

Optimization studies on the adsorption of Malachite green from quaternary dye mixture using modified sawdust of locust bean tree

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ABSTRACT

A novel study on optimization of biosorption of Malachite green dye from a mixture of four dyes onto acid-modified sawdust of *Parkia biglobosa* was conducted. The Design of Experimental (DoE) and Response Surface (RS) methodology, that provides detailed information from minimum number of experiment, was employed in this study rather than the traditional one-variable-at-a-time technique which is both time consuming and cost ineffective. The adsorbent was characterized using different methods. Four factors each from the mixture components (malachite green, methylene blue, crystal violet and rhodamine B) and process parameters (adsorbent dose, contact time, temperature and pH) were considered. A total of 64 duplicate batch runs were performed using Crossed Composite design of experiment, and the results were analysed using Analysis of variance (ANOVA). The model developed was predictive (standard deviation = 0.37; $R^2 = 0.974$; adjusted $R^2 = 0.963$ and predicted $R^2 = 0.945$). The optimum conditions required for the adsorption (98.58 % removal) were 1.0 g dose of adsorbent at 60 °C, pH of 9.42 and contact time of 146 min.

KEYWORDS

adsorption; dye mixture; optimization; sawdust

1. INTRODUCTION

Dyes are one of the most common contaminants disposed into water bodies (El-Maghraby and El-Deeb, 2010). They are used in large quantities being widely applied in many industries including textiles, paper, pharmaceutical, petroleum, food, rubber, carpet, plastic, paint, cosmetics, ceramic and leather industries (Chandra et al., 2007; Tahir et al., 2009). In textile dyeing processes, a large volume of dye contaminated effluent is discharged and about 15 % of the dyes used are lost in the effluent (Kaushik et al., 2008). This effluent is discharged to the nearby land or channelled into rivers without any prior treatment because the conventional treatment methods are very expensive (Verma and Mishra, 2010).

The presence of even a small amount of dye in

water is undesirable as it is highly visible, and may be toxic and carcinogenic (Sun and Yung, 2003). Hence, the dye wastewaters has to be treated before the eventual discharge of wastewater into the environment (Regine and Volesky, 2000; Dionysiou et al., 2004). Therefore there is the need to develop efficient and effective treatment methods for wastewaters containing dye molecules. Several methods such as coagulation, membrane separation, oxidation, ozonation and adsorption are used for wastewater treatment (Crini, 2008; Giwa et al., 2015). In recent years, adsorption with economical and eco-friendly materials such as melon husk (Giwa et al., 2013), lime peel (Ahmad et al., 2015) and durian peel (Chandra et al., 2007) were used for various pollutants. Effectiveness of other substances such as maize cob, fruit peels, wood, husks, tree barks, leaf powders, tea leaves have also been investigated

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(Gupta and Suhas, 2009). For removing mixture of dyes, granular activated carbon, tamarind kernel and rice hull are some of the adsorbent materials that have been studied (Gupta et al., 2015). Different models have been used to interpret the experimental results obtained from the various studies that have been conducted (Babak and George, 2013). Raw sawdust of *Parkia biglobosa* was used also by Giwa et al. (2015) for the adsorption of Rhodamine B in ternary mixture of dyes. The present study, however, uses sulphuric acid-treated sawdust obtained from locust bean tree for the adsorption of Malachite green from quaternary mixture of dyes.

Although the traditional step-by-step approach (batch adsorption) is widely used, it involves a large number of independent runs and does not consider the simultaneous interaction of multiple parameters. Apart from this, the method is also time and material consuming and requires a large number of experimental trials to capture the effects of all the factors. These limitations of this method can be reduced by optimization using statistical experimental design (Khamparia et al., 2015). With experimental designs, the effects of individual factors and interactions on any objective function can be adequately captured. Also, all the process variables can be optimized using response surface methodology to understand the system better and also to minimize the cost.

The few reported studies (Jaikumar et al., 2009; Ahmad et al., 2015; Khamparia et al., 2015) on optimization of dye adsorption were focused only on color removal from solutions containing single dye. However, in this study, optimization of dye removal from quaternary dye mixture at different operating conditions was performed using DoE and RS methodologies.

