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Modeling and Process Parameters Optimization of Colour Pigments Removal from Palm Oil Using Activated Ibusa Clay

[1]Okafor, V. N., *[2]Nnanwube, I. A., [1]Onukwuli, O. D., [2]Obibuenyi, J. I., [1]Ajemba, R. O.

[1]Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria.

[2]Department of Chemical Engineering, Madonna University, Akpugo, Nigeria.

Abstract: *In the present study, central composite design of response surface methodology was utilized to optimize the bleaching of palm oil using local clay from Ibusa. The XRF and FTIR analyses carried out revealed that the clay exists as kaolinite. Hydrochloric acid was used for the chemical activation of the clay. The process parameters used for the design include bleaching time, bleaching temperature, clay dosage and particle size. The result showed that the optimum condition for the bleaching process was a bleaching temperature of 111.07°C, bleaching time of 2.3 hours, clay dosage of 3.16 g and particle size of 0.16 mm which resulted in 75.34% bleaching of the palm oil. The statistical tests carried out showed a close correlation between the experimental and predicted data. This study has shown that Ibusa kaolinite is a good adsorbent for palm oil bleaching.*

Keywords: *Bleaching, Response surface methodology, Optimization, Clay, ANOVA.*

1. INTRODUCTION

Clay is a naturally occurring sedimentary rock composed of one or more minerals which usually develops plasticity when pulverized and wetted. The word clay is used in ceramics to mean several different kinds of materials. It is often taken to mean one of the particular groups of purified clay minerals, each having a definite composition and characteristic crystal structure. Clay is composed mainly of silica, alumina, and water, and frequently appreciable quantities of iron, alkalis and alkali earth metals. Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygen or hydroxyls. Due to their low cost, abundance in most continents of the world, high dissolubility in acidic solutions, high sorption properties, and potential for ion exchange, clay materials are regarded as source of metals and adsorbents (Ajemba and Onukwuli, 2012)

Bleaching involves a mass concentration of the colour pigment at the interface between the fluid and the bleaching agent. It is achieved as a result of intermolecular forces between molecules of solid and the substances adsorbed and is readily reversible (Richardson, Harke and Backhurst, 2002). Adsorptive bleaching is the most effective form of bleaching in which various absorbents like carbon, silica gel, activated alumina and activated clay are used. The bleaching agent should be one that will change the tint of the oil without altering the chemical properties of the oil (Parker, 1987). Several bleaching agents, especially clays, have been studied in recent times for various bleaching temperature and times. Clays that have been studied include acid, neutral and caustic activated clays (Brophy et al., 2004; Arumughan et al., 2004; Kamalu et al., 2012).

The traditional method of optimization involves one-factor-at a-time approach and keeping the other factors constant. This method is strenuous; it does not represent the total effects of the variables in the process (Bas and Boyaci, 2007) and ignores the combined interactions between the variables. One of the methods used to address these problems in the last three decades is the application of response surface methodology (RSM). It defines the effect of the independent variables, alone or in combination, in the processes (Betiku et al., 2015). In addition, the methodology also generates a mathematical model (Bas and Boyaci, 2007). Several authors have applied the tool effectively to pigment removal from palm oil using activated clay (Ajemba and Onukwuli, 2012; Nwabanne and Ekwu, 2012).

This work focused on RSM optimization of process variables such as bleaching temperature, bleaching time, clay dosage and particle size for colour pigments removal from palm oil using HCl activated Ibusa clay.

2. MATERIALS AND METHODS

2.1 Material

The clay sample used in this research was sourced from Ibusa (Lat 6'11N, Long 6'38E) in Delta State of Nigeria. The crude palm oil (CPO) was bought from local oil mill at Ezema village, Ojoto in Idemili South local government area of Anambra State, Nigeria.

2.1.1 Characterization of Clay Sample

X-ray fluorescence analysis of the clay sample was carried out using ARL 9400XP+ Wavelength-dispersive XRF Spectrometer while FTIR analysis was done using Shimadzu FTIR-8400S spectrophotometer.

