OPTIMUM CONDITIONS FOR THE ADSORPTION OF METHYLENE BLUE ONTO ADSORBENT PREPARED FROM TEA WASTES

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Abstract: The optimum adsorption conditions for the removal of methylene blue (MB) dye onto activated carbon produced from Nigerian tea waste were studied with the help of response surface methodology (RSM) statistical software. The effect of two adsorption variables (adsorbent dosage and adsorbate concentration) were investigated using central composite design (CCD), a subset of response surface methodology (RSM) with the targeted response being percentage removal of MB. The optimum adsorption conditions obtained were the adsorbent dosage of 0.7 g and the initial concentration of 87 mg L^{-1} with the desirability of 0.96. The predicted and experimental adsorption efficiency values for MB adsorption were 90.23 and 91.07%, respectively, showing desirable agreement between the experimental and the predicted value from the models with a relatively small error of 0.84. The results show that tea waste has the potential of being a very good precursor for activated carbon production.
Keywords: Tea waste, activated carbon, adsorption, response surface methodology

Introduction

The growing use of dyes which are classified as hazardous compounds has recorded a significant increase in recent years due to their wide range of industrial applications. They are mostly used considerably in various industrial processes such as paper and pulp manufacturing, plastics, dying of clothes, leather treatment and printing which later result into soil and water contamination due to the presence of industrial effluents containing dyes (Argun*et al.,* 2014). The presence of these dyes is unwanted in the environment due to their toxicity with most of them being recalcitrant to microbial degradation. Some of the dyes also lead to the formation of compounds that are potentially carcinogenic due to their ability to undergo anaerobic degradation (Banat *et al.,* 2007). Another threat posed by the presence of dyes in the environment is that the highly color wastewaters they form may impede sunlight and oxygen from reaching various aquatic organisms which lead to their demise (Crini, 2006).

What has always been a challenge to industrialists and environmentalists is the safe and effective disposal of wastewater containing these dyes because cost-effective treatment alternatives are not available. Physical and chemical treatment processes, such as coagulation, chemical precipitation, membrane filtration, and electrochemical methods, were applied for the removal of dyes and heavy metals from wastewater (Alslaibi *et al.,* 2013) but most of these methods lack significance mainly due to their high capital and operational cost, disposal of residual metal sludge, continuous need of chemicals and sometimes failure to meet acceptable limits of environmental protection agencies (Baccar *et al.,* 2013). Therefore, there is a pressing need for more cost-effective and environmentally friendly methods. One of the most commonly used techniques involves the process of adsorption, which is the adhesion of chemicals onto a solid surface (Adetokun *et al.,* 2019; Cheng *et al.,* 2018; Garba & Afidah, 2016; Garba *et al.,* 2015; Garba *et al.,* 2019a; Garba *et al.,* 2019b; Gogoi *et al.,* 2018; Huang *et al.,* 2017; Jeon, 2018; Pongener *et al.,* 2017; Prashanthakumar *et al.,* 2018; Santos *et al.,* 2018; Zango *et al.,* 2016) with activated carbon being the most widely used solid surface.

Proficient and effective adsorptions are achieved with the aid of experimental design which helps in identifying the significant factors (input), improving the process or product robustness and minimizing process variation. Response surface methodology (RSM) is the statistical technique that has been used by many researchers to determine equations of regression model under certain operating conditions(Garba & Afidah, 2014).

The aim of this research is to study the role of response surface methodology software in optimizing methylene blue (MB) adsorption conditions using activated carbon prepared from Nigerian tea waste.

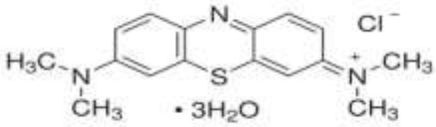
Materials and Methods

The chemicals and materials employed in this work include phosphoric acid (H_3PO_4), methylene blue dye, purified nitrogen gas, furnace, oven, ultraviolet-visible (UV-Vis) spectrophotometer, isothermal shaker, and tea waste. All reagents used were of analytical grade.

The tea waste obtained from different eateries at Ahmadu Bello University, Zaria was ground and sieved (500 µm) to get a uniform size. 30 g of the raw material was impregnated with 0.5 M phosphoric acid. The adsorbate is methylene blue (MB), a basic aniline dye with the molecular formula $C_{16}H_{18}ClN_3S$. It is also known as methylthioninium chloride which at room temperature appears as a solid and odourless. The basic properties and characteristics of the MB dye are listed in Table 1.