2. MATERIALS AND METHODS

2.1. Preparation and characterization of adsorbent

An agrowaste, sawdust of locust bean tree (*Parkia biglobosa*) was used as adsorbent in this research. It was collected from a sawmill in Ogbomoso, sieved with 10-20 mesh and mixed with concentrated H_2SO_4 acid in ratio 1:1 W/V, then activated in an electric oven at 160 °C for 15 h. Excess acid on the adsorbent was washed with $NaHCO_3$ solution (5% W/V), then with distilled water till a stable pH was obtained. It was then stored in an air tight container as concentrated acid modified

sawdust adsorbent. Pore characteristics, surface area, surface charge, surface morphology, surface chemistry analysis using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) Spectroscopy and elemental diffraction X-ray spectroscopy (EDS) were employed to characterize the adsorbent. The characterization was conducted before and after modification.

2.2. Preparation of adsorbate

The artificial wastewater used in the study was an aqueous solution of a mixture of four dyes; malachite green (MG), methylene blue (MB), crystal violet (CV) and rhodamine B (RB). Malachite green (MG) with the wavelength of maximum absorbance (λ_{max}) of 616 nm was the reference dye. A stock solution (1000 mg/L) of each dye was prepared; working solutions of different desired concentrations were obtained by careful dilution of the stock.

2.3. Adsorption experiments

Batch adsorption experiments were conducted to investigate the effects of different operational parameters on the removal of crystal violet from the quaternary dye mixture. This was conducted by shaking a series of glass volumetric flasks, each containing 30 mL solution of the desired concentrations of the dye mixture, in a horizontal thermostated shaker (SM 101 by Surgafriend Medicals) at a contact agitation speed of about 120 rpm for predetermined contact times, pH, adsorbent doses and temperature. The dye-adsorbent mixture was filtered and the residual concentration of crystal violet at any given time was measured in the filtrate on Genesys UV-vis scanning spectrophotometer at the earlier determined wavelength of maximum absorbance, λ_{max} (616 nm) of the dye.

2.4. Design of crossed composite experiment

The selection of crossed composite design for the adsorption of dye mixture was due to the fact that it can simultaneously be used for mixture of dyes and process parameters. The process parameters and the dye mixture factors are presented in Table 1 at different levels. The response was expressed as % dye removal.

The percentage dye removal (% R) was calculated using the equation:

$$\% R = \frac{100(C_o - C_e)}{C_o} \quad (1)$$

Table 1. Design variables for crossed composite design.

Factors	Units	Type	Actual value		Coded value	
			Low	High	Low	High
Methylene blue	mg/L	Mixture	10	100	0	1
Malachite blue	mg/L	Mixture	10	100	0	1
Crystal violet	mg/L	Mixture	10	100	0	1
Rhodamine B	mg/L	Mixture	10	100	0	1
Dosage	g	Numeric	0.1	1	-1	1
Temperature	°C	Numeric	30	60	-1	1
pH		Numeric	4	10	-1	1
Time	min	Numeric	30	180	-1	1

where C_0 and C_e are the initial and equilibrium concentrations of the dye in mg/L respectively.

elemental analysis. This evidence further confirms the successful chemical modification of sawdust.

3. RESULTS AND DISCUSSION

3.1. Characterization of the sawdust adsorbent

Scanning electron microscope (SEM) was used to study the surface morphology of the adsorbent. The surface textural structure before and after modification are presented at $\times 200$ magnification in Figure 1. The scanning electron microscopy image as depicted in Figure 1 shows that the surface of the sawdust was porous and the porosity increased after the treatment with concentrated sulphuric acid, as shown in Figure 1.

The FTIR spectrum of the sawdust before modification (Figure 2) shows some absorption peaks that indicate the complexity of the material. The spectrum indicates that the adsorbent has potential adsorption sites as represented by functional groups OH, COOH, C = O, and C = C. After modification (Figure 2), a new band that indicates C = S functional group appeared at 1104 cm^{-1} . This shows a change in the composition of the sawdust thereby confirming the chemical modification. A shift in the position of the OH functional group from wave number of 3321 cm^{-1} to 3240 cm^{-1} and that of C = C from 1593 cm^{-1} to 1574 cm^{-1} were also observed. The elemental analysis of raw sawdust of locust bean tree as shown in Figure 3 shows a high percentage of carbon (57.62 %) which makes it a good adsorbent. The percentage of carbon component of the sawdust increased after modification (Figure 3) to 66.77 % which makes the modified form of sawdust of locust bean tree a better adsorbent than the raw form. The presence of sulphur in the acid-treated sawdust as suggested by the appearance of C = S bond in the FTIR spectrum was also confirmed by the results of the