2.1.2 Acid Activation of Clay Sample

The clay material was prepared for activation by drying it under the sun at an ambient temperature of 35°C to make them amenable to grinding. The clay sample was then pulverized and sieved to a particle of 300µm. 50g of the clay sample was mixed with 250 ml of the prepared acid. The resulting suspension was heated on a magnetically-stirred hot plate at a temperature of 98°C for 2.0 hours. The clay residue was washed free of the acid several times with distilled water until a neutral point was obtained with pH meter. The clay was then dried at a temperature of 110°C for 3 hours, then ground again using laboratory mortar and pestle, sieved with 75µm sieve and stored in desiccators.

2.2 Bleaching Process

100 g of the refined unbleached palm oil was measured out into a 250 ml conical flask and heated on a magnetically-stirred hot plate to an already determined temperature from the experimental design. The required mass of the activated clay sample was then added to the heated oil and stirred continuously via a magnetic stirrer carefully inserted into the beaker up to the bleaching time in the experimental design. At the completion of the time, the hot oil and clay mixture was filtered under gravity using Whatman filter paper No.42 (15 cm diameter), before measuring the absorbance. The bleaching/adsorption efficiency of the activated clay samples was then determined by measuring the color of the bleached oil using UV-VIS Spectrophotometer (Model WFJ 525) at 450nm. The bleaching efficiency is defined by the expression in Equation (1).

$$Bleaching\ Efficiency\ (\%) = \frac{A_{\text{unbleached}} - A_{\text{bleached}}}{A_{\text{unbleached}}} \times 100 \qquad (1)$$

Where $A_{\text{unbleached}}$ and A_{bleached} are absorbencies of unbleached and bleached palm oil respectively, at 450 nm.

2.3 Experimental Design

To examine the combined effect of the four (4) independent variables (factors): bleaching temperature, bleaching time, clay dosage and particle size on bleaching efficiency and derive a model, a central composite factorial design of $2^4 = 16$ plus 6 center points and $(2 \times 4 = 8)$ star point leading to a total of 30 experiments were performed. The factors levels with the corresponding real values are shown in Table 1, while the design matrix is shown in Table 2. The matrix for the four (4) variables was varied at five (5) levels (-a, -1, 0, +1, and +a). The lower level of variable was designated as "-1", intermediate lower level as "-α", middle level as "0", intermediate higher level as "+α" and higher level as "+1". The experiments were performed in random order to avoid systematic error. The results were analyzed using the coefficient of determination, analysis of variance (ANOVA), and response surface plots. In RSM, the most widely used second-order polynomial equation developed to fit the experimental data and identify the relevant model terms is shown in Equation 2.

$$Y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{\substack{i=1 \\ j>1}}^{n-1} \sum_{j=2}^{n} \beta_{ij} x_i x_j + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \varepsilon \qquad (2)$$

where Y is the predicted response variable which is the bleaching efficiency in this study, β_0 is the constant coefficient, β_i is the ith linear coefficient of the input variable x_i, β_{ii} is the ith quadratic coefficient of the input variable x_i, β_{ij} is the different interaction coefficients between the input variables x_i and x_j and ε is the error of the model.

Table 1: *Experimental range of the independent variables, with different levels, to study the adsorption/bleaching properties of Ibusa clay after activation with hydrochloric acid.*

Independent variables	Symbol	Range and Levels				
		-a	-1	0	+1	+a
Bleaching Temp.(°C)	A	40	75	110	150	200
Bleaching Time (hrs)	B	-0.50	1.50	2.50	3.00	3.50
Clay Dosage (g)	C	-1.50	1.25	2.95	5.50	8.50
Particle Size (mm)	D	-0.05	0.05	0.25	0.40	0.55

Table2: *Experimental design/plan for adsorption/ bleaching studies of Ibusa clay in hydrochloric acid.*

