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Application of the box-behnken design for modelling and optimization of direct red 81 dye adsorption using raffia palm (*Raphia hookeri)* fruit epicarp activated carbon

[*1] Nkeng Severin Muluh, [2] Julius Numbonui Ghogomu, [3] Njoyim Estella Buleng Tamungang
[1, 2] Department of Chemistry, Faculty of Science, University of Dschang, P.O. Box 67 Dschang, Cameroon
[3] Department of Chemistry, Higher Teacher Training College, University of Bamenda, P.O. Box 39 Bambili, Cameroon

Abstract

Raffia Palm (*Raphia Hookeri*) fruit epicarp biomass waste was used for the preparation of activated carbon by chemical activation using $ZnCl_2$. The surface characteristics of the adsorbent were determined by Fourier transform infrared spectroscopy, Boehm titration, iodine number and bulk density. Later on, the *Raphia hookeri* fruit epicarp activated carbon (RHFE-AC) was employed for Direct Red 81 (DR81) dye colour removal from aqueous solutions. The experiment made up of 15 runs was setup with the help of Box-Behnken design to modelled and optimized the effects of the primary operating parameters such as adsorbent dosage (0.1-2 g), solution pH (2-10), and contact time (10-60 min), while the initial DR81 dye concentration was fixed at 100 mg/L. Analysis of variance showed that the suggested quadratic model successfully explained the experimental data with a correlation coefficient of R^2=0.9997 and adjusted R^2=0.9993. The optimum pH, contact time, and adsorbent dosage were determined to be 2, 60 min, and 1.73 g respectively. The predicted % removal acquired from the RSM under optimal conditions was 78.82%. A confirmatory test of the optimal conditions supported the validity of the model yielding a % removal of 80.21%. The adsorption equilibrium data were best described by the Langmuir isotherm with R^2=0.96584 and the pseudo-second order kinetic model fitted the experimental data best. The study showed the pertinence of RHFE-AC utilized in batch mode for the removal of dyes.

Keywords: adsorption, ANOVA, box-behnken design, direct red 81 dye, optimization, response surface methodology

Introduction

The removal of recalcitrant contaminants such as dyes from wastewater is essential as they pose serious health and environmental hazard. The increasing use of a wide variety of dyes, pollution caused by dyes wastewater is becoming increasingly alarming. Moreover, dyes are toxic to some organisms. Among the synthetic dyes, about 70% of the dyes used by the dying industries are azo dyes. An azo dye contains one or more azo bonds (-N=N-) that act as chromophores in the molecular structure in association with an aromatic structure containing functional groups such as -OH and $-SO_3H$ [1].

Water contaminated with dyes is not only unfit for drinking both by humans and animals, it is also not suitable for agricultural irrigation due to its inhibitory action on the photosynthetic process in water plants and phytoplankton [2]. In addition, dyes reduce the dissolved oxygen of the aquatic ecosystem leading to an increase in the chemical oxygen demand (COD) [3]. Direct Red 81, is a toxic sulfonated azo dye which is carcinogenic in nature. Ingestion of the dye can result in gastrointestinal problems, nausea, and vomiting. Direct Red 81 dye is equally harmful to the eyes and skin [4]. Hence, there is a need to develop technologies that can remove the toxic pollutants from wastewater streams.

Different technologies used in the treatment of wastewater such as precipitation, ion-exchange, membrane separation, adsorption and biological treatment methods have been used for the removal of dyes and organic pollutants from wastewater [5]. However, most of these methods are costly and require high levels of expertise, consequently, these methods are not applied by many end-users. Adsorption is one of the most popular methods for removing dyestuff from aqueous media since the proper design of the adsorption process will produce high quality treated effluents.

The success of an adsorption process starts with choosing the appropriate adsorbent. Several adsorbents can be used to treat wastewater, namely: commercial activated carbon, silica-gel, zeolite and activated alumina, but they are very expensive. For this reason, the use of low-cost adsorbents derived mainly from agricultural waste has attracted wide attention in recent years. Raphia hookeri fruit epicarps, an agricultural waste material, was favorably selected as an adsorbent for the removal of dyestuff from wastewater due to its local availability, low production cost, insolubility in water, high mechanical strength and chemical stability [6].

In adsorption processes, factors such as pH, the initial concentration of adsorbate, adsorbent dose, contact time and stirring speed, influence the process efficiency. The efficiency of the process may thus be optimized by adjusting these factors [7].

In traditional multifactor experiments, optimization is usually carried out by varying one factor while keeping all the other factors fixed that is the one-factor-at-a-time (OFAT) method. However, this method is time-consuming and expensive because it requires a large number of experiments to be performed [8]. Also, the OFAT method does not include interactive effects among the factors and does not depict the complete effects of the parameters on the process [7]. The limitations of the traditional methods such as the OFAT method can be eliminated by optimizing all the factors collectively by statistical experimental designs such as response surface methodology (RSM) [9].

Response Surface Methodology which is based on factorial design is a statistical method that uses quantitative data from appropriate experiments to analyzed and evaluate the effects of variables as well as to determine the optimum operating conditions for the system [10]. The application of statistical experimental design techniques in the development of the adsorption process can result in reduced process variability and overall cost [8]. However, RSM has not been used for the optimization of the removal of Direct Red 81 dye from aqueous solution using Raphia hookeri fruit epicarp activated carbon (RHFE-AC).

The main purposes of this study are to investigate the feasibility of using RHFE-AC for the sequestration of Direct Red 81 dye from aqueous solution, to model and optimized the adsorption process of Direct Red 81 dye onto *raphia hookeri* fruit epicarp activated carbon using RSM, and lastly, to investigate the interactive effects of process parameters such as solution pH, contact time and adsorbent dose on the adsorption capacity of RHFE-AC towards Direct Red 81 dye. The Box-Behnken Design (BBD), a standard response surface design method was employed in this study to design the experiment.

Materials and Methods

Chemicals

Direct Red 81, an anionic, acidic sulfonated disodium azo dye with molecular formula $C_{29}H_{19}N_5Na_2O_8S_2$ and molecular weight 675.60 g mol^{-1} was obtained from BDH company, and supplied by Lab Sec, was used without further purification. The structure of the dye is shown in Figure 1. A stock solution of the dye with concentration 1000 ppm was prepared by dissolving 1 g of the dye using distilled water. Solutions for the adsorption study were prepared by diluting an aliquot of the stock solution with distilled water. Other chemicals used were of analytical reagent grade quality and all other solutions were prepared with distilled water.

