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Optimizing Removal of Azo Dyes from Aqueous Solution by Kaolinite Clay using Response Surface Methodology

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Abstract: *Optimization of Azo dyes removal from aqueous solution by kaolinite clay from Alkaleri North-East Nigeria using Response Surface Methodology (RSM) was carried out in this study. The Presence of colour in natural water is aesthetically undesirable coupled with the possible harmful effects to humans, aquatic lives and plants. With the aid of Design Expert and using the Central Composite Design (CCD) of the Response Surface Methodology, fifteen (15) experiments were generated for methyl red dye and methyl orange dye respectively and run. The results obtained revealed that quadratic models show better performance that correlate kaolinite clay-dye interaction variables, removal efficiencies and analysis of variance (ANOVA). The experimental constant conditions of pH 7.0 and temperature 298 K was adopted which gave 80.25% optimum removal efficiency of Methyl red from an aqueous solution at 1.29 g adsorbent dose, 23.18 mg/L initial concentration, 103.89 minutes contact time while the optimum removal efficiency for methyl orange from aqueous solution was 90.51% at 440 rpm agitation speed, 105.05 mg/L initial concentration, 77.65 contact time respectively. Therefore, the application of Response Surface Methodology to optimize the adsorptive removal efficiency of Azo dyes from aqueous solutions by kaolinite clay has been successfully demonstrated, thus the potential application of indigenous kaolinite clay for wastewater treatment in Nigeria.*

Keywords*: Adsorption, Analysis of Variance (ANOVA), Azo dyes, Central Composite Design (CCD), Kaolinite Clay, Response Surface Methodology (RSM).*

1.0 INTRODUCTION

The azo dyes are the largest and most versatile of all dyes used in the textile and dyeing industries and they are characterized by the presence of one or more azo groups [-N=N-] in association with one or more aromatic rings [1,2]. The azo dyes are relatively resistant to biological and chemical degradation in addition to their being toxic and/or carcinogenic [3,4]. It is therefore essential that any effluent containing azo dyes must not be discharged into natural water bodies without prior treatment [5]. Methyl red (MW=269.30 $gmol^{-1}$) and methyl orange (MW=327.33 $gmol^{-1}$) are synthetic dyes of chemical formulae $[(CH_3)_2NC_6H_4N=NC_6H_4CO_2H]$ and $[(CH_3)_2NC_6H_4N=NC_6H_4NaO_3S]$ respectively as shown in Fig. 1:

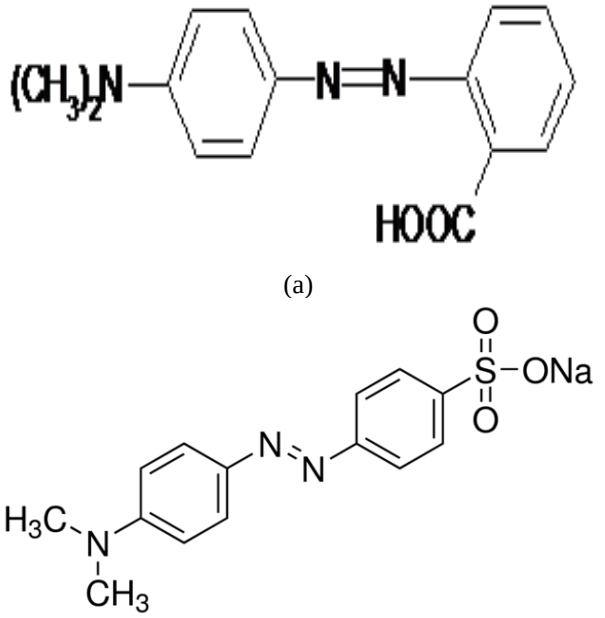


Figure 1: Molecular structure of synthetic azo dyes: (a) methyl red and (b) methyl orange

It was estimated that 10-15 % of the dye is lost in the effluent which cause damages to the environment, significantly affect photosynthetic activity in aquatic life due to reduced light penetration into water and toxic to aquatic life due to the presence of metals, chlorides and lead [6,7,8]. In different toxicological studies indicated that 98 % of dyes have a lethal concentration value LC50 for fishes higher than 1 mg/L and 59 % have an LC50 value higher than 100 mg/L [9].

A number of treatment methods for the removal of dyes from aqueous solutions have been reported, namely reduction, ion exchange, electrochemical precipitation, evaporation, chemical coagulation, flocculation, chemical oxidation, photochemical degradation, membrane filtration, including aerobic and anaerobic biological degradation,

solvent extraction and adsorption [10,11]. Due to its simplicity and easy operational conditions, adsorption is a widely used process for either separation or purification [12,13].

The most classic and popular way to achieved highest removal efficiency is by the use of one variable at a time approach, but it involves a huge number of independent run and time consuming. Optimization can be done by using Response Surface Methodology (RSM) which is a collection of mathematical and statistical techniques useful for modelling and analysis of problems in which the response of interest is influenced by several variables and the objective is to optimize this response [14,15], which has proved very effective and time saving model for studying the influence of process parameters on the response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions [16].

This study is set out to achieve wastewater treatment by optimizing the conditions of adsorption of disperse azo dyes (methyl red and methyl orange) onto kaolinite clay in a batch system. It will elucidate the interactions between kaolinite clay and azo dyes in aqueous solution to assess the removal efficiency of the waste dyes residue and its potential application in Nigeria, hence the use of Kaolinite clay from Alkaleri.