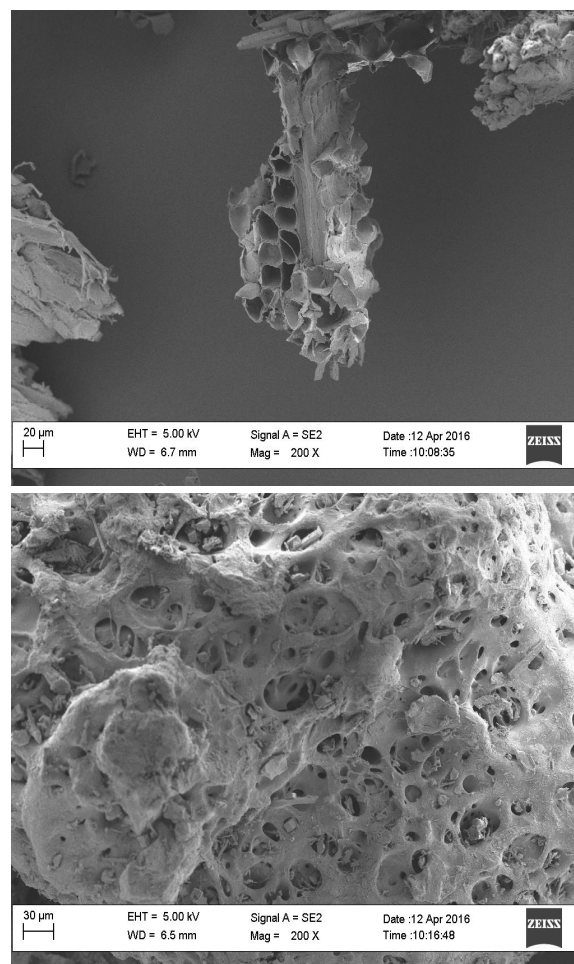


Figure 1. Scanning electron microscopy (SEM) images of sawdust before modification (top image) and after modification (bottom image).

3.2. Model evaluation and selection

Table 2 show the results based on the evaluation of different models for adsorption of malachite green from a quaternary dye mixture using five statistical indexes. The standard deviation showed the degree of deviation of predicted values from the global mean experimental values. The correlation coefficient (R^2) value reflects the efficiency of the prediction relative to the actual experimental data. The closer the R^2 and adjusted R^2 value to unity, the better the model. The predicted R^2 also show the efficiency of the model prediction within the experimental range. Linear model was selected for both the mixture components and process parameters as a result of its high correlation coefficients ($R^2 = 0.974$; adjusted $R^2 = 0.963$ and predicted $R^2 = 0.945$).

3.3. Evaluation of model parameters using analysis of variance (ANOVA)

Analysis of variance (ANOVA) was used in the selection of model term for the % removal of malachite green. The analyses were done using Fisher's 'F'-test and Student't'-test. The student't'-test was used to determine the significance of the regression coefficients of the parameters. The P-values were used as a tool to check the significance of the main variables and interactions among the variables, which in turn may indicate the patterns of the interactions among the variables. It also evaluates the desirability of the model through adequate precision (the signal to noise ratio). If the model is desirable, it can be used to navigate the design space.

Table 3 shows the analysis of variance for the model and parameter selection. The model F-value of 87.06 implies that the model is significant relative to the pure error. This high value indicates that it was certainly a signal (desired meaningful information) and not noise (undesired response, background noise). The probability that a "Model F-Value" this large could occur due to noise was low (0.01%). There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. This therefore shows that it is certainly a signal and not noise. For all model parameters, values of "Prob > F" was less than 0.0500 which indicate that the terms were significant. The final model equation is presented in Eqn. 2.

$$\% R = 92.675MB + 88.657MG + 91.174CV + 91.926RB + 2.068MB*dose + 0.027MB*temp + 0.135MB*pH + 0.012MB*time + 2.265MG*dose + 0.033MG*temp + 0.165MG*pH + 0.013MG*time + 1.904CV*dose$$