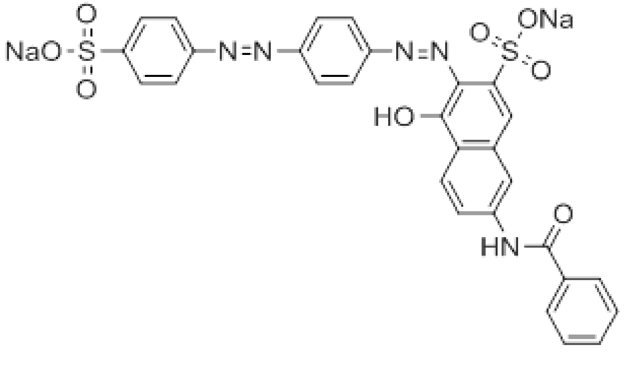

Fig 1: Structure of Direct Red 81

Preparation of the adsorbent

Raffia palm (*Raphia Hookeri*) bunch was collected from a fresh water swamp bush. The fruits were removed from the bunch, put in a plastic bag and left for about a week. Thereafter, the epicarps were separated from the mesocarp and endocarp, washed and sun dried. The dried epicarp was then first crushed into smaller fragments with a mortar and pestle and later further ground into finer particles using an electric blender. The pulverized precursor material was sieved using a 75 µm sieve. 100 g sample of the precursor material was impregnated using a solution of $ZnCl_2$ in a 1:1 (weight basis) impregnations ratio. The impregnation was carried out at 110 °C in a hot air oven for 24h to achieve good penetration of chemicals into the interior of the precursor material. The impregnated sample was then dried at 110 °C in an oven for 12h. The impregnated sample was transferred into porcelain crucibles with lids. The crucibles were then placed inside an electric Muffle furnace and carbonized at 400 °C for 1h, in the absence of air. The carbonized sample was then cooled to room temperature and washed with 0.1 M hydrochloric acid (HCl) to remove the residual chemical agent followed by distilled water until the pH value of the rinsed water was neutral. The washed activated carbon was then dried in the oven at 110 °C for 5 hours. The dried sample was pulverized using a porcelain mortar and pestle and stored in an airtight bottle for later use.

Batch adsorption studies

The batch experiments were carried out with the various combinations of the different factors. The batch experiments were performed by mechanical agitation using a multi-agitator system (Edmund Bühler GmbH SM 30) at room temperature. The initial concentration of the dye solution was fixed at 100 ppm. After agitation, the solution was filtered using a what man No. 1 filter paper. The residual concentration of the dye in the filtrate was determined spectrophotometrically using a UV-Vis Spectrophotometer (JENWAY) at a maximum wavelength of 508 nm. The adsorption capacity (q_e) and the predicted percentage removal (Y) were calculated using the following expressions:

$$q_e = \frac{(C_o - C_e)\,V}{M} \tag{1}$$

$$Y = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

Where C_o is the initial concentration of Direct Red 81 dye and C_e is the concentration of Direct Red 81 dye at equilibrium.

Statistical Design of Experiment

The process parameters affecting the removal of Direct Red 81 dye by *raphia hookeri* fruit epicarps activated carbon were optimized using a three factorial, three-level Box-Behnken experimental design combines with response surface methodology, established using Minitab software (17.0 version). The input parameters adsorbent dosage, pH, and contact time and the three levels of the design were low, medium and high and coded as (-1, 0, and +1) respectively. The process variables and their levels are presented in Table 1.

Table 1: Process factors and their levels

Factors	Factors Code	Box-Behnken Levels		
		Low (-1)	**Medium (0)**	**High (+1)**
Adsorbent dosage (g)	A	0.1	1.05	2
pH	B	2	6	10
Contact time (min)	C	10	35	60

A total of 15 experimental runs were carried out to optimize the process parameters and the experiments were performed according to the actual experimental design matrix as shown in Table 2.

Table 2: Experimental design matrix with response

Run	A: Adsorbent dosage (g)	B: pH	C: Contact time (min)	Removal (%)
1	2.00	6.00	10.00	42.17
2	1.05	6.00	35.00	55.69
3	1.05	10.00	60.00	50.55
4	2.00	2.00	35.00	66.73
5	1.05	6.00	35.00	56.70
6	1.05	10.00	10.00	26.65
7	2.00	10.00	35.00	28.82
8	0.10	2.00	35.00	36.17
9	1.05	6.00	35.00	56.70
10	1.05	2.00	10.00	56.60
11	1.05	2.00	60.00	75.82
12	2.00	6.00	60.00	69.59
13	0.10	10.00	35.00	18.88
14	0.10	6.00	60.00	43.48
15	1.05	6.00	35.00	55.68

The results were analyzed by applying the Analysis of variance (ANOVA), correlation coefficients (R^2) and response plots. For RSM, the most widely employed second-order polynomial equation developed to fit the experimental data and identify the relevant model terms may be written as equation (3) [11].

$$Y = b_o + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \qquad (3)$$

Where *Y* is the predicted % removal of Direct Red 81 dye, which is used as the dependent variable; it is defined as equation (1) above. In this model, b_o is the constant coefficient, b_i is the linear coefficient, b_{ij} is the interaction coefficient, b_{ii} is the quadratic coefficient, X_i and X_j are the coded values for the factors.

Adsorption Equilibrium and Kinetic Studies

Adsorption isotherm and kinetic models are usually employed to represent the interaction between the adsorbent and adsorbate at equilibrium and to establish the mechanism of the adsorption process. In order to find the most appropriate isotherm and kinetic model for Direct Red 81 adsorption, the results obtained were analyzed with the following isotherm models, Langmuir [12], Freundlich [13], Temkin [14], and Halsey isotherms [15]. While the kinetics of the adsorption process was analyzed with the pseudo-first order [16], pseudo-second order [17], liquid film diffusion [18], and intraparticle diffusion [19] models. For both equilibrium and kinetic studies, the adsorption experiments were performed at predetermined time intervals for analyzing the residual dye concentration using optimized conditions previously obtained from the Box-Behnken design analysis. The equations for the kinetics and isotherm models employed in this study are presented in Table 3.

Table 3: Isotherms and Kinetics model equations

Model	Linear equation	Symbol representation
Isotherm models		
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	where q_e (mg/g) and q_m (mg/g) are the equilibrium and maximum adsorption capacity of DR81 dye, respectively, C_e (mg/L) is the concentration of DR81 dye at equilibrium, k_1 (L/mg) is the Langmuir constant.
Freundlich isotherm	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	Where K_F (L/g) and n are Freundlich isotherm constants which are related to the adsorption capacity and the adsorption intensity, respectively.
Temkin isotherm	$q_e = B \mathrm{In} A + B \mathrm{In} C_e$	where A is the Temkin isotherm energy constant (L/g) and B is the Temkin isotherm constant
Halsey isotherm	$\mathrm{In} q_e = \frac{1}{n_H} \mathrm{In} K_H - \frac{1}{n_H} \mathrm{In} C_e$	Where K_H (mg/L) and n_H are the Halsey isotherm constants.
Kinetic models		
Pseudo-first order model	$\log(q_e - q_t) = \log q_e + \frac{k_1}{2.303} t$	Where q_t is the adsorption capacity at time t (mg/g); k_1 is the rate constant of first-order (min^{-1}).
Pseudo-second order model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	Where k_2 is the second-order adsorption rate constant (g/mg min).
Liquid film diffusion model	$\mathrm{In}(1\text{-}F) = k_{fd} t$	Where F is the fractional attainment of equilibrium ($F = q_t/q_e$) at time t, and K_{fd} (min^{-1}) is the adsorption rate constant.
Intraparticle diffusion model	$q_t = k_{id} t^{1/2} + I$	Where K_{id} is the intraparticle diffusion rate constant (mg/g $min^{1/2}$) and I is the intercept.