1.1 Response Surface Methodology (RSM)

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques used in significance of several affecting factors in an optimum manner, even in the presence of complex interactions [17]. The main reason for implementing RSM is to determine the optimum operational conditions for the process or to determine a region that satisfies the operating specifications [18]. If the selected variables are assumed to be measurable, the response surface can be expressed as follows (Eq. 1) [19,20].

$$Y = f(X_1, X_2, X_3 \ldots X_n) \quad (1)$$

where Y is the answer of the system, and X_i the variables of action called factors. The task then is to find a suitable approximation for the true functional relationship between independent variables and the response surface [21,22]. Usually a second-order model is utilized in response surface methodology as shown in Eq. 2:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j \quad (2)$$

where Y=predicted response; X_1, X_2, ⋯, X_k are input factors which influence the response Y; β_0=constant coefficient; β_i=linear coefficients; β_{ii}=quadratic coefficients; β_{ij}=cross product (interaction) coefficients and k=number of factors.

1.2 Central Composite Design (CCD)

The central composite designs (CCD) gives almost as much information as a three-level factorial, requires many fewer tests than the full factorial design and has been shown to be sufficient to describe the majority of steady-state process responses [23]. The number of tests required for CCD includes the standard 2^k factorial with its origin at the center, $2k$ points fixed axially at a distance, say β, from the centre to generate the quadratic terms, and replicate tests at the center; where k is the number of variables. The axial points are chosen such that they allow rotatability, which ensures that the variance of the model prediction is constant at all points equidistant from the design centre. Replicates of the test at the center are very important as they provide an independent estimate of the experimental error. The number of experiments can be detected from (Eq. 3) [22]:

$$N = 2^k + 2k + cp \quad (3)$$

where N=total number of experiments required, k=number of variables and cp= number of central points.

2.0 EXPERIMENTAL PROCEDURE

2.1 Preparation of adsorbent

Kaolinite clay was obtained from mines site in Alkaleri Local Government Area of Bauchi State, Northeast-Nigeria, which was subjected to preliminary treatment and physical beneficiation, reported in a separate publication [24] was used.

2.2 Preparation of adsorbate

Analytical grade of azo dyes manufactured by BDH Chemical Ltd England while NaOH, H_2SO4 and HCl manufactured by GGC Chemical Factory & Co. Ltd were obtained and used for this study. A stock solution of azo dyes was prepared as follows: 100 mg/L methyl red and 200 mg/L methyl orange. The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration adjusted using HCl, H_2SO_4 and NaOH to neutral measured by digital pH meter (Micro pH 200, CRISON). The absorbances of the azo dyes solutions were predetermined at maximum wavelengths of 429.5 nm for methyl red and 463 nm for methyl orange respectively using UV Spectrophotometer (6100 Spectrophotometer, JENWAY).

2.3 Statistical optimization procedure

Central composite design (CCD) was designed for optimization according to three selected variables: initial concentration (mg/L), adsorbent dosage (g) and contact time (min.) for methyl red and agitation speed (rpm), initial concentration (mg/L) and contact time (min.) for methyl orange respectively. The upper and lower limits values were presented in Tables 1 and 2 for methyl red and methyl orange

respectively. Therefore, 15 sets of experiments were generated which including the 2^3 factorial experiments, 5 axial points and 5 replicates of center points. The azo dyes stock solutions were prepared by dissolving adsorbate in de-ionize water according to the concentrations suggested by the experimental design shown in Tables 3 and 4, pH was adjusted using dilute H_2SO_4 and NaOH for methyl red while dilute HCl and NaOH for methyl orange respectively.

The experiments were performed at 298 K using 45 µm pore filter paper to obtain the supernatant solution according to statistical design at 400 rpm stirring speed for methyl red and 0.03 g/mL adsorbent dosage for methyl orange respectively.

The removal efficiency of the azo dyes was calculated using Eq. 4 [22,25]:

$$Removal\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (4)$$

where C_O and C_t are the azo dyes initial and equilibrium concentrations (mg/L) respectively.

Table 1: Independent variables and their coded levels CCD for methyl red.

Variables	Coding	Units	Levels				
			+α	+1	0	-1	-α
Initial concentration	A	mg/L	10	23.18	55	86.86	100
Adsorbent dose	B	g	0.05	0.26	0.78	1.29	1.50
Contact time	C	min.	10	26.11	65	103.89	120

Table 2: Independent variables and their coded levels CCD for methyl orange.

Variables	Coding	Units	Levels				
			+α	+1	0	-1	-α
Agitation speed	A	rpm	100	158.58	300	441.42	500
Initial concentration	B	mg/L	50.00	64.64	100	135.35	150
Contact time	C	min.	15	25.98	52.50	79.02	90

The data obtained were fitted to a second-order polynomial equation as shown by Eq. 5 [26]:

$$Y = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} {X_1}^2 + \beta_{22} {X_2}^2 + \beta_{33} {X_3}^2 \qquad (5)$$

where Y is the predicted response, β_0, intercept, β_1, β_2 and β_3, linear coefficients, β_{11}, β_{22} and β_{33}, squared coefficients and β_{13}, β_{12} and β_{23}, the interactions coefficients of the equation and X_1, X_2 and X_3 are the independent variables. Subsequent regression analyses, analyses of variance (ANOVA) and response surfaces were performed using the Design Expert Software (Version 7.0.0). The quality of the developed model can be determined from the value of correlation (R^2) while evaluation of the statistical significance of the equations developed can be determined by using ANOVA.