A stock solution was prepared by dissolving 1 g of MB dye in 1 L of distilled water with MB solutions of different concentrations (10, 23, 55 and 87 mg L^{-1}) were prepared by diluting the stock solution with distilled water. The concentrations of residual MB dye were measured using a UV spectrophotometer (Multi-user lab Cary 300 UV/Vis 1601 Spectrophotometer). The maximum wavelength (λ_{max}) of this dye is 668 nm.

Table 1 Properties and characteristics of MB

Generic Name	Methylene Blue
Chemical formula	$C_{16}H_{18}ClN_3S$
Molecular weight (g mol^{-1})	319.85
Molecular volume (cm^{3}mol^{-1})	241.9
Molecular diameter (nm)	0.8
Maximum wavelength (nm)	668
Colourindex	52.014
Chemical structure and sample	 

Preparation of activated carbon

The impregnated tea waste sample was put into the stainless steel vertical tubular reactor that was placed in a furnace. The sample was carbonized under purified nitrogen gas (99.99%) with a flow rate of 150 mL min^{-1} and at a heating rate of 10 Kmin^{-1} until 1073 K and held for 2 h. The product was cooled to room temperature (303 K), washed with distilled water and dried at 373 K in an oven. The activation process took place using carbon dioxide gas under the same condition as the carbonization but it was held for 1 h, 30 min. The activated product was cooled to room temperature (303 K), washed with distilled water and dried in an oven at 373 K.

Batch adsorption experiment

The adsorption experiment was carried out to determine the removal efficiency of MB in aqueous solution at a different combination of variables as shown it Table 2. Each sample was kept in a shaker until it reached equilibrium. In order to analyze the solutions, all samples were filtered to separate the adsorbate from the solutions and to minimize the interference. The remaining concentration of the MB solution was determined using the ultraviolet-visible (UV-Vis) spectrophotometer at 668 nm. The MB % removal was calculated using equation 1:

$$\text{MB removal}(\%\ R) = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

Where: C_o and C_e represent the liquid-phase concentrations at initial and equilibrium states (mg/L), respectively.

Central composite design (CCD) was chosen and applied for the statistical design of experiments and data analysis because it aid in optimizing the effective variables with the least number of experiments as well as probe the interaction among the parameters. The detailed CCD process was described in our previously published papers (Afidah & Garba, 2015; Garba & Afidah, 2015).

Results and Discussion

Development of regression model equations using CCD

The design matrix of the preparation variables, their ranges and the response (Y_{MB}) respectively were displayed in Table 2. Y_{MB} is the percentage removal of MB calculated from equation 1 which was recognized as a response by the software.

CCD was applied for the development of the polynomial regression equation which was two factor interaction (2FI) expressions as suggested by the software. The model expression was selected in accordance with sequential model sum of square that is based on the polynomial's highest order where the model was not aliased and the additional terms were significant (Garba & Afidah, 2014).

Table 2: Experimental design matrix using central composite design

Run	MB adsorption variables: Adsorbent dosage (g)	MB adsorption variables: Initial Concentration (mg L^{-1})	MB removal: Y_{MB} (%)
1	0.20 (-1)	23 (-1)	87.74
2	0.20 (-1)	55 (0)	88.77
3	0.20(-1)	87(+1)	89.72
4	0.70(+1)	87(+1)	91.07
5	0.50(0)	23(-1)	88.00
6	0.10(-α)	55(0)	86.07
7	0.50(0)	55(0)	85.29
8	0.80(+α)	55(0)	87.69
9	0.50(0)	55(0)	89.29
10	0.50(0)	55(0)	85.62
11	0.50(0)	55(0)	86.90
12	0.50(0)	100(+α)	78.60
13	0.50(0)	10(-α)	88.80

+1 and −1 for high and low values respectively, representing the factorial points; ±α, 0 and 0, ±αfor the axial points; 0, 0 for the replicates at the center points

The correlation between predicted and experimental data was obvious as shown by the model's R^2 value of 0.9252 which was within desirability range (Gómez-Pacheco *et al.*, 2012). The final empirical model's equations for percentage removal of MB (Y_{MB}) response was given as equation 2.

$$Y_{MB} = 11.61 + 2.59x_1 - 1.91x_2 + 0.70x_1x_2 \qquad 2$$

The positive and negative signs before the terms indicate the synergetic and antagonistic effect of the respective variables (Garba & Afidah, 2014). The appearance of a single variable in a term signified a uni-factor effect and two variables imply a double factor effect (Ahmad & Alrozi, 2010).

The MB percentage removal ranges from 78.60–91.07% as can be seen on the total experimental design matrix and the values of the response in Table 1.