Results and Discussion

Regression Model Equation Development

The results of the % removal of Direct Red 81 dye for 15 experimental runs are presented in Table 2. From the results, it can be observed that the maximum removal efficiency of dye was found to be 75.82%. ANOVA and α level of 0.05 (95% confidence level) was used to determine the statistical significance of the independent parameters and their interactions. Table 4 presents the analysis of variance (ANOVA) results for each term of the quadratic model. A term is significant if the F-value is large and the P-value is less than 0.005 [20]. From the results as depicted in Table 3, the F-value of 2696.28 and the corresponding P-value of 0.0001 for the model term is an indication that the model is significant. Also, from the results, it can be inferred that the linear terms A, B and C, the interaction terms AB, AC and BC and the quadratic terms A^2, B^2 and C^2 are all significant since their corresponding P-values are < 0.05.

Table 4: Analysis of Variance for DR81 removal efficiency

Source	Sum of Squares	DF	Mean Square	F-Value	P-Value	Comments
Regression Model	4286.15	1	476.24	2696.28	< 0.0001	significant
A-Adsorbent dosage	820.33	1	820.33	4644.38	< 0.0001	significant
B-pH	1524.07	1	1524.07	8628.72	< 0.0001	significant
C-Contact time	929.88	1	929.88	5264.64	< 0.0001	significant
AB	106.38	1	106.38	601.81	< 0.0001	significant
AC	34.28	1	34.28	194.09	< 0.0001	significant
BC	5.48	1	5.48	31.00	0.0008	significant
A^2	673.59	1	673.59	3813.63	< 0.0001	significant
B^2	151.36	1	151.36	856.97	< 0.0001	significant
C^2	18.69	1	18.69	105.80	< 0.0001	significant
Residual Error	1.24	7	0.18			
Lack-of-fit	1.04	3	0.36	0.18	0.9072	Not significant
Pure Error	1.24	4	0.31			
Total	4287.38	16				

The ANOVA analysis also shows the Lack-of-Fit (LoF) of the test result, which can be used to investigate the model's adequacy. The hypothesis is, if the LoF is not significant, then the model is adequate and if there is a significant LoF then the model is unfit to represent the data [21]. The LoF P-value of 0.9072, implies the lack-of-fit is not significant indicating the model adequately fit the data. Besides the Lack-of-Fit test, the model sufficiency can also be confirmed by doing the residual analysis to validate the three ANOVA assumptions (normality, constant variance, and independence). Based on the residual normality test, the normal probability plot of residual should form a straight line with the data points spread around the line. The constant variance assumption can be checked with residual versus fit plot. This plot should show a random pattern of residuals on both sides of the zero line and should not show any recognizable patterns and the independence assumption can be checked using the residual versus order plot. If the plot does not reveal any pattern, then the independence assumption is satisfied [22]. From the results, the normality plot of residuals as depicted in Figure 2a shows that the residuals follow a normal distribution. Both plots of residuals versus fitted values (Figure 2b) and plot of residual versus run order (Figure 2c) do not show any pattern. Thus, both constant variance and independent assumptions are satisfied, indicating the model is correct.

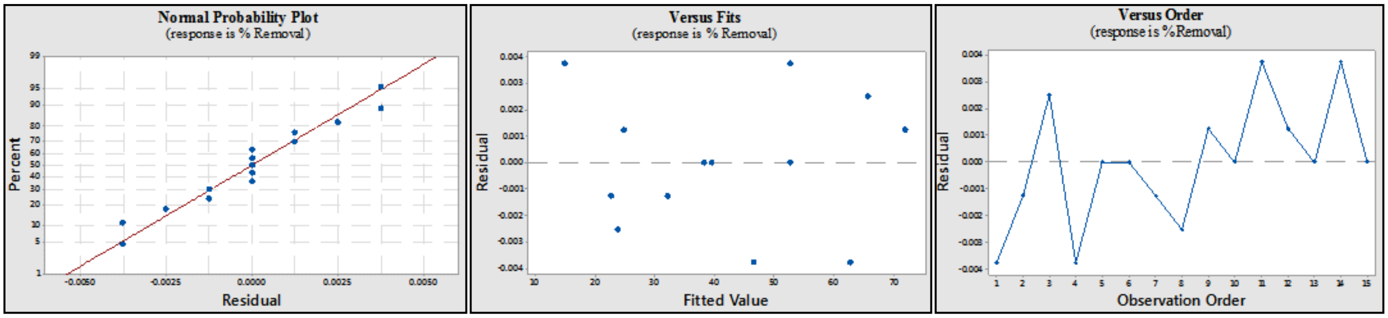

Fig 2: (a) Normal probability plot, **(b)** Residual versus fits plot and **(c)** Residual versus run order plot of adsorption of DR81 dye by RHFE-AC

Table 5, shows results for the estimated coefficients for both the coded and actual values along with the correlation coefficient (R^2), the adjusted correlation coefficient (adj. R^2) and the predicted correlation coefficient (pred. R^2). The model equation fitted between the response (color removal efficiency) and the input variables: adsorbent dosage (A), pH (B), and contact time (C) in terms of coded and uncoded (actual) values of the variables are shown in Equation 4 and 5 respectively.

$$\begin{aligned} Y = {} & 52.6900 + 10.1262A - 13.8025B + 10.7813C \\ & - 12.8512A^2 - 6.19875B^2 + 1.90375C^2 \\ & - 5.15500AB + 2.92750AC + 1.17000BC \qquad (4) \end{aligned}$$

$$\begin{aligned} Y &= 19.6333 + 44.3877A + 2.21335B + 0.018404C \\ &\quad - 14.2396A^2 - 0.387422B^2 + 0.003046C^2 \\ &\quad - 1.35658AB + 0.123263AC + 0.01170BC \qquad (5) \end{aligned}$$

The fitness of the model was also tested using the correlation coefficients. In this case, the value of the predicted correlation coefficient (pred, $R^2 = 0.9995$) is in good agreement with the value of the adjusted correlation coefficient (adj. $R^2 = 0.9993$), indicating that the regression was statistically significant.