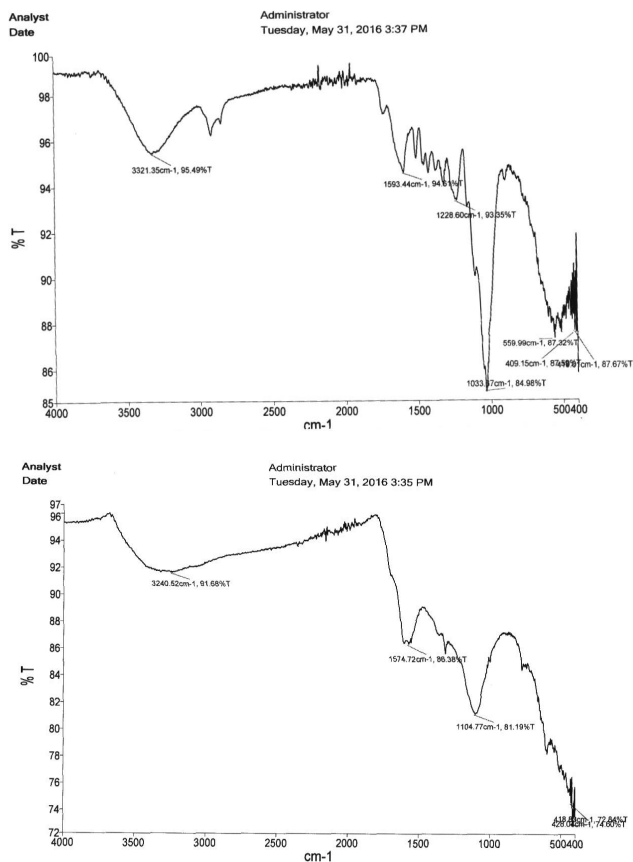


Figure 2. Fourier transform infrared (FTIR) spectroscopy micrographs of sawdust before modification (top image) and after modification (bottom image).

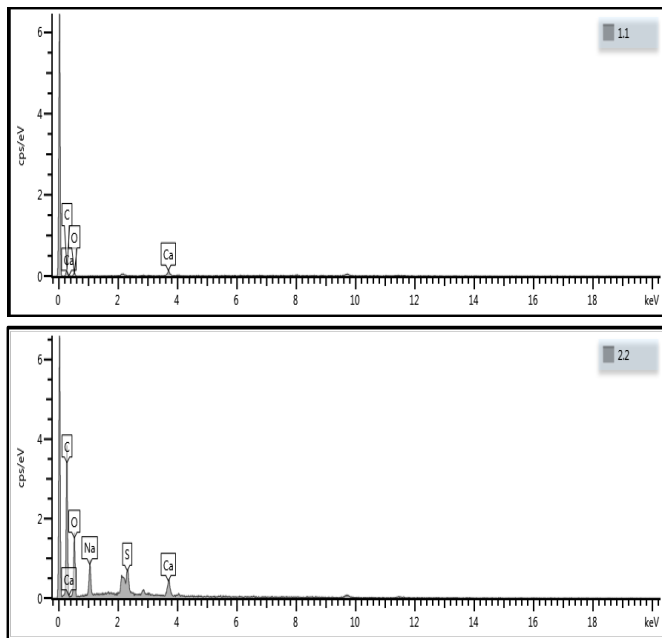


Figure 3. Elemental Diffraction X-ray Spectroscopy (EDS) of sawdust before modification (top image) and after modification (bottom image).

Table 2. Summary of model evaluation.

Source [Mix]*Process	Standard deviation	R-squared	Adjusted R-squared	Predicted R-squared	PRESS	Comment
[Mean]*Linear	1.09	0.69	0.67	0.64	82.95	
[Mean]*2FI	1.14	0.70	0.64	0.56	101.12	
[Mean]*Quadratic	1.14	0.70	0.64	0.56	101.12	Aliased
[Mean]*Cubic	1.19	0.70	0.61	0.48	117.66	Aliased
[Linear]*Mean	1.66	0.28	0.24	0.18	187.32	
[Linear]*Linear	0.37	0.97	0.96	0.95	12.51	Suggested
[Linear]*2FI	0.34	0.99	0.97	0.90	23.81	
[Linear]*Quadratic	0.34	0.99	0.97	0.90	23.81	Aliased
[Linear]*Cubic	0.56	0.99	0.91	-0.42	323.84	Aliased
[Quadratic]*Mean	1.66	0.28	0.24	0.18	187.32	Aliased
[Quadratic]*Linear	0.37	0.97	0.96	0.95	12.51	Aliased
[Quadratic]*2FI	0.34	0.99	0.97	0.90	23.81	Aliased
[Quadratic]*Quadratic	0.34	0.99	0.97	0.90	23.81	Aliased
[Quadratic]*Cubic	0.56	0.99	0.91	-0.42	323.84	Aliased
[Special Cubic]*Mean	1.66	0.28	0.24	0.18	187.32	Aliased
[Special Cubic]*Linear	0.37	0.97	0.96	0.95	12.51	Aliased
[Special Cubic]*2FI	0.34	0.99	0.97	0.90	23.81	Aliased
[Special Cubic]*Quadratic	0.34	0.99	0.97	0.90	23.81	Aliased
[Special Cubic]*Cubic	0.56	0.99	0.91	-0.42	323.84	Aliased
[Cubic]*Mean	1.66	0.28	0.24	0.18	187.32	Aliased
[Cubic]*Linear	0.37	0.97	0.96	0.95	12.51	Aliased
[Cubic]*2FI	0.34	0.99	0.97	0.90	23.81	Aliased
[Cubic]*Quadratic	0.34	0.99	0.97	0.90	23.81	Aliased
[Cubic]*Cubic	0.56	0.99	0.91	-0.42	323.84	Aliased

$$+ 0.044CV*temp + 0.219CV*pH + 0.015CV*time + 2.269RB*dose + 0.033RB*temp + 0.164RB*pH + 0.013RB*time \quad (2)$$

