with SSAC followed pseudo second order kinetic model. The optimum parameters do confirm that CCD is better design tool in comparison to BBD. Hence, the Central Composite Design can be used to get closer optimal values of the parameters in case of exothermic and spontaneous adsorption process.

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