Table 5: Estimated regression coefficients for the model

Term	Estimated Coefficients	
	Coded	Uncoded (actual)
Intercept	52.6900	19.6333
A-Adsorbent dosage	10.1262	44.3877
B-pH	-13.8025	2.21335
C-Contact time	10.7813	0.018404
A^2	-12.8512	-14.2396
B^2	-6.19875	-0.387422
C^2	1.90375	0.003046
AB	-5.15500	-1.35658
AC	2.92750	0.123263
BC	1.17000	0.011700
$R^2 = 0.9997$		
Adjusted $R^2 = 0.9993$		
Predicted $R^2 = 0.9995$		

Analysis of response surface plots

In order to explain the interaction effects of factors on the adsorption of Direct Red 81 by raphia hookeri fruit epicarp activated carbon, 2-Dimensional contour and 3-Dimensional surface plots for the predicted response were analyzed.

Interaction effect of pH and adsorbent dosage at constant contact time

The combined effect of pH and adsorbent dose at a constant contact time of 35 mins was analyzed using RSM and the results of the contour and response surface plots are presented in Figure 3a and 3b. It can be inferred from the plots that the % removal of Direct Red 81 dye from solution onto RHFE-AC decreased with increasing pH and increased with increasing adsorbent dose up to a dose of 1.05 g, thereafter, it decreases. This trend foreboded by the model is coherent with the experimental results presented in Table 2 that is the highest % removal of 75.82%, was observed at low pH and an adsorbent dose of 1.05 g (run 7). From our findings, it is evident that pH plays a vital role in the removal of dyes. At low pH, the adsorbent surface is protonated and is positively charged, which provides an electrostatic attraction between the adsorbent surface and the anionic dye molecules. At higher pH, the electrostatic repulsion between the negatively charged adsorbent surface and the dye molecules reduces the amount of dye uptake by the adsorbent. Similar results were reported by [24, 26]. The increase in the % removal with increasing mass of adsorbent can be attributed to the accessibility of more binding sites available to the dye molecules. Beyond a dose of 1.05 g, the decrease in % removal can be explained in terms of the agglomeration of adsorption sites which leads to a decrease in the total adsorbent surface accessible by the dye molecules. This result is consonant with that obtained by [7].

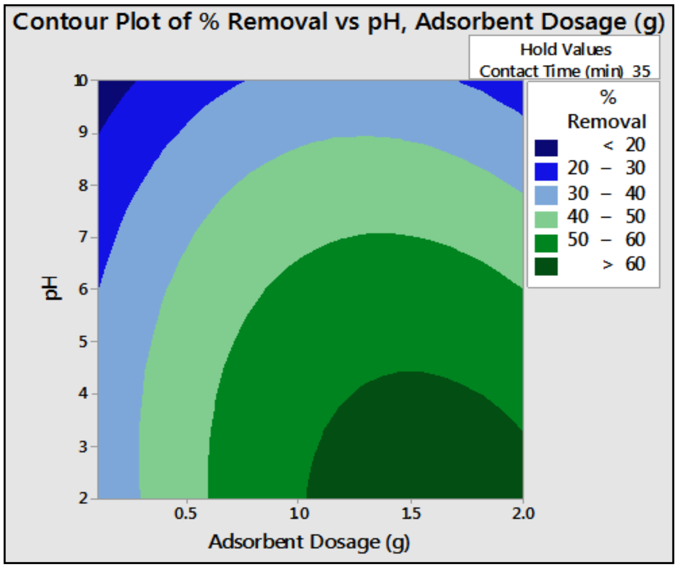

Fig 3a: Contour plot of % removal of DR81 vs pH and adsorbent dosage

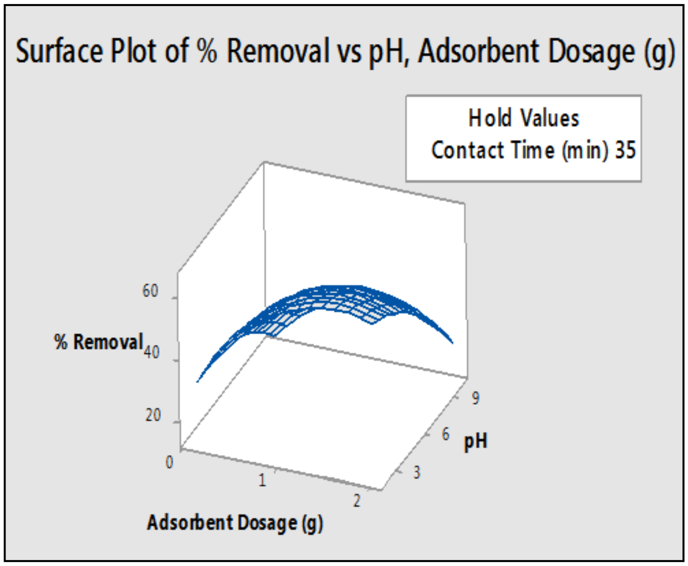

Fig 3b: Response surface plot of interaction effect of pH and adsorbent dosage on % removal of DR81

Interaction effect of contact time and adsorbent dosage at constant pH

The results of the analysis of the relationship between the % removal, contact time and adsorbent dosage at constant pH are presented in the contour and surface plots in Figure 4a and 4b. It can be observed from the plots that, the % removal increased with increasing the adsorbent dose to a maximum at 1.05 g, then decreased thereafter. On the other hand, the % removal increased with increasing contact time, which can be ascribed to the presence of vacant sites on the adsorbent surface which are available to the dye molecules, in accordance with that obtained by [23].