Statistical analysis

In order to evaluate the individual as well as the interaction effects of the variables influencing the MB removal efficiency, analysis of variance (ANOVA) was performed. The sum of squares and mean square of each factor, F-value as well as Prob.>F values are shown in Table 3 for MB percentage removal.

ANOVA validated the importance and how adequate the models are. From Table 2, dividing the sum of the squares of each of the variation sources, the model and the error variance by the respective degrees of freedom give the mean square values. The model terms with a value of Prob.>F less than 0.05 are considered as significant (Ahmad & Alrozi, 2010; Garba *et al.*, 2016a; Garba *et al.*, 2016b).

From Table 3, it can be seen that the model F-value is 16.10 and Prob. >F of 0.0186 signifies the model's significance for MB removal. The only significant model term was x_2 with

x_1 as well as x_1x_2 being insignificant to the response. From the statistical results obtained, it can be seen that the models were suitable in predicting MB removal within the range of the studied variables. Additionally, Fig. 1 shows the predicted values versus the experimental values for MB removal, portraying that the developed models successfully captured the relationship between the adsorption process variables to the response.

Table 3 ANOVA for (2FI) response surface of MB % removal

Source	Sum of squares	Degree of freedom	Mean square	F-value	Porb>F
Model	85.52	2	42.76	16.10	0.0186
x_1	33.66	1	33.66	14.80	0.0533
x_2	51.86	1	51.86	17.39	0.0216
x_1x_2	26.15	1	26.15	11.05	0.0590
Residual	70.15	10	7.01		
Lack of fit	68.89	6	11.48	2.85	0.0879
Pure Error	1.26	4	0.32		

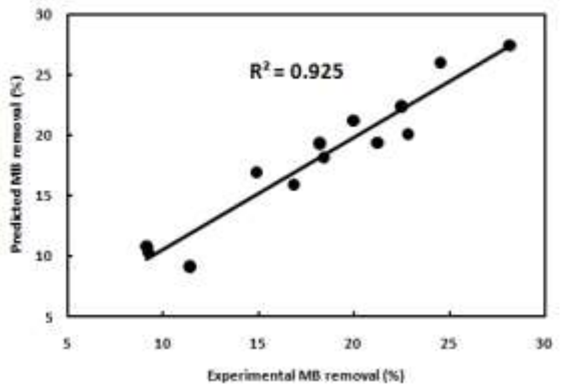


Fig. 1: Relationship between predicted and experimental data for MB removal

Individual and interaction effects of the variables

From Table 3, it can be observed that the individual effect inflicted by initial concentration on MB percentage removal was superior to that of adsorbent dosage having F-values of 17.39 and 14.80, respectively. The interaction effect between the studies variables (Adsorbent dosage and Initial concentration) was slightly insignificant with F- and Prob>F values of 11.05 and 0.0590, respectively.

Figure 2 showed the 3D response surface plots for the studied variables demonstrating the effect of adsorbent dosage and initial concentration on the response (Y_{MB}). From Figure 2, the percentage MB removal can be seen to increase with an upsurge in all the studied variables.