3.4. Model validation

3.4.1. Diagnostic Case Study

The results of the diagnostic case study are given in Figure 4. It is a plot of residual values against predicted values. The actual values indicate the percentage of dye removed and the predicted values indicate the standard generated by the software. The residual shows the closeness of the actual values to the predicted values, it can therefore be either positive or negative or zero. Negative values of residuals indicate that the actual value is greater than the predicted value while positive value indicates that the predicted value is greater than the actual value. Residual value of zero is an indication that the actual amount is equal to the predicted value

on which the comparison is made.

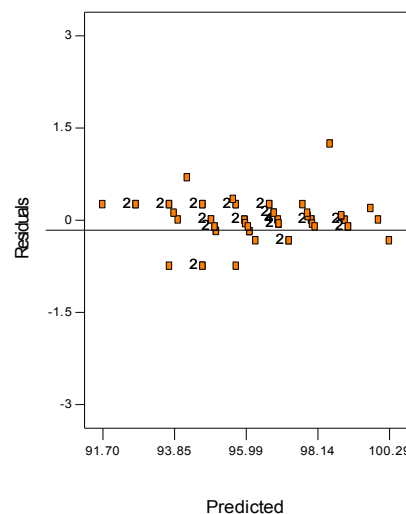


Figure 4. Diagnostic case plot of residual values and predicted values.

Table 3. Analysis of variance (ANOVA) of % R.

Source	Sum of squares	DF	Mean square	F Value	Prob > F	
Model	222.39	19	11.70	87.06	< 0.0001	significant
Linear Mixture	63.66	3	21.22	157.86	< 0.0001	
AE	14.10	1	14.10	104.88	< 0.0001	
AF	3.05	1	3.05	22.65	< 0.0001	
AG	3.06	1	3.06	22.78	< 0.0001	
AH	14.06	1	14.06	104.60	< 0.0001	
BE	16	1	16	119.01	< 0.0001	
BF	4	1	4	29.75	< 0.0001	
BG	4	1	4	29.75	< 0.0001	
BH	16	1	16	119.01	< 0.0001	
CE	12.60	1	12.60	93.74	< 0.0001	
CF	6.00	1	6.00	44.65	< 0.0001	
CG	6.00	1	6.00	44.65	< 0.0001	
CH	19.80	1	19.80	147.30	< 0.0001	
DE	16.04	1	16.04	119.31	< 0.0001	
DF	3.98	1	3.98	29.61	< 0.0001	
DG	3.98	1	3.98	29.61	< 0.0001	
DH	16.04	1	16.04	119.31	< 0.0001	
Residual	5.92	44	0.13			
Cor Total	228.30	63				

* AE- Methylene blue* Dose; AF- Methylene blue* Temperature; AG- Methylene blue* pH; AH- Methylene blue* Time; BE- Malachite green* Dose; BF- Malachite green * Temperature; BG- Malachite green * pH; BH- Malachite green * Time; CE- Crystal violet* Dose; CF- Crystal violet * Temperature; CG- Crystal violet * pH; CH- Crystal violet * Time; DE- Rhodamine B* Dose; DF- Rhodamine B * Temperature; DG- Rhodamine B * pH; DH- Rhodamine B * Time; Significant terms at alpha= 0.005

3.4.2. Stastical Error Analysis

The performance indices used in the study are summarized in Table 4. Each index was used to estimate the production forecast for each data set. Table 5 shows the result from the error analysis. In addition to the estimated errors, the coefficients of correlation are also indicated. The value for each error index was low and the R² values were high which implies that the model is very reliable(Arinkoola and Ogbe, 2015).