Run	Bleach Temp. (°C) A		Bleaching Time (hrs) B		Clay Dosage (g) C		Particle Size (mm) D	
	Coded	Real	Coded	Real	Coded	Real	Coded	Real
1	-1	75	-1	1.50	-1	1.25	-1	0.05
2	+1	1.50	-1	1.50	-1	1.25	-1	0.05
3	-1	75	+1	3.00	-1	1.25	-1	0.05
4	+1	150	+1	3.00	-1	1.25	-1	0.05

5	-1	75	-1	1.50	+1	5.50	+1	0.40
6	+1	150	-1	1.50	+1	5.50	+1	0.40
7	-1	75	+1	3.00	+1	5.50	+1	0.40
8	+1	150	+1	3.00	+1	5.50	+1	0.40
9	-1	75	-1	1.50	-1	1.25	+1	0.40
10	+1	150	-1	1.50	-1	1.25	+1	0.40
11	-1	75	+1	3.00	-1	1.25	+1	0.40
12	+1	150	+1	3.00	-1	1.25	+1	0.40
13	-1	75	-1	1.50	+1	5.50	+1	0.40
14	+1	150	-1	1.50	+1	5.50	+1	0.40
15	-1	75	+1	3.00	+1	5.50	+1	0.40
16	+1	150	+1	3.00	+1	5.50	+1	0.40
17	-2	40	0	2.50	0	2.95	0	0.25
18	+2	200	0	2,50	0	2.95	0	0.25
19	0	110	-2	-0.50	0	2.95	0	0.25
20	0	110	+2	3.50	0	2.95	0	0.25
21	0	110	0	2.50	-2	-1.50	0	0.25
22	0	110	0	2.50	+2	8.50	0	0.25
23	0	110	0	2.50	0	2.95	-2	-1.50
24	0	110	0	2.50	0	2.95	+2	5.50
25	0	110	0	2.50	0	2.95	0	0.25
26	0	110	0	2.50	0	2.95	0	0.25
27	0	110	0	2.50	0	2.95	0	0.25
28	0	110	0	2.50	0	2.95	0	0.25
29	0	110	0	2.50	0	2.95	0	0.25
30	0	110	0	2.50	0	2.95	0	0.25

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1 XRF analysis

The result of XRF analysis of the clay shows that Alumina (Al_2O_3), Iron Oxide (Fe_2O_3) and Silicon Oxide (SiO_2) are present in major quantities while other components are present in trace amounts. The following compositions were obtained: Al_2O_3 (17.5 %), SiO_3 (56.60 %), Fe_2O_3 (19.29 %), SO_3 (1.52 %), CaO (2.36 %), TiO_2 (2.36 %), V_2O_5 (0.14%), Cr_2O_3 (0.09%), Mn_2O_3 (0.20%), P_2O_5 (0.43%), NiO (0.04%), CuO (0.03%), ZnO (0.06%), MoO_3 (0.30%), Rh_2O_3 (1.10%), Ta_2O_5 (0.10%), Re_2O_7 (0.10%), IrO_2 (0.27%), Se_2SO_3 (0.03%), CdO (0.60%). The high silica content of the clay suggests its use as source of silica for the production of floor tiles (Nwabanne and Ekwu, 2013)

3.1.2 FTIR analysis

The FTIR spectrum of Ibusa clay is shown in Figure 1. The result revealed the functional groups present in the clay. The band at 524 cm^{-1} is attributed to C-C=O bend, C-Br and C-I stretches. The band at 792.77 cm^{-1} is attributed to C-Cl stretch and CH out-of-phase deformation while the band at 1020.38 cm^{-1} is attributed to Si-O-Si and P-O-C anti-symmetrical stretches. The band at 1107.18 cm^{-1} is attributed to C-N, C-O and C=S stretches as well as C-O-C anti-symmetrical stretch while the band at 1635.65 cm^{-1} could be attributed to Al-O-H stretching. The band at 3399.65 cm^{-1} is attributed to OH stretch for solids and liquids as well as NH stretch for dilute solution.