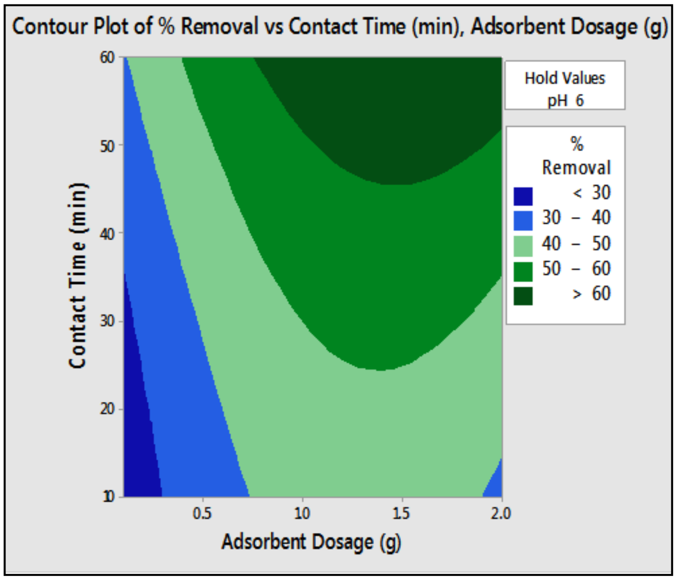

Fig 4a: Contour plot of % removal of DR81 vs contact time and adsorbent dosage

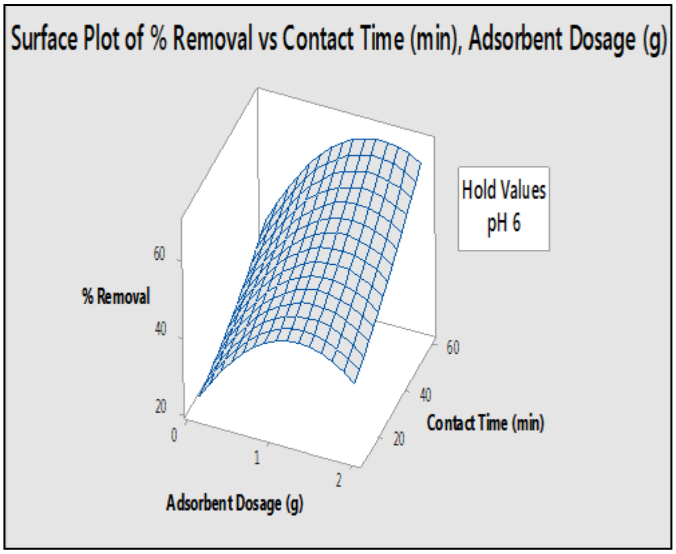

Fig 4b: Response surface plot of interaction effect of contact time and adsorbent dosage on % removal of DR81

Interaction effect of contact time and pH at constant adsorbent dosage

The interaction effect between contact time and pH on the % removal of Direct Red 81 is shown on the contour and the response surface plots in Figures 5a and 5b. It can be inferred from the plots that the % removal of Direct Red 81 by RHFE-AC increases with increase in the contact time between the activated carbon and the dye solution, but decreases with increasing pH. Thus high % removal of Direct Red 81 (greater than 70%) is obtained at the maximum level of contact time and a minimum level of pH, with the mass of adsorbent held at 1.05 g. Conversely, a low % removal of Direct Red 81 dye from solution (less than 30%) is obtained at lower values of contact time and higher pH values.

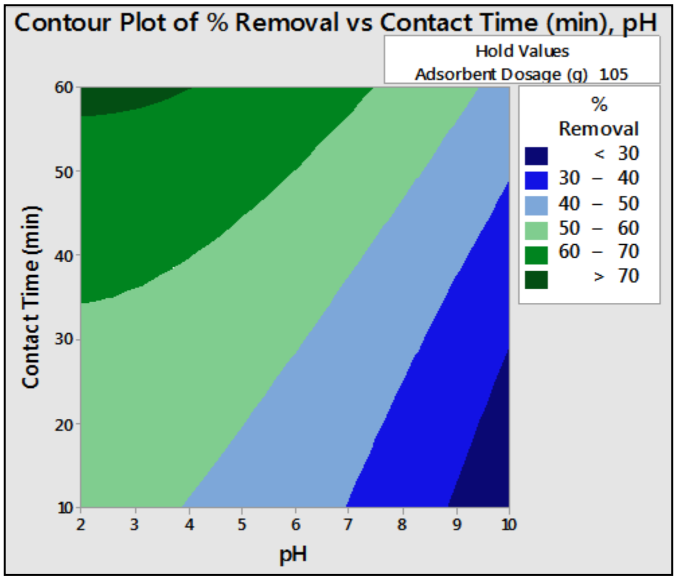

Fig 5a: Contour plot of % removal of DR81 vs pH and contact time

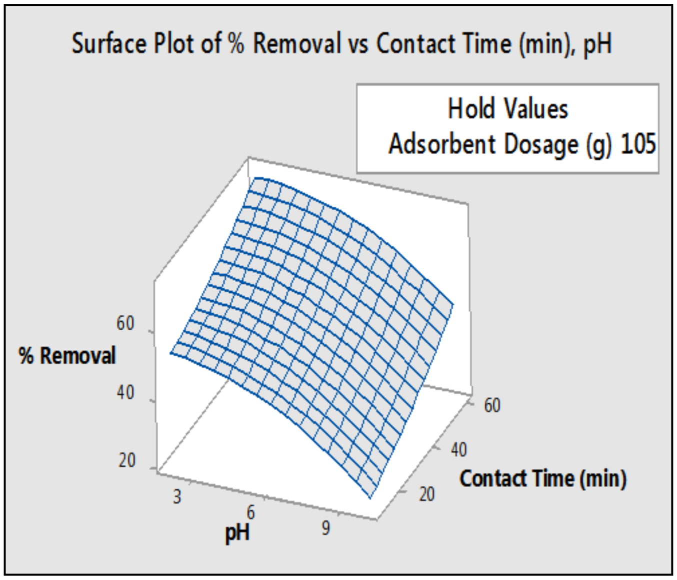

Fig 5b: Response surface plot of interaction effect of pH and contact time on % removal of DR81

Optimization and Validation of model

One of the primary objectives of the present study is to optimize and validate the results obtained. In order to find the maximum % removal of Direct Red 81 dye that collectively fulfills all process conditions, optimization was performed using RSM response optimizer in MINITAB 17 software. The optimum conditions for the batch adsorption of Direct Red 81 dye using raphia hookeri fruit epicarp activated carbon, are as follows: adsorbent dosage of 1.73 g, pH of 2, and contact time of 60 mins. Validation experimental runs were carried out using the optimum conditions in replicate and the average value of the % removal of Direct Red 81 of 80.21% was obtained. A maximum, which validated the design.

Adsorption isotherm studies

From the results as presented in Figure 6 and in Table 6, the correlation coefficient R^2 (0.96584) for the Langmuir isotherm model was highest in comparison to the values gotten for the Freundlich, Halsey and Temkin models. Also, the correlation coefficient R^2 (0.96584) and the adjusted R^2 (0.96242) for the Langmuir isotherm was in good agreement and is an indicator of the homogeneous nature of the RHFE-AC surface and the monolayer adsorption nature of the Direct Red 81 dye onto the adsorbent. Therefore, the Langmuir isotherm was found to best represent the equilibrium data for the adsorption of Direct Red 81 dye onto RHFE-AC. The monolayer adsorption capacity of 10.37 mg/g is slightly higher compared to values obtained using other low-cost adsorbents, as shown in Table 7. The favourability of the Langmuir adsorption isotherm was further assessed using the dimensionless separation factor (R_L) which can be defined as $R_L=1/1+K_LC_o$. If the Langmuir isotherm is favourable for the adsorption process, then $0<R_L<1$. From the value of R_L in Table 6, it could be seen that the Langmuir isotherm was favourable for the adsorption of DR81 dye on RHFE-AC since R_L (0.51) was less than 1 but greater than zero.