Table 4. Performance indices For model evaluation (Arinkoola and Ogbe, 2015)

Name of Measure	Formula
Absolute Deviation	$AD = \frac{1}{N} \sum (Pred - Exp)$
Average Deviation	$AAD = \frac{1}{N} \sum (Pred - Exp)$
Room Mean Square	$RMSE = \sqrt{\frac{1}{N} \sum (Actual - Predicted)^2}$
Average Absolute Percentage Relative Error	$AAPRE = \frac{1}{N} [\sum E_i / I]$
Maximum Error	$E_{max} = \frac{\text{Max } E_i }{\frac{Pred-Exp}{Exp}} * 100$
Standard Deviation	$SD = \frac{1}{N-1} * \sum E_i^2$

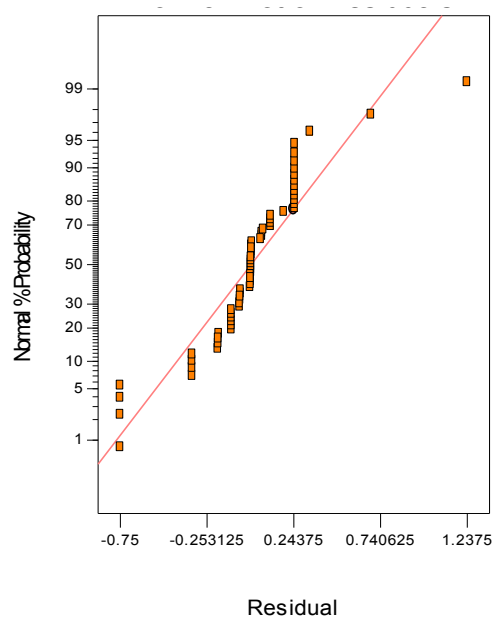


Figure 5. Probability distribution of residual values

The relationship between the actual, predicted and the residual values are graphically represented by the design expert diagnostic graphs as depicted in

Figures 5 and 6. Figure 5 shows that the probability of having the actual values greater than the predicted values (that is negative values for the residual) is low, while the probability of having positive residual values is very high. The actual values are very close to the predicted values hence the plot of actual values against predicted values almost align as a straight line graph as depicted in Figure 6.

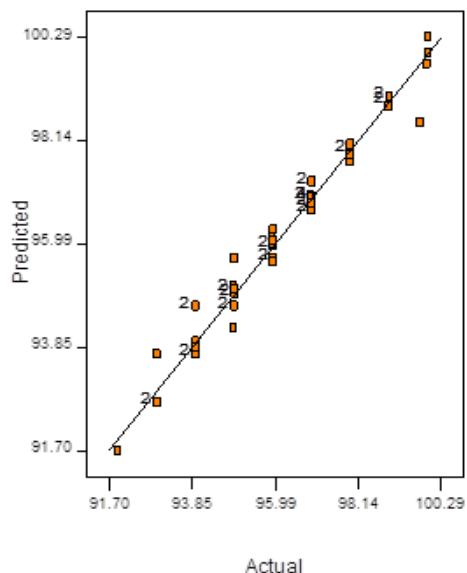


Figure 6. Relationship between the predicted and actual values of percentage removal.

Table 5. Model error analysis.

Performance Index	Value
AD	7.84981E-14
AAD	0.135110544
RMSE	0.247980105
AAPRE	0.14223179
E_{max}	0.921
SD	0.003716161
R^2	0.974
Adjusted R^2	0.963

3.5. Effects of adsorption parameters

The adsorption parameters that are examined in the present study, including adsorbent dose, pH, time and temperature have significant effects on the percentage removal of the dye. The interaction between the operative parameters and percentage removal (% R) when mixture components were fixed at 32.5 mg/L are depicted in Figures 7 – 10. The percentage removal increased with increase in (i) dose when temperature

was fixed at 51.89 °C, 7.32 pH and 153.65 min (Figure 7), (ii) temperature when dose was fixed at 0.60 g, 8.05 pH and 145.54 min (Figure 7), (iii) pH when temperature was fixed at 45 °C, 8.05 pH and an adsorbent dose of 0.60 (Figure 7), and (iv) time when temperature was fixed at 45 °C, 8.05 pH and an adsorbent dose of 0.60 (Figure 7).