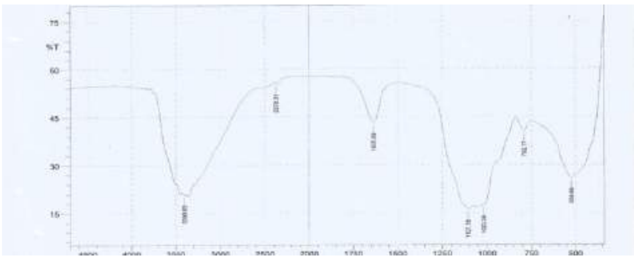

Figure 1: *FTIR spectrum of Ibusa clay.*

3.2 Statistical Analysis of Bleaching Efficiency

To optimize the bleaching efficiency (BE) of the clay sample, response surface method was used to determine the optimum values of the process variables. Response surface methodology (RSM) consists of a group of empirical techniques used for evaluation of relationship between cluster of controlled experimental factors and measured response. The central composite design (CCD) of RSM was used to obtain a quadratic model, consisting of factorial trials and star points to estimate quadratic effects and central points to estimate the pure process variables with bleaching efficiency as response. Response surface methodology (RSM) was employed to optimize the selected four significant process variables such as bleaching time (A), bleaching temperature (B), clay dosage (C) and particle size (D). The design plan shown in Table 2 was used to optimize the bleaching efficiency (BE) of Ibusa clay. Mathematical relationship was generated between the factors (independent variables) and response (dependent variable) using the statistical package Design-Expert 10.0 Trial Version for determining the levels of factors which yield optimum bleaching efficiency. A second order polynomial regression equation that fitted the data is shown in Equation (3).

$$BE\ (\%) = 42.58 + 7.13*A + 4.82*B + 0.38*C + 7.05*D + 0.46*AB - 1.64*AC + 2.19*AD + 1.64*BC + 0.37*BD - 0.79*CD + 0.54*A^2 + 2.97*B^2 - 1.46*C^2 + 2.82*D^2 \quad (3)$$

The above equation represents the quantitative effect of the factors (A, B, C, and D) upon the response (BE). Coefficients with one factor represent the effect of that particular factor, while the coefficients with more than one factor and those with second order terms represent interaction between those factors and the quadratic nature of the phenomena, respectively. Positive sign in front of the terms indicates synergistic effect while negative sign indicates antagonistic effect of the factor. The adequacy of the above proposed model was tested using the Design-Expert sequential model sum of squares and the model summary statistics. From the model summary statistics shown in Table 3, the regression coefficient (R^2 =0.9895) is high, and the adjusted R^2 (0.9798) is in close agreement with the predicted R^2 (0.9528) value. From the analysis of variance shown in Table 4, it can be observed that the model F-value (101.44) of the quadratic model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, D, AC, AD, BC, CD, B^2, C^2, D^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. Based on this, the insignificant terms of the model are removed and model reduces to Equation 4.

$$BE\ (\%) = 42.58 + 7.13*A + 4.82*B + 7.05*D - 1.64*AC + 2.19*AD + 1.64*BC - 0.79*CD + 2.97*B^2 - 1.46*C^2 + 2.82*D^2 \quad (4)$$

In terms of actual factor values, the bleaching efficiency is given in Equation (5).

$$BE\ (\%) = 46.32308 + 0.097620*\text{Bleaching Time} + 0.52856*\text{Bleaching Temp.} + 21.30461*\text{Particle Size} - 0.014611*\text{Bleaching Time}*\text{Dosage} + 0.12963*\text{Bleaching Time}*\text{Particle Size} + 0.031286*\text{Bleaching Temp.}*\text{Dosage} - 2.32963*\text{Dosage}*\text{Particle Size} + 2.42253E\text{-}003*\text{Bleaching Temp.}^2 - 20.64733*\text{Dosage}^2 + 55.65630*\text{Particle Size}^2. \quad (5)$$

The "Lack of Fit F-value" of 1.15 implies the Lack of Fit is not significant relative to the pure error. There is a 46.64% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good as it shows that the model is well fitted.

Table 3: *Model summary statistics.*

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remark
Linear	4.12	0.8537	0.8302	0.7816	634.41	
2FI	3.60	0.9151	0.8704	0.7946	596.54	
Quadratic	1.42	0.9895	0.9798	0.9528	137.12	Suggested
Cubic	1.41	0.9952	0.9801	0.6476	1023.50	

Table 4: *ANOVA for the quadratic model.*

Source	Sum of Squares	Df	Mean Square	F-Value	p-value Prob > F	
Model	2874.32	14	205.31	101.44	< 0.0001	Significant
A-Bleaching Time	1017.05	1	1017.05	502.49	< 0.0001	
B-Bleaching Temp	464.37	1	464.37	229.43	< 0.0001	
C-Dosage	2.88	1	2.88	1.42	0.2514	
D-Particle Size	995.30	1	995.30	491.75	< 0.0001	
AB	3.33	1	3.33	1.65	0.2190	
AC	43.23	1	43.23	21.36	0.0003	
AD	76.56	1	76.56	37.83	< 0.0001	
BC	43.16	1	43.16	21.33	0.0003	

BD	2.24	1	2.24	1.10	0.3100	
CD	9.89	1	9.89	4.89	0.0430	
A^2	2.67	1	2.67	1.32	0.2685	
B^2	82.20	1	82.20	40.61	< 0.0001	
C^2	19.80	1	19.80	9.78	0.0069	
D^2	74.10	1	74.10	36.61	< 0.0001	
Residual	30.36	15	2.02			
Lack of Fit	21.15	10	2.12	1.15	0.4664	not significant
Pure Error	9.21	5	1.84			
Cor Total	2904.68	29				

The coefficient of variation (CV) value of 3.10 illustrate that the model can be considered reasonably reproducible (Chen and Chen, 2011). The signal to noise ratio which is given as the value of the adequate precision is 39.348 as shown in Table 5. It indicates that an adequate relationship of signal to noise ratio exists and that the result can be used to navigate the design space.

Table 5: *Summary of regression values*

Std. Dev.	Mean	C.V. %	PRESS	Adeq. Precision
1.42	45.82	3.10	137.12	39.348

The experimental data were also analyzed to check the correlation between the experimental and predicted bleaching efficiencies as shown in Figure 1. It can be seen from Figure 1 that the data points on the plot were reasonably distributed near to the straight line, indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis were appropriate. The result also suggests that the selected quadratic model was adequate in predicting the response variables for the experimental data (Ajemba and Onukwuli, 2012).

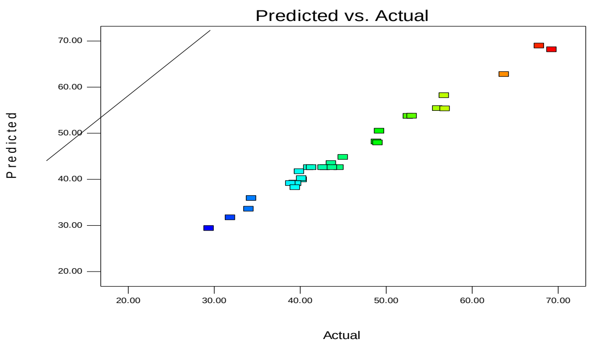

Figure 1: *Plot of predicted values versus the actual experimental values.*

3.3 Response Surface Plots

The 3D response surface plots which represent the interactive effects of two of the process variables on the bleaching efficiency while keeping the other factors at their central (0) level are shown in Figures 2(a-f). The interactive effect of bleaching time and bleaching temperature is positive as shown in Equation 2 and Figure 2a. This implies that increasing both variables increases the bleaching efficiency of the clay. The response surface plot of bleaching time and clay dosage is negative as shown in Equation 2 and Figure 2b. This implies that a simultaneous increase of both variables will have adverse effect on the bleaching efficiency. Figure 2c shows the interactive effect of particle size and bleaching time. The result indicates a positive effect on the bleaching efficiency as depicted in Equation 2. The response variance as a function of clay dosage and bleaching temperature shown in Figure 2d indicates a positive effect. This suggests that both factors will have positive simultaneous influence on