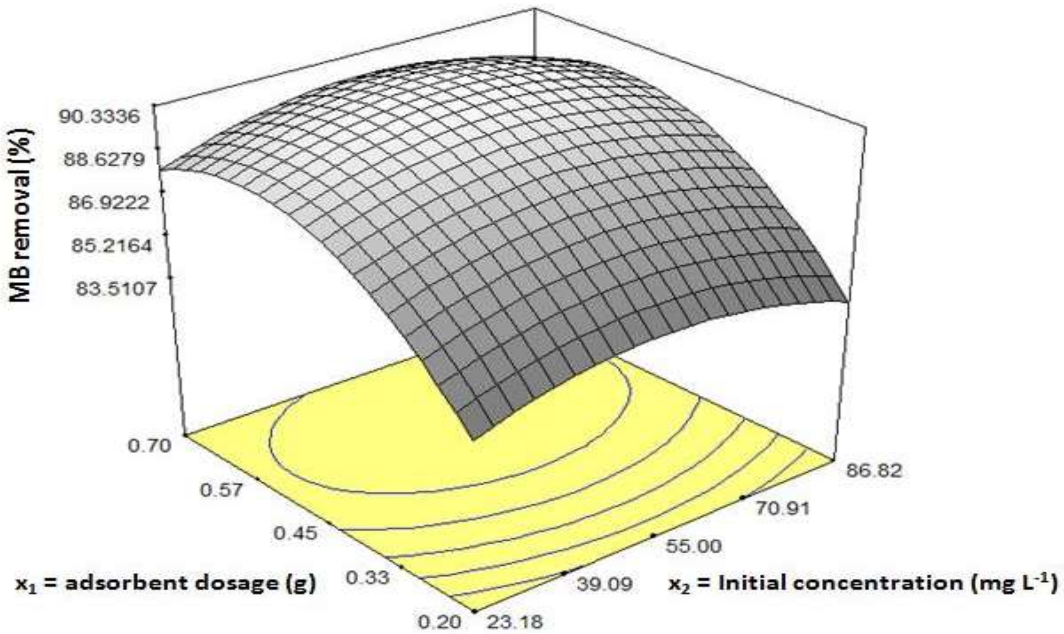


Fig. 2: Three-dimensional response surface plot demonstrating the effect of adsorbent dosage and initial concentration for MB removal

Process optimization

The optimization of MB adsorption onto WTAC was carried out using design-expert software (Stat-Ease, Inc., Minneapolis, MN 55413, USA). In the optimization analysis, the target criterion was set as maximum value for the response. The optimum adsorption conditions obtained were initial concentration of 87 mg L^{-1} and adsorbent dosage of 0.70 g with desirability of 0.96 as shown on Table 4.

Table 4: The optimum MB adsorption parameters onto WTAC

Parameters		WTAC
MB adsorption (%)	Predicted	90.23
	Experimental	91.07
	Error	0.84
Model Desirability		0.96
x_1, Adsorbent dosage (g)		0.70
x_2, Initial concentration (mg L^{-1})		87.00

At the optimum conditions, the predicted and experimental MB removals were found to be 90.23 and 91.07%, respectively showing good agreement between the experimental values and those predicted from the model with a relatively small error of 0.84.

Several researchers reported adsorbent dosage ranging from 0.1g to up to about 20g for MB adsorption by employing several adsorbents such as fly ash (Kumar *et al.,* 2005), modified sawdust (Zou *et al.,* 2013), raw mango seed (Kumar *et al.,* 2013)and modified mango seed (Kumar *et al.,* 2013).

Conclusion

Two adsorption parameters were optimized with the help of CCD, a subset of RSM for the adsorption of MB dye onto waste tea activated carbon with the dye percentage removal (Y_{MB}) as the analysis response. Based on the results obtained, the two factors (adsorbent dosage and initial concentration) have varying impacts on the adsorption processes. Highest removal percentage of the MB dye was obtained at the optimum conditions of adsorbent dosage (0.68 g) and initial concentration (85 mg L^{-1}) with the desirability of 0.96. Results of the optimization analysis revealed that good removal of MB can be achieved which is comparable to some conventional adsorbents.

Conflict of Interest

Authors have declared that there is no conflict of interest.

References

Adetokun AA, Uba S & Garba ZN 2019. Optimization of adsorption of metal ions from a ternary aqueous solution with activated carbon from Acacia senegal (L.) Willd pods using Central Composite Design. *J. King Saud Univ. - Sci.,* Article in Press, https://doi.org/10.1016/j.jksus.2018.12.007.

Afidah AR & Garba ZN 2015. Optimization of preparation conditions for activated carbon from Prosopis africana seed hulls using response surface methodology. *Desalin. Water Treat.,* 57:17985-17994.

Ahmad MA & Alrozi R 2010. Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology. *Chem. Eng. J.,* 165:883-890.

Alslaibi TM, Abustan I, Ahmad MA & Abu Foul A 2013. Kinetics and equilibrium adsorption of iron (II), lead (II), and copper (II) onto activated carbon prepared from olive stone waste. *Desalin. Water Treat.,* 1-11.

Argun ME, Güclü D & Karatas M 2014. Adsorption of Reactive Blue 114 dye by using a new adsorbent: Pomelo peel. *J. Ind. Eng. Chem.,*20(3):1079-1084.

Baccar R, Blánquez P, Bouzid J, Feki M, Attiya H & Sarrà M 2013. Modeling of adsorption isotherms and kinetics of a tannery dye onto an activated carbon prepared from an agricultural by-product. *Fuel Proces. Technol.,* 106:408-415.

Banat F, Al-Asheh S, Al-Ahmad R & Bni-Khalid F 2007. Bench-scale and packed bed sorption of methylene blue using treated olive pomace and charcoal. *Bioresour. Technol.,* 98:3017-3015.

Cheng Z-L, Li Y-X & Liu Z 2018. Study on adsorption of rhodamine B onto Beta zeolites by tuning SiO_2/Al_2O_3 ratio. *Ecotoxicol. Environ. Safety,* 148:585-592.

Crini G 2006. Non-conventional low-cost adsorbents for dye removal: A review. *Bioresour. Technol.,* 97:1061-1085.