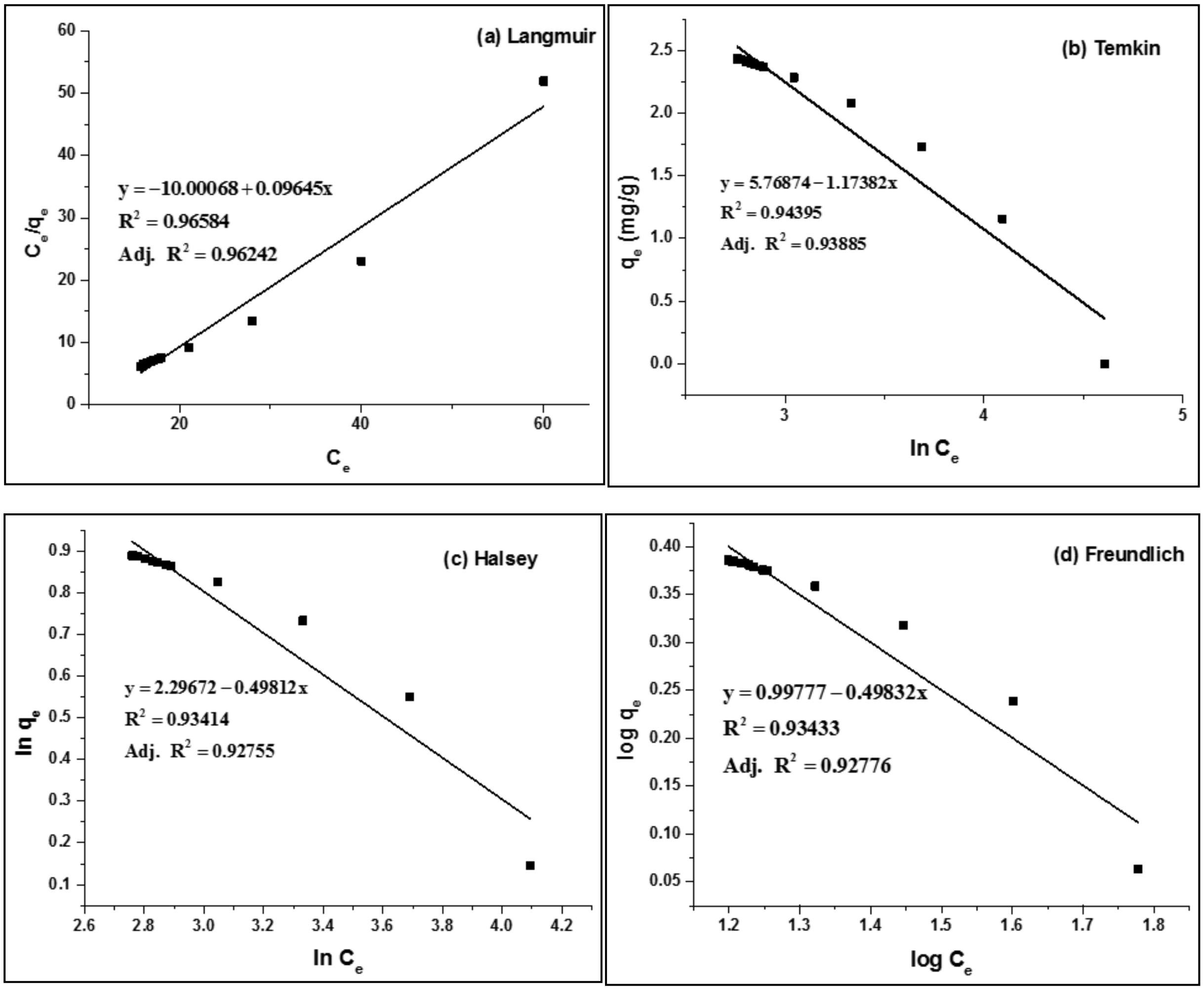

Fig 6: (a) Langmuir, (b) Temkin (c) Halsey, and (d) Freundlich plots for DR81 dye adsorption onto modified RHFE.

Table 6: Isotherm constants for DR81 dye adsorption

Langmuir				Freundlich			Halsey			Temkin		
q_m (mg/g)	K_L	R_L	R^2	n	K_f	R^2	n_H	K_H	R^2	B_T	K_T	R^2
1.037	0.096	0.51	0.96584	2.007	9.949	0.93433	2.008	100.56	0.93414	2100	132.13	0.94395

Table 7: Comparison of monolayer adsorption capacities of DR81 dye onto different adsorbents

Adsorbents	q_m (mg/g)	References
Treated Bamboo sawdust	13.83	[24]
Bamboo sawdust	6.43	[24]
Modified silk maze	5.55	[25]
Argemone Mexicana	3.66	[26]
RHFE-AC	10.37	This study

Adsorption kinetic studies

From the plots of the different kinetic models as depicted in Figure 7 and the different kinetic parameters for the uptake of DR81 dye presented in Table 8, it was noticed that the pseudo-second order model described the adsorption process best due to the fact that it correlation coefficient (0.99960) was the highest for the kinetic models studied. Also, the theoretical adsorption capacity ($q_{e,cal}$ of 24.789 mg/g) for the pseudo-second order model was consistent with the experimental adsorption capacity ($q_{e,exp}$ of 24.326 mg/g). The liquid film diffusion and intraparticle diffusion plots were used to determine the mechanism of Direct Red 81 dye uptake by RHFE-AC. From the plots in Figure 7, it can be deduced that the liquid film diffusion plot is a straight line but it does not pass through the origin, thus, the liquid film diffusion is not the only prevailing mechanism in the sorption process. From the intraparticle diffusion plot, it was also noticed that the plot exhibited two linear portions indicating that two intervening mechanisms affect the adsorption process. From these results, it can be concluded that the mechanism of DR81 dye uptake by activated RHFE was controlled by both liquid film and intraparticle diffusion.