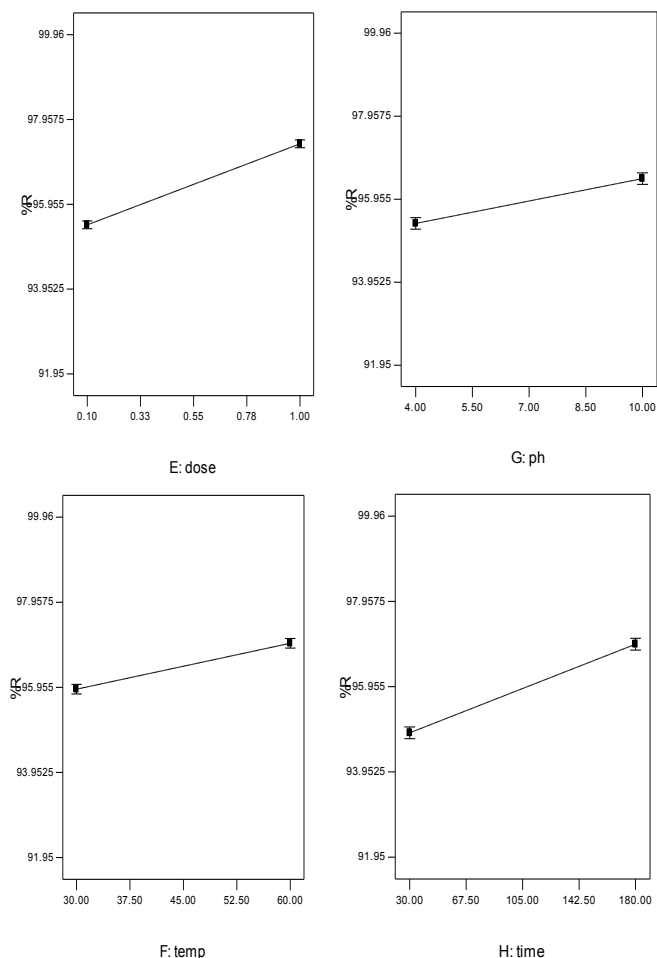


Figure 7. Interactive effects of dose and percentage removal; temperature and percentage removal; pH and percentage removal; time and percentage removal.

At a minimum temperature, the percentage removal increased with increase in dose and vice-versa when time was fixed at 109.05 min and pH at 7 (Figure 8). At a minimum pH, the percentage removal increased with increase in time and vice-versa when dose was fixed at 0.6 g and temperature fixed at 45 °C (Figure 8). A simultaneous increase in temperature and time when dose and pH are fixed at 0.6 g and 8.05 respectively results in an increase in percentage removal (Figure 9) and a simultaneous increase in dose and pH increases the percentage removal when temperature and time are fixed at 45 °C and 109.05 min, respectively (Figure 9). An increase in the value of one of the parameters

led to an increase in the percentage removal of the dye. When the values of two parameters were increased, the percentage removal increased further (Figure 10).

a temperature of 60 °C, pH of 9.42 and 146.04 min. The process was validated by performing the selected optimum experiments and percentage removal (% R) of 98.51 was obtained. This is 99.93 % in accordance with the model prediction. Hence the model was very predictive.

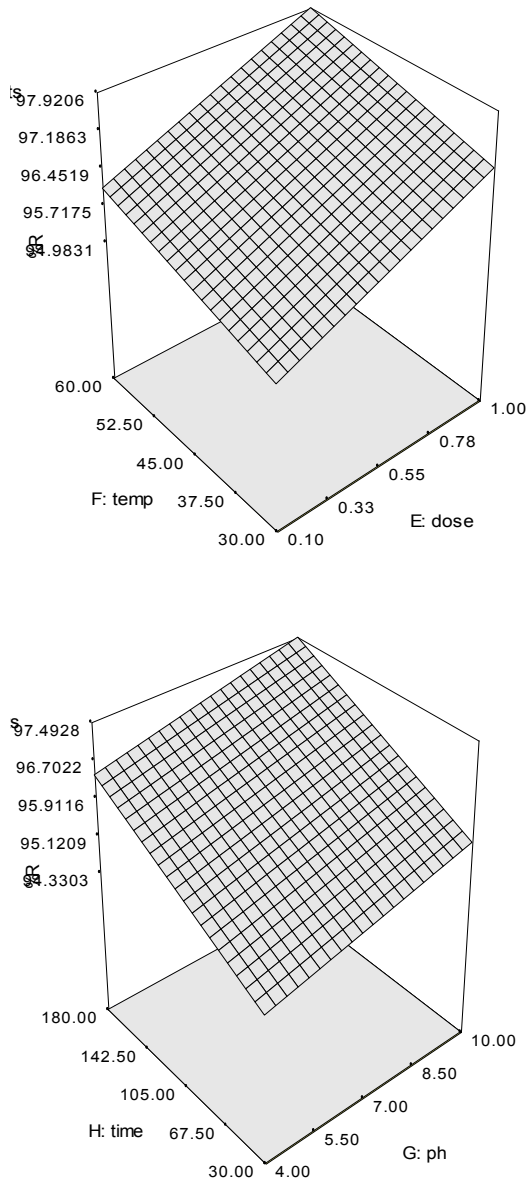


Figure 8. 3D interactive effects of: (top image) temperature and dose on percentage removal; (bottom image) time and pH on percentage removal.