Garba ZN & Afidah AR 2016. Evaluation of optimal activated carbon from an agricultural waste for the removal of para-chlorophenol and 2,4-dichlorophenol. *Proc. Safety Environ. Protec.,* 102:54-63.

Garba ZN & Afidah AR 2015. Optimization of activated carbon preparation conditions from Prosopis africana seed hulls for the removal of 2,4,6-Trichlorophenol from aqueous solution. *Desalin. Water Treat.,* 56:2879-2889.

Garba ZN & Afidah AR2014. Process optimization of $K_2C_2O_4$-activated carbon from Prosopis africana seed hulls using response surface methodology. *J. Anal. Appl. Pyrol.,* 107:306-312.

Garba ZN, Afidah AR & Bello BZ 2015. Optimization of preparation conditions for activated carbon from Brachystegia eurycoma seed hulls: A new precursor using central composite design. *J. Environ. Chem. Eng.,* 3:2892–2899.

Garba ZN, Bello I, Galadima A & Aisha YL 2016a. Optimization of adsorption conditions using central composite design for the removal of copper (II) and lead (II) by defatted papaya seed. *Karbala Intl. J. Modern Sci.,* 2:20-28.

Garba ZN, Hussin MH, Galadima A & Lawan I 2019a. Potentials of *Canarium schweinfurthii* seed shell as a novel precursor for CH_3COOK activated carbon: statistical optimization, equilibriumand kinetic studies. *Appl. Water Sci.,* 9(31):1-13.

Garba ZN, Ugbaga NI & Amina KA 2016b. Evaluation of optimum adsorption conditions for Ni (II) and Cd (II) removal from aqueous solutionby modified plantain peels (MPP). *Beni-Suef Univ. J. Basic Appl. Sci.,* 5:170–179.

Garba ZN, Zhou W, Lawan I, Xiao W, Zhang M, Wang L, Chen L& Yuan Z 2019b. An overview of chlorophenols as contaminants and their removal from wastewater by adsorption: A review. *J. Environ. Manage.,* 241:59-75.

Gogoi S, Chakraborty S & Saikia MD 2018. Surface modified pineapple crown leaf for adsorption of Cr(VI) and Cr(III) ions from aqueous solution. *J. Environ. Chem. Eng.,* 6:2492-2501.

Gómez-Pacheco CV, Rivera Utrilla J, Sánchez Polo M & López Peñalver JJ2012. Optimization of the preparation process of biological sludge adsorbents for application in water treatment. *J. Hazard. Mater.,* 217:76-84.

Huang R, Liu Q, Huo J & Yang B 2017. Adsorption of methyl orange onto protonated cross-linked chitosan. *Arab. J. Chem.,* 10:24-32.

Jeon C2018. Adsorption behavior of cadmium ions from aqueous solution using pen shells. *J. Ind. Eng. Chem.,* 58:57-63.

Kumar KV, Ramamurthi V & Sivanesan S 2005. Modeling the mechanism involved during the sorption of methylene blue onto fly ash. *J. Colloid Interface Sci.,* 284:14-21.

Kumar PS, Palaniyappan M, Priyadharshini M, Vignesh AM, Thanjiappan A, Fernando SAP& Ahmed RT 2013. Adsorption of basic dye onto raw and surface-modified agricultural waste. *Environ. Prog. Sust. Energ.,* 33:87-98.

Pongener C, Kibami D, Rao KS, Goswamee RL& Sinha D 2017. Adsorption studies of fluoride by activated carbon prepared from Mucuna prurines plant. *J. Water Chem. Technol.,* 39:108–115.

Prashanthakumar TKM, Kumar SKA & Sahoo SK 2018. A quick removal of toxic phenolic compounds using porous carbon prepared from renewable biomass coconut spathe and exploration of new source for porous carbon materials. *J. Environ. Chem. Eng.,* 6:1434-1442.

Santos AG, Leite JO, Souza MJB, Gimenez IF & Garrido-Pedrosa AM 2018. Effect of the metal type in perovskites prepared by modified proteic method in dye adsorption from aqueous medium. *Ceram. Int.,* 44:5743-5750.

Zango ZU, Garba ZN, Abu-Bakar NHH, Tan WL & Abu-Bakar M 2016. Adsorption studies of Cu^{2+}–Hal nanocomposites for the removal of 2,4,6-trichlorophenol. *Appl. Clay Sci.,* 132-133:68-78.

Zou W, Bai H, Gao S& Li K 2013. Characterization of modified sawdust, kinetic and equilibrium study about methylene blue adsorption in batch mode. *Korean J. Chem. Eng.,* 30: 111-122.