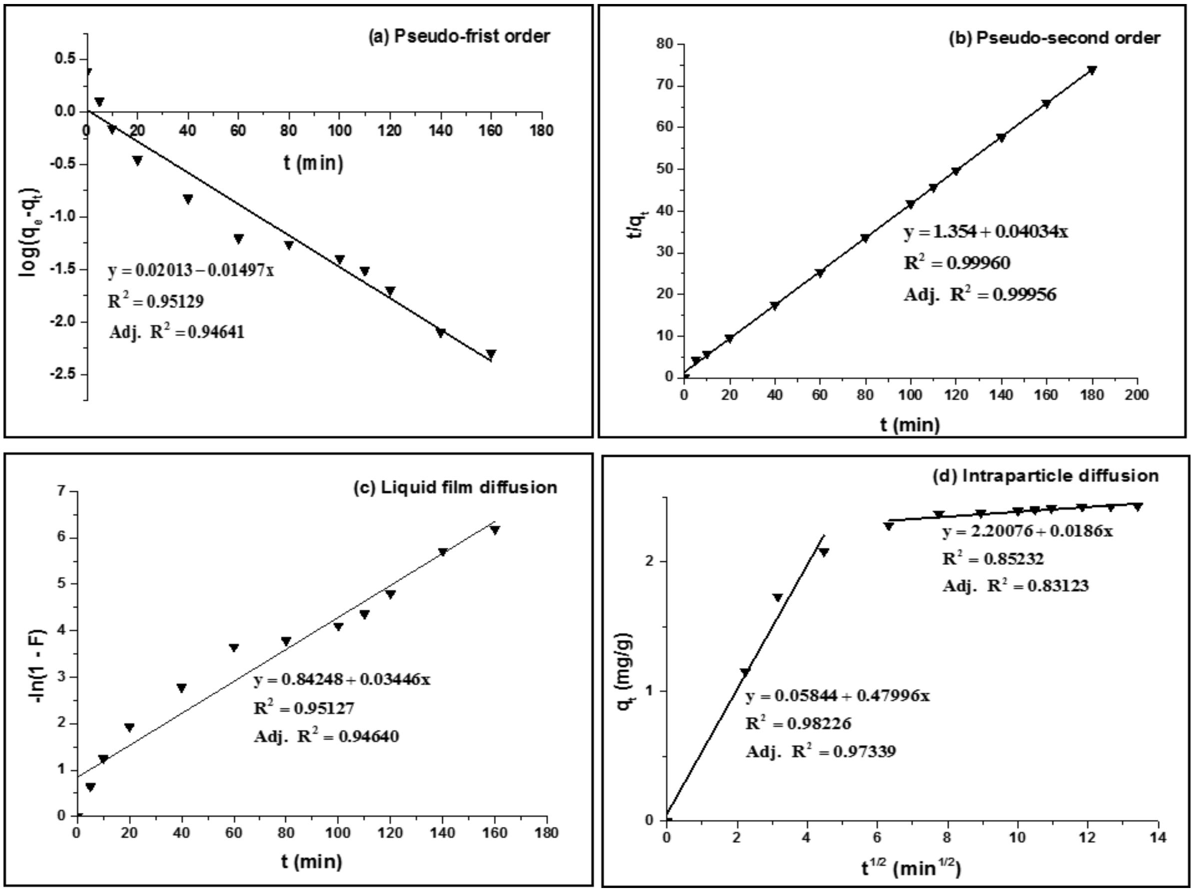

Fig 7: Adsorption kinetic plots for adsorption of DR81 dye on modified RHFE: (a) pseudo-first-order kinetics, (b) pseudo-second-order kinetics, (c) liquid film diffusion and (d) intraparticle diffusion.

Table 8: Kinetic parameters for the uptake of DR81 dye

Kinetic Models		Parameters	
		$q_{e,\ exp}$ (mg/g)	24.326
Pseudo-first order model		$q_{e,\ cal}$ (mg/g)	1.0474
		K_1 (1/min)	0.0345
		R^2	0.95129
Pseudo-second order model		$q_{e,\ cal}$ (mg/g)	24.789
		K_2 (mg/g.min)	1.202
		R^2	0.99960
Liquid film diffusion model		K_{fd}	0.03446
		R^2	0.95127
Intraparticle diffusion model	First line segment	K_{id} (mg/g.min)	0.47996
		I	0.05844
		R^2	0.98226
	Second line segment	K_{id} (mg/g.min)	0.0186
		I	2.20076
		R^2	0.85232

Characterization of adsorbent

Physicochemical Properties of adsorbent: The physico-chemical properties of RHFE-AC were obtained from previous studies [6] and presented in Table 9.

Table 9: Physicochemical properties RHFE-AC

Boehm titration (meq/g)					Iodine number (m^2/g)	Bulk density (g/cm^3)	Surface area (m^2/g)
Carboxylic	Lactonic	phenolic	Total basic	Total			
0.431	0.023	0.068	0.34	0.637	576.84	0.63	712.64

Fourier Transform Infra-Red Spectra Analysis

In order to determine the functional groups existing on the surface of the adsorbent, FTIR was carried out on the sample using infrared spectrophotometer (Brüker alpha-p Spectrometer) with ethanol as a solvent with a resolution of 4 cm^{-1} within the interval 400 - 4000 cm^{-1}.

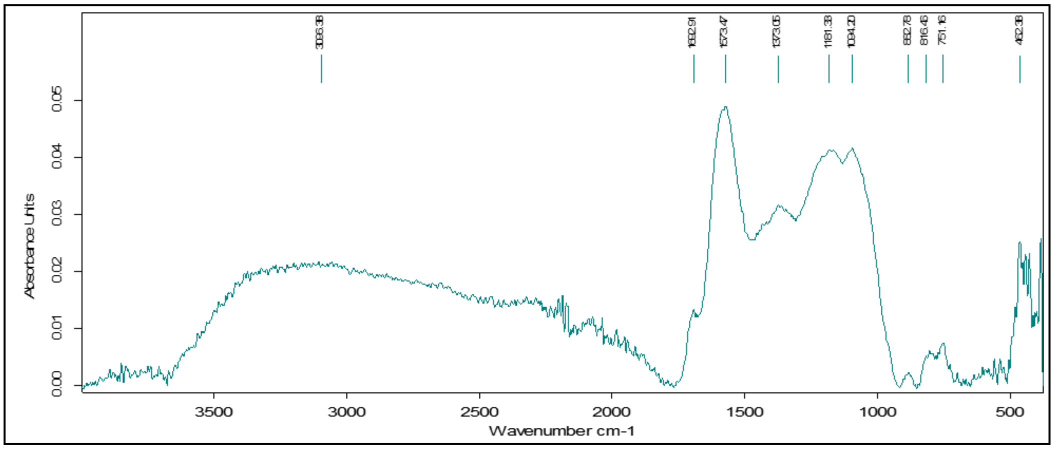

Fig 8: FTIR spectrum of RHFE-AC

The Fourier Transform Infra-Red spectrum of RHFE-AC is presented in Figure 8. From the spectrum, it can be observed that the absorption band between 3600-3000 cm^{-1} can be attributed to the OH of carboxylic acids, phenols, alcohols or water. The band at 2928 cm^{-1} is due to CH of aromatic methoxyl groups. The band centered at 1698 cm^{-1} is due to absorption by C=O of ketones, aldehydes, lactones or of carboxylic groups. The bands in the region 1550-1650 cm^{-1} may be allocated to carboxylic acid derivatives and amino acids. The absorption band at 1416 cm^{-1} may be due to vibrations of C=C bonds in the aromatic rings. The peaks situated between 1456-1420 cm^{-1} corresponds to CH2 and/or O-H vibrations of carboxylic acids and phenols while the peak centered at 1102 cm^{-1} corresponds to C-O vibrations of a secondary alcohol. Between the range 700-900 cm^{-1} the peaks correspond to para substitutions on the benzene ring and the peak at 462.36 cm^{-1} can be attributed to halogeno alkanes.