3.6. Optimization of percentage removal

Optimization was used by the model to give the specific values (level) for each of the independent variables that gave optimum adsorption. The optimum conditions required for the adsorption of 40.02 mg/L of MG (98.58 % removal with a desirability of 0.861) in the presence of 48.35 mg/L of MB, 10.00 mg/L of CV, 31.63 mg/L of RB are 1.0 g dose of adsorbent at

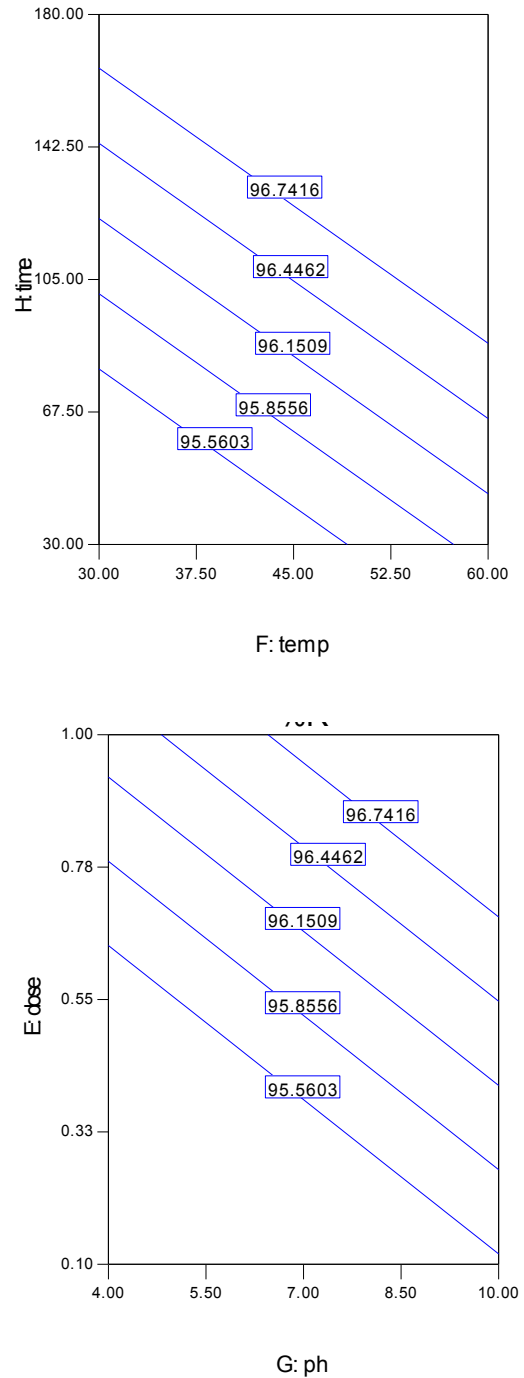


Figure 9. Effect of time and temperature on percentage removal (top image); and time and pH on percentage removal (bottom image).

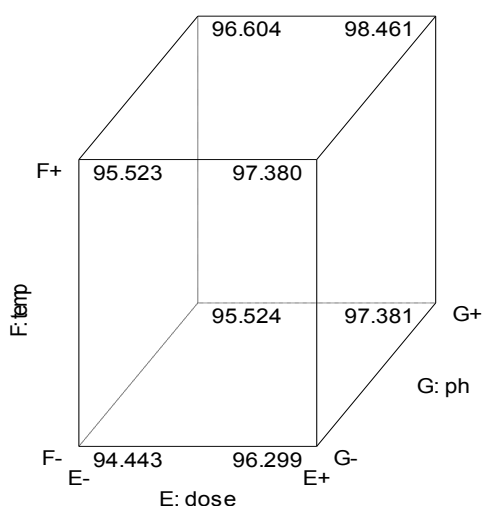


Figure 10. Interactive effect of adsorbent dose, temperature and pH on percentage removal.

4. CONCLUSIONS

The characterization analysis indicates that the adsorbent has potential adsorption sites (represented by functional groups OH, COOH, C = O, C = C, and C = S) with several pores and carbon content as high as 66.77%. The model developed is predictive (Standard deviation = 0.37, $R^2 = 0.974$, Adjusted $R^2 = 0.963$ and predicted $R^2 = 0.945$). The optimum conditions required for the adsorption of 40.02 mg/L of MG (98.58 % removal) in the presence of 48.35 mg/L of MB, 10.00 mg/L of CV, 31.63 mg/L of RB were 1.0 g dose of adsorbent at a temperature of 60 °C, 9.42 pH and 146.04 min.

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