3.0 RESULTS AND DISCUSSION

3.1 Statistical analysis of azo dyes

In order to study the combined effect of three factors, 15 experiments were performed in different combinations of the parameters. Tables 3 and 4 present an average of three (3) experimental value and predicted value related to percentage removals of methyl red and methyl orange respectively. The performance of the model can be observed by the plots of predicted versus experimental percentage removal by Fig. 2.

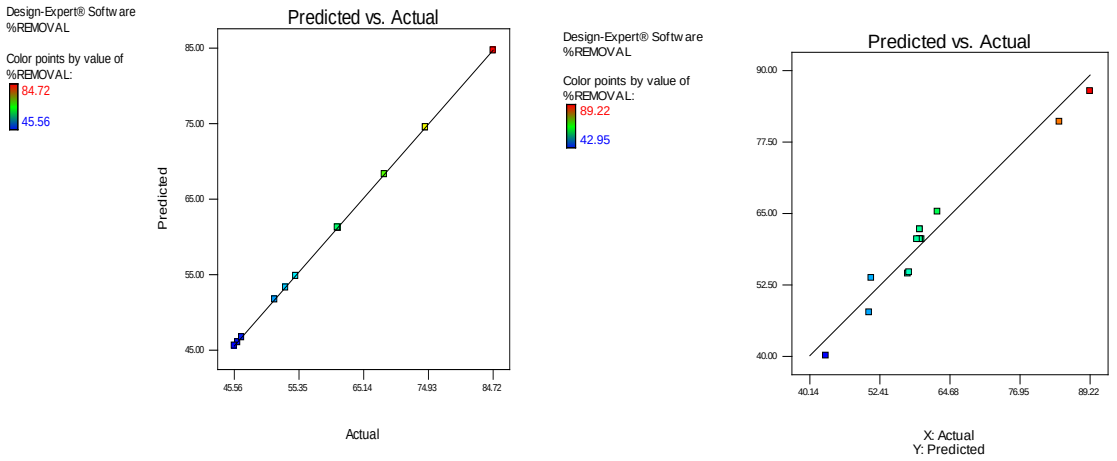
Table 3: Experimental factors in coded and actual units for experimental responses for methyl red.

RUN	A mg/L	B g	C min	Experimental value %	Predicted value %	Residual values (w/w)%
1	86.82	1.29	26.11	54.86	54.82	0.035
2	86.82	0.26	103.89	46.08	46.04	0.035
3	23.18	1.29	103.89	84.72	84.68	0.035
4	23.18	0.26	26.11	53.33	53.29	0.035
5	10.00	0.78	65.00	74.47	74.51	-0.035
6	100.00	0.78	65.00	46.67	46.71	-0.035
7	55.00	0.05	65.00	45.56	45.60	-0.035
8	55.00	1.50	65.00	74.49	74.53	-0.035
9	55.00	0.78	10.00	51.68	51.72	-0.035
10	55.00	0.78	120.00	68.26	68.30	-0.035
11	55.00	0.78	65.00	61.27	61.25	0.024
12	55.00	0.78	65.00	61.15	61.25	-0.095
13	55.00	0.78	65.00	61.28	61.25	0.034
14	55.00	0.78	65.00	61.29	61.25	0.044

15	55.00	0.78	65.00	61.31	61.25	0.064

Table 4: Experimental factors in coded and actual units for experimental responses for methyl orange.

RUN	A rpm	B mg/L	C min	Experimental value %	Predicted value %	Residual values (w/w)%
1	300.00	100.00	52.50	50.91	50.78	0.126
2	158.58	64.64	25.98	59.41	60.28	-0.870
3	300.00	100.00	52.50	62.50	62.37	0.126
4	441.42	135.36	25.98	59.42	60.29	-0.870
5	300.00	100.00	52.50	57.31	57.44	-0.130
6	300.00	50.00	52.50	83.86	83.99	-0.130
7	300.00	100.00	52.50	57.53	57.66	-0.130
8	300.00	100.00	52.50	50.52	50.65	-0.130
9	300.00	100.00	90.00	42.95	42.98	-0.030
10	500.00	100.00	52.50	89.22	89.35	-0.130
11	300.00	150.00	52.50	59.72	59.20	0.516
12	158.58	135.36	79.02	59.41	59.20	0.206
13	441.42	64.64	79.02	59.38	59.20	0.186
14	300.00	100.00	15.00	59.44	59.20	0.236
15	100.00	100.00	52.50	57.31	57.20	0.106



(a) (b)

Figure 2: Predicted versus actual removal of (a) methyl red and (b) methyl orange from aqueous solution

3.2 Fitness of the Statistical Model

The RSM software generate a series of models (linear, two factor interaction (2FI), quadratic and cubic polynomial) that fitted to the response as well as suggest the best fitted model as shown in Tables 5 and 7. According to the sequential model sum of square, the best model to fit the response was quadratic model due to its highest order polynomial with significance of additional terms and the model was not aliased. Using the experimental results from Tables 3 and 4, the full quadratic second order polynomial equation (Eqs. 6 and 7) was fitted to the appropriate data in terms of coded (Y_1) and (Y_2) factors for the central composite response surface quadratic model for methyl red and methyl orange respectively expressed as follows:

$$Y_1 = 61.25 - 9.83A + 10.23B + 5.86C + 0.21AB + 0.19AC - 0.55BC - 0.3A^2 - 0.59B^2 - 0.62C^2 \quad (6)$$

$$Y_2 = 60.204 + 9.389A - 2.478B + 16.359C + 13.464AB - 1.123AC + 12.287BC + 3.754A^2 + 4.526B^2 + 1.504C^2 \quad (7)$$

where Y_i is the removal efficiency and the coded terms 'A' represent initial concentration, 'B' represent adsorbent dose and 'C' represent contact time for methyl red while coded terms 'A' represent agitation speed, 'B' represent initial concentration and 'C' represent contact time for methyl orange respectively. Positive sign in front of the terms indicates synergic effect (increasing the adsorption rate) while negative sign indicates antagonistic effect (decrease the adsorption rate) [27].

Table 5a give the lack of fit test for methyl red with Quadratic versus 2F1 model been suggested having probability value (P-value) of <0.0001. The estimated coefficients of regression model are given in Table 5b. The large value of the coefficient of multiple determinations (R^2 =0.99998) indicate good fitness of the result. The high adjusted and predicted R^2 values of 0.99996 and 0.99919

respectively revealed that the model adequately represents the experimental result.

Table 5a: Lack of fit model test for methyl red removal

Source	Sum of Squares	Df	Mean Square	F-Value	P-value Prob > F	
Mean vs Total	54773.150	1	54773.150			
Linear vs Mean	1817.074	3	605.691	968.586	< 0.0001	
2FI vs Linear	0.7646	3	0.2549	0.3335	0.8017	
Quadratic vs 2FI	6.0847	3	2.0282	345.288	< 0.0001	Suggested
Cubic vs Quadratic	0.0134	1	0.0134	3.343	0.1415	Aliased
Residual	0.0160	4	0.0040			
Total	56597.1	15	3773.140			

Table 5b: Model summary statistics for methyl red removal

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	0.79078	0.99623	0.99520	0.99251	13.65902	
2FI	0.87422	0.99665	0.99413	0.96531	63.28071	
Quadratic	0.07664	0.99998	0.99996	0.99919	1.46959	Suggested
Cubic	0.06325	0.99999	0.99997		+	Aliased

The analysis of variance (ANOVA) has been summarized in Table 6. It was observed that the variable with most significance effect on methyl red removal were the linear terms of contact time (P<0.0001 and F-value 71240.58), initial concentration (P<0.0001 and F-value 65183.98) and adsorbent dose (P<0.0001 and F-value 23399.13), followed by the quadratic term of contact time with (P<0.0001 and F-value 505.427), adsorbent dose (P<0.0001 and F-value 461.610) and initial concentration (P<0.0001 and F-value 134.791). The least significant term that has minimal contribution in methyl red removal is the interaction term AC (P = 0.0187 and F-value 11.754). The model having an F-value of 34500.45 and P<0.0001 is significant while its lack of fit with F-value 3.342593 and P=0.1415 is not significant.

Table 6: ANOVA of the second-order polynomial equation for methyl red

Source	Sum of Squares	Df	Mean Square	F-Value	P-value Prob > F	
Model	1823.92	9	202.65	34500.45	< 0.0001	Significant
A= Initial concentration	386.42	1	386.42	65783.98	< 0.0001	
B= Adsorbent dose	418.47	1	418.47	71240.58	< 0.0001	
C= Contact time	137.45	1	137.45	23399.13	< 0.0001	
AB	0.0877	1	0.0877	14.932	0.0118	
AC	0.0690	1	0.0690	11.754	0.0187	
BC	0.6078	1	0.6078	103.476	0.0002	
A^2	0.7918	1	0.7918	134.791	< 0.0001	
B^2	2.7115	1	2.7115	461.610	< 0.0001	
C^2	2.9689	1	2.9689	505.427	< 0.0001	
Residual	0.0294	5	0.0059			
Lack of Fit	0.0134	1	0.0134	3.343	0.1415	not significant
Pure Error	0.0160	4	0.0040			
R^2=0.9999 Adjusted R^2=0.9989						

Table 7a give the lack of fit test for methyl orange with Quadratic versus 2F1 model been suggested having probability value (P-value) of 0.0244. The estimated coefficients of regression model are given in Table 7b. The large value of the coefficient of multiple determinations (R^2 = 0.95122) indicate good fitness of the result. The high adjusted and predicted R^2 values of 0.8635 and 0.96444 respectively revealed that the model adequately represents the experimental result.

Table 7a: Methyl orange removal lack of fit model test

Source	Sum of Squares	Df	Mean Square	F-Value	P-value Prob > F	
Mean vs Total	38.844	1	38.840			
Linear vs Mean	2.450		0.817	11.294	0.0011	Suggested
2FI vs Linear	0.481	3	0.160	4.087	0.0494	
Quadratic vs 2FI	0.259	3	0.086	7.865	0.0244	Suggested
Cubic vs Quadratic	0.055	1	0.055	901.921	< 0.0001	Aliased
Residual	0.00024	4	6E-05			
Total	42.090	15	2.806			

Table 7b: Methyl orange removal model summary statistics

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	
Linear	0.55194	0.96229	0.87455	0.95742	
2FI	0.6819	0.95329	0.85329	0.95634	
Quadratic	0.06572	0.95122	0.86358	0.96444	Suggested
Cubic	0.06743	0.96132	0.96131		Aliased

The analysis of variance (ANOVA) has been summarized in Table 8. It was observed that the variable with most significance effect on methyl orange removal were the linear terms of Contact Time with (P= 0.0006 and F-value 57.49), Agitation Speed (P= 0.0074 and F-value 18.93), while the Initial concentration (P= 0.3026 and F-value 1.32) is not significant and has less contribution in methyl orang removal in the experiment. The interaction and quadratic terms AC and Contact Time (C^2) are the least significant terms that have minimal contributions in methyl orange removal with F-values of 0.14 and 0.94 respectively. The model having an F-value of 10.84 and P= 0.0086 is significant while its lack of fit with F-value 92.13 and P =0.0007 is significant.

Table 8: ANOVA of the second-order polynomial equation for methyl orange

Source	Sum of Squares	Df	Mean Square	F-Value	P-value Prob > F	
Model	1816.55	9	201.84	10.84	0.0086	Significant
A=Agitation speed	352.45	1	352.45	18.93	0.0074	
B= Initial concentration	24.57	1	24.57	1.32	0.3026	
C= Contact time	1070.46	1	1070.46	57.49	0.0006	
AB	362.55	1	362.55	19.47	0.0069	
AC	2.52	1	2.52	0.14	0.7278	
BC	301.93	1	301.93	16.22	0.0101	
A^2	108.69	1	108.69	5.84	0.0604	
B^2	158.06	1	158.06	8.49	0.0333	
C^2	17.44	1	17.44	0.94	0.3776	
Residual	93.1	5	18.62			
Lack of Fit	89.22	1	89.22	92.13	0.0007	significant
Pure Error	3.87	4	0.97			
R^2=0.9512 Adjusted R^2=0.8635						

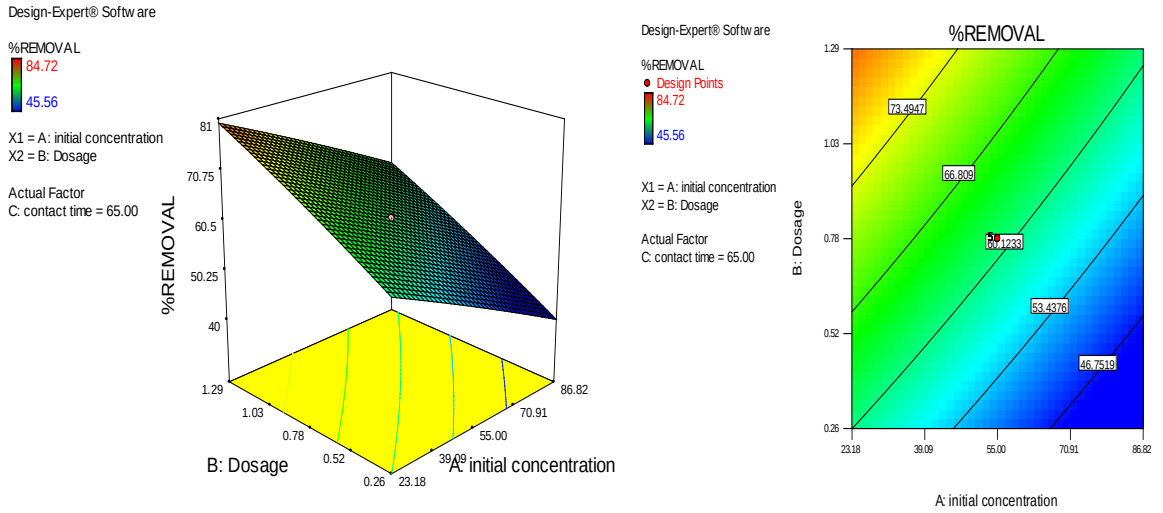
3.3 Effect of Process parameters on azo dyes removal efficiencies

Effect of the selected variables and the interaction between them during removal of azo dyes from aqueous solutions using kaolinite clay is expressed in 3D and cube response surface diagrams. Response surface plots in terms of two selected factors at any one time maintaining all other factors at fixed levels are suitable in understanding either the main or the interaction effects of these two factors and represented by 3D diagrams. The shape of the curve indicates good interaction of the two variables and circular shape indicates no interaction between the variables [28].

Interaction between adsorbent dose and initial concentration of methyl red

The relation between adsorbent dosage and initial concentration and their effect on the required responses is represented in Figs. 3(a) and 3(b). This was performed at pH

7, thus the removal efficiency increase with increasing the dose at any given concentration but appear to be more promising at lower concentrations.

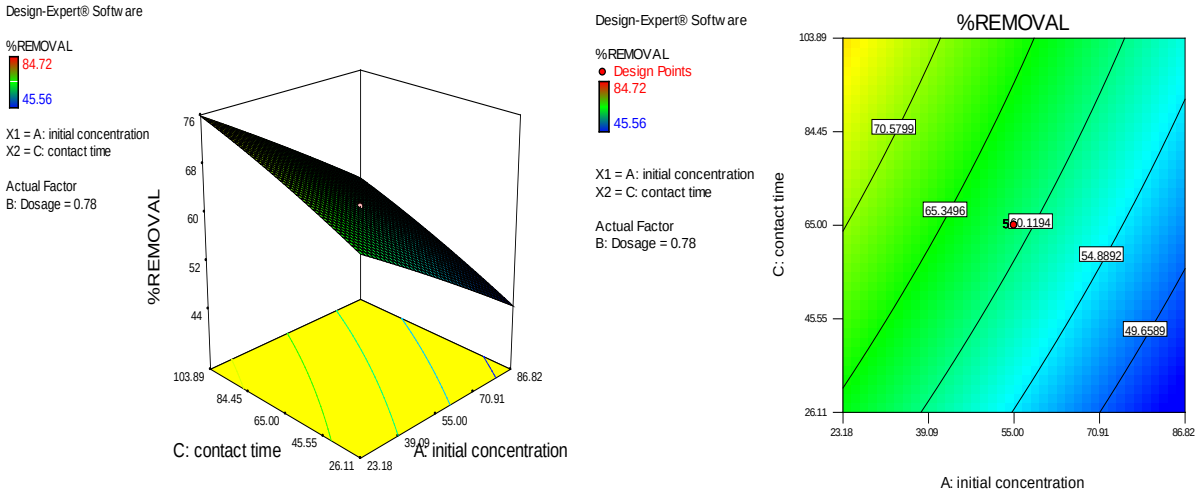


(a) (b)

Figure 3: Methyl red removal efficiency response surface plot (a) Three-dimensional and (b) Contour

Interaction between contact time and initial concentration of methyl red

The pH and the applied dosage were kept constant at 7 and 0.78 gm, respectively, throughout the experiment. The plots Figs. 4(a) and 4(b) showed that higher removal efficiency (> 60%) can be obtained between intermediate and low level of initial concentration (55 to 23.18 mg/L) and between the investigated ranges of reaction time (26.11 to 103.8 min). The 3D respond surface also showed that the removal efficiency was increased with increasing reaction time and increasing the dye concentration lead to decrease in percentage removal.

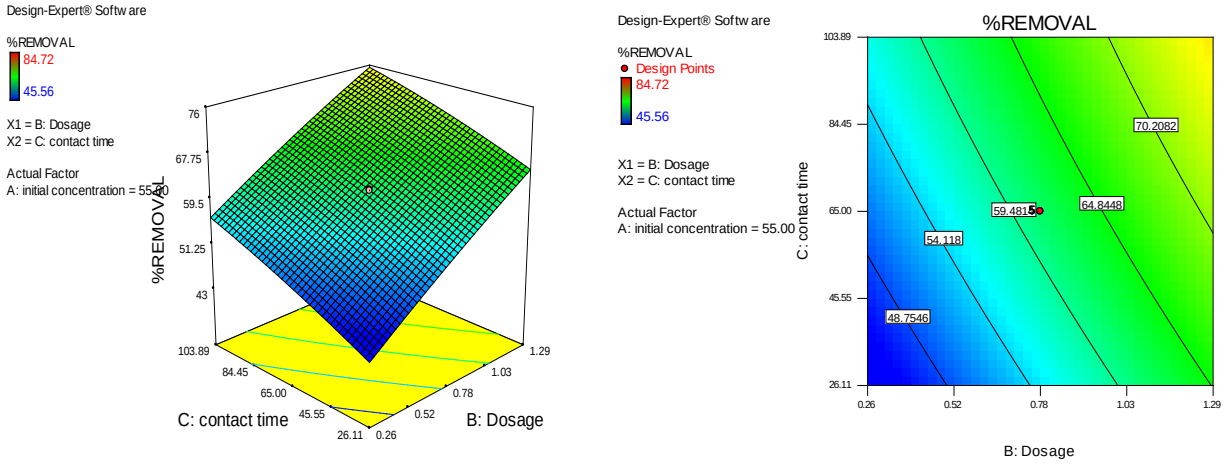


(a) (b)

Figure 4: Methyl red removal efficiency response surface plot (a) Three-dimensional and (b) Contour

Interaction between adsorbent dose and contact time of methyl red

The two parameters showed positive influence on methyl red removal as illustrated in Figs 5(a) and 5(b) which shows the effects of the two significant variables (B and C) where A was fixed at zero level (55 mg/L). It was observed that the methyl red removal efficiency (>50%) was achieved at the reaction time range between 65 and 103.89 min and adsorbent dose 0.78–1.29 g. These results were in agreement with the findings of [29] which used treated banana pseudo stem fibres to prepare activated carbon, they found that the adsorbent dose and contact time have significant effect on removal of methyl red from aqueous solution using RSM.

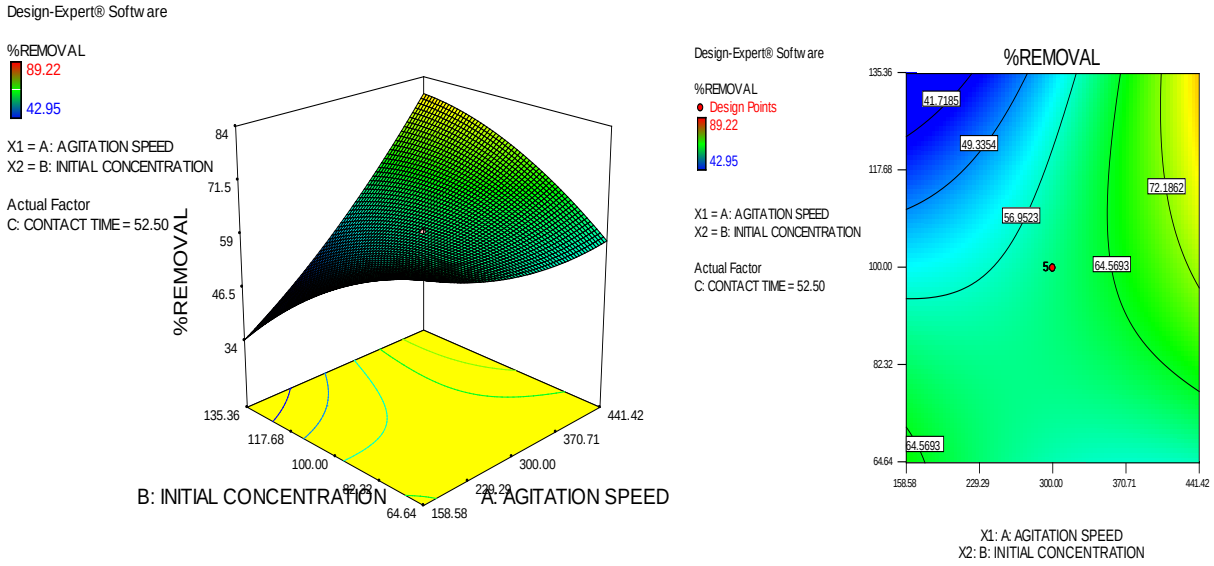


(a) (b)

Figure 5: Methyl red removal efficiency response surface plot (a) Three-dimensional and (b) Contour

Interaction between agitation speed and initial concentration of methyl orange

The relation between agitation speed and initial concentration at constant pH 7 and 52.50 minutes contact time is presented in Figs. 6(a) and 6(b). The removal efficiency increases with increasing the agitation speed at any given concentration but appear to be more promising at lower concentrations.

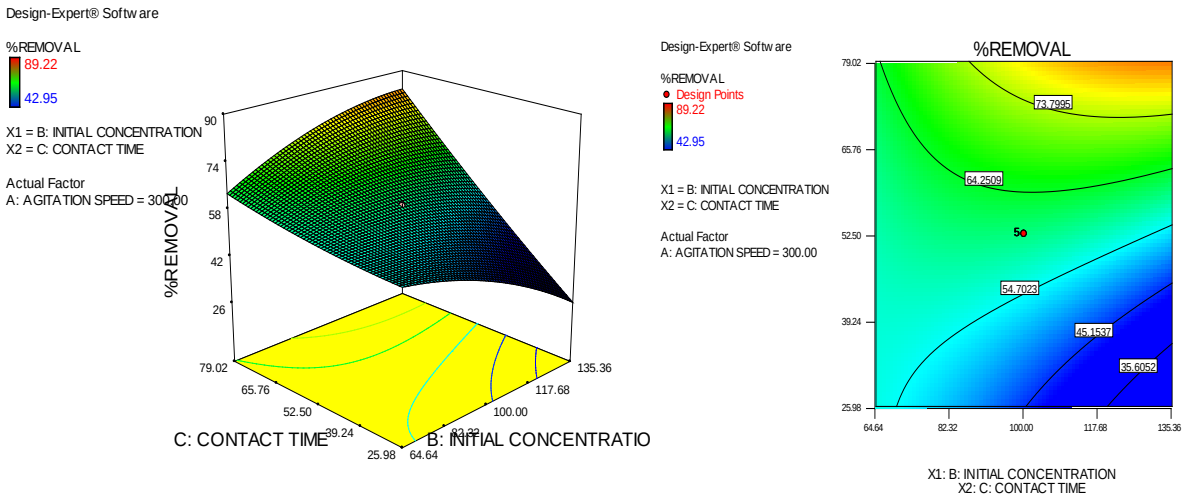


(a) (b)

Figure 6: Methyl orange removal efficiency response surface plot (a) Three-dimensional and (b) Contour

Interaction between contact time and initial concentration of methyl orange

The methyl orange contact time and initial concentration interaction 3D and contour response surface plots at pH 7 and 300 rpm as presented Fig. 7 which shows higher removal efficiency (> 42.95%) can be obtained between intermediate and high level of initial concentration (100 to 135.18 mg/L) and between the investigated ranges of reaction time (64.25 to 79.02 min). The 3D response surface also showed that the removal efficiency increased with increasing reaction time while increasing the dye concentration lead to decrease in removal efficiency. The significant increment of the removal efficiency (42.95 to 89.22%) was observed when the reaction time was raised from low level (25.98 min) to high level (79.02 min) and at low level methyl orange concentration (64.64 mg/L).

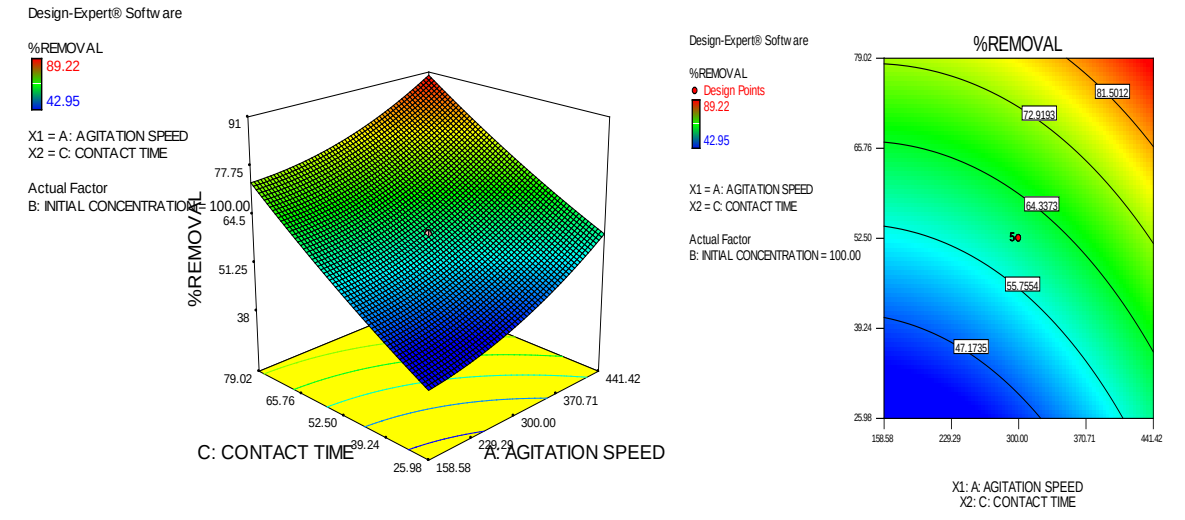


(a) (b)

Figure 7: Methyl orange removal efficiency response surface plot (a) Three-dimensional and (b) Contour

Interaction between agitation speed and contact time of methyl orange

Figure 8(a) and 8(b) illustrate the 3D and contour plot response surface which shows the effects of the two significant variables (agitation speed and contact time) where the initial concentration was fixed at zero level (100 mg/L). The highest methyl orange removal efficiency was achieved when both variables were at maximum point. The falling trend in removal efficiency could be explained that at lower concentration the ratio of initial dye molecules to the available surface is low, subsequently the fractional adsorption becomes independent of initial concentration. However at higher concentration the available sites of adsorption becomes fewer, hence the removal efficiency is dependent upon initial concentration.

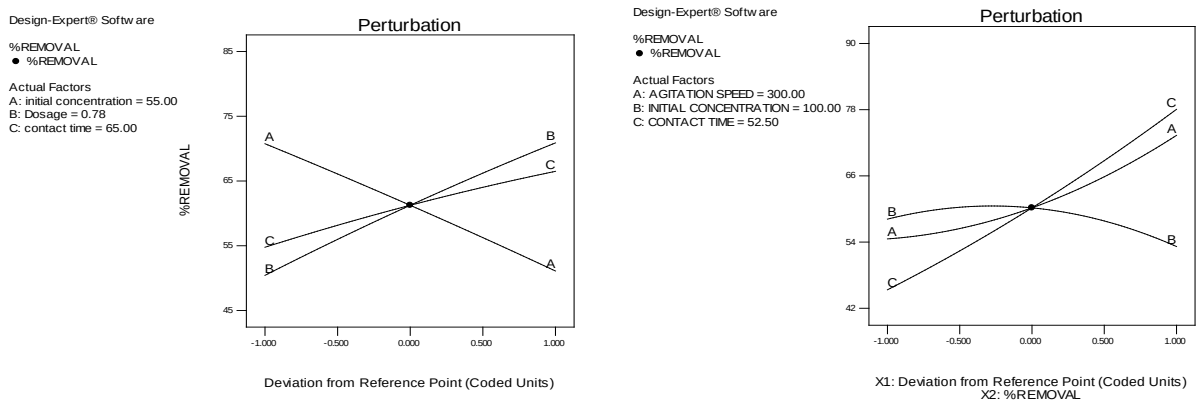


(a) (b)

Figure 8: Methyl orange removal efficiency response surface plot (a) Three-dimensional and (b) Contour

Interaction of variables for removal efficiency of azo dyes

The interaction of selected variables at fixed pH 7 and their effect on the removal efficiency of azo dyes is represented by perturbation plots in Figs. 9(a) and 9(b) for methyl red and methyl orange respectively. The removal efficiencies (%) of methyl red by kaolinite clay increases with increasing the contact time and applied dosage but decreases with increasing the initial concentration. The maximum quantity of methyl red removed by kaolinite clay occurs at the upper limits when the reaction time was raised from low level (26.11 min) to high level (103.89 min) and adsorbent dose of low level (0.26 g) to high level (1.29 g).



(a) (b)

Figure 9: Perturbation plot (a) Methyl red and (b) Methyl orange

The removal efficiency (%) of methyl orange by kaolinite clay increases with increasing the contact time and the agitation speed but decrease with increasing the initial concentration. The maximum quantity of methyl orange removed by kaolinite clay occurs at the upper limits when the reaction time was raised from low level (25.98 min) to high level (79.02 min) and agitation speed of low level (158.58 rpm) to high level (441.42 rpm).

3.4 Optimization and Validation of the model

Model desirability approaching unity and with low error value portrays the applicability of the model towards the responses, relatively small errors of less than 5 % were obtained for the predicted and the actual values, indicating that the models are suitable and sufficient to predict the responses as presented in Tables 9 and 10 for methyl red and methyl orange respectively. Model validation was done by preparing azo dyes according to the condition given by the software and batch experiments were conducted to find out experimental removal efficiency. It was found that the values given by the software was in accordance with the experimental values with relatively small error percentage.

Table 9: Predicted optimize solutions for removal efficiency of methyl red

RUN	Initial concentration (mg/L)	Adsorbent dose (g)	Contact time (min)	Removal efficiency (%)	Desirability	
1	23.18	1.29	103.73	84.67	0.99263	Selected
2	23.50	1.29	103.89	84.60	0.99105	
3	23.19	1.25	103.89	84.04	0.97872	
4	23.18	1.29	77.85	81.81	0.92902	

Table 10: Predicted optimize solutions for removal efficiency of methyl orange

RUN	Agitation speed (rpm)	Initial concentration (mg/L)	Contact time (min)	Removal efficiency (%)	Desirability	
1	439.74	105.050	77.650	92.075	1	Selected
2	417.41	118.760	72.250	91.107	1	
3	379.53	134.360	75.770	92.781	1	
4	158.58	134.950	79.020	65.519	0.60817	

4.0 CONCLUSION

From the findings of this study, the 'Alkaleri' kaolinite clay can be used to remove azo dyes (methyl red and methyl orange) from their aqueous solutions thereby resulted in reduction of environmental hazards without compromising plant and animal productivity.

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