Conclusion

In this study, the practicability of colour uptake from aqueous solution by raphia hookeri fruit epicarp activated carbon was studied. RSM with Box-Behnken design was successfully used to determine the effects of the cardinal process factors such as the adsorbent dosage, the pH and contact time on the dye removal. The results from ANOVA (correlation coefficient, R^2 of 0.9997, adj-R^2 of 0.9993, a P value for the model less than 0.0001) affirms that the model was very much significant. The suggested quadratic model used to elaborate the relationship between the % removal of DR81 dye and the pH, adsorbent dosage, and contact time fitted the experimental data well. The maximum DR81 dye colour removal was accomplished with a pH of 2, an adsorbent dose of 1.73 g, and contact time of 60 mins. This optimal response obtained from the RSM was 78.26%, which is in close agreement with the experimental value of 80.21%. The equilibrium of the adsorption process was best described by the Langmuir isotherm model with a monolayer adsorption capacity of 10.37 mg/g. Although the kinetic data for the sorption of DR81 dye was analyzed using four kinetic models, only the pseudo-second order kinetic model was the most appropriate (R^2 of 0.99960) and the mechanism of DR81 removal was controlled by both intraparticle diffusion and liquid film diffusion of dye molecules through the liquid adjoining the solid adsorbent. It is evident from the results obtained that activated carbon produced from RHFE could be utilized as a low-cost adsorbent for the removal of dyes from solution.

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References

1. Crini G. Non-Conventional low-cost adsorbent for dye removal: A reviewer. Bioresource Technology. 2006; 97:1061-1085.
2. Aguila DMM, Ligaray MV. Adsorption of Eriochrome Black Ton MnO_2-Coated zeolite. International Journal of Environmental Science and Development. 2015; 6(11):824-827.
3. Neetu Sharma, Tiwari DP, Singh SK. Decolourisation of Synthetic Dyes by Agricultural Waste- A Review.

International Journal of Scientific & Engineering Research. 2012; 3(2):1-10.

4. Sharma N, Tiwari DP, Singh SK. Efficiency of chemically treated potato peel and Neem bark for sorption of Direct Red-81 dye from aqueous solution. Rasayan Journal of Chemistry. 2014; 7:399-409.
5. Azhar SS, Liew AG, Suhardy D, Hafiz KF and Hatim MDI. Dye removal from aqueous solution by using adsorption on treated sugarcane bagasse. American Journal of Applied Sciences. 2005; 2:1499.
6. Ghogomu JN, Muluh SN, Ajifack DL, Alongamo AAB, and Noufame DT. Adsorption of lead (II) from aqueous solution using activated carbon prepared from Raffia Palm (Raphia Hookeri) Fruit epicarp. IOSR Journal of Applied Chemistry IOSR-JAC. 2016; 9(7)1:74-85.
7. Musapatika ET, Onyango MS, Aoyi O. Cobalt (II) removal from synthetic wastewater by adsorption on South African coal fly ash. South African Journal of Science, 2010; 106(9/10), Art. #167: 1-7. DOI: 10.4102/sajs.v106i9/10.167.
8. Elibol M. Response Surface Methodology Approach for inclusion of perfluorocarbon in actinorhodin fermentation medium. Process Biochemistry. 2002; 38:667-773.
9. Kasman M. and Ibrahim S. Application of Response Surface Methodology in Optimization of Cadmium Adsorption by Raw Rice Husk. International Conference on Chemistry and Chemical Engineering, 2010: 157-161.
10. Krishna D, Padma Sree R. Response surface modelling and optimization of Cu (II) removal from wastewater using Borasus Flabellifer Coir Powder. International Journal of Applied Science and Engineering. 2014; 12(3):157-167.
11. Qiu P, Cui M, Kang K, Park B, Son Y, Khim E, *et al*. Application of Box-Behnken design with Response Surface Methodology for modelling and optimizing ultrasonic oxidation of arsenite with H_2O_2. Central European Journal of Chemistry. 2014; 12(2):164-172.
12. Langmuir I. Adsorption of gases on plane surfaces of glass, mica and platinum. Journal of American Chemical Society. 1918; 40:1361-1368.
13. Freundlich HMF. Over the adsorption in solution. Journal of Physical Chemistry. 1906; 57:385-471.
14. Temkin MJ, Pyzhev V. Kinetics of ammonia synthesis on promoted Iron catalyst. *Acta Physicochima* USSR, 1940; 12:217-256.
15. Halsey G. Physical adsorption on non-uniform surface. Journal of Chemical Physics. 1948; 16:931-937.
16. Lagergren S. About the Theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskapsakademiens: Handlinger. 1898; 24(4):1-39.
17. Ho YS, Mckay G. Pseudo-Second order model for sorption processes, Process Biochemistry. 1999; 34:451-465.
18. Boyd GE, Adamson AM and Myers LS. The exchange adsorption of ions from aqueous solution bioorganic zeolites II, kinetics. Journal of American Chemical Society. 1949; 69:2836-2842.
19. Weber WJ and Morris JC. Kinetics of adsorption on carbon from solution. Journal Sanitary. Engineering Division. American Society of Civil Engineering. 1963; 89:31-60.
20. Aravind J, Lenin C, Nancyflavia C, Rashika P, Saravanan S. Response surface methodology optimization of nickel (II) removal using pigeon pea pod biosorbent. International Journal of Environmental Science and Technology. 2015; 12:105-114. DOI 10.1007/s13762-013-0391-0.
21. Elmoubarki R, Taoufik M, Moufti A, Tounsadi H, Mahjoubi FZ, Bouabi Y, *et al*. Box-Behnken experimental design for the optimization of methylene blue adsorption onto Aleppo pine cones. Journal of Materials and Environmental Sciences. 2017; 8 (6):2184-2191.
22. Yi Liu, Yian Zheng, and Aiqin Wang. Response Surface Methodology for Optimizing Adsorption Process Parameters for Methylene Blue Removal by a Hydrogel Composite. Adsorption Science & Technology. 2010; 28(10):913-922.
23. Tchuifon TDR, Ndifor-Angwafor NG, Ngakou SC, Kamgaing T, Ngomo HM, Anagho SG, Ketcha JM. Optimization of cadmium (II) adsorption onto modified and unmodified lignocellulosics (rice husk and egussi peeling), International Journal of Basic and Applied Sciences. 2016; 5(1):45-51.
24. Khan TA, Dahiya S, Ali I. Removal of Direct Red 81 Dye from aqueous solution by native and citric acid modified bamboo sawdust. Kinetic study and equilibrium isotherm analysis. Gazi University Journal of Science. 2012; 25(1):59-87.
25. Heravi MM, Ardalan P, Vafaie A. Equilibrium and kinetic studies of Direct Red 81 biosorption onto modified silk maze as an economical biosorbent. Journal of Chemical Health Risks. 2014; 4(1):63-73.
26. Khamparia S and Jaspal D. Adsorptive removal of Direct Red 81 dye from aqueous solution onto Argemone Mexicana. Sustainable Environmental Research. 2016; 26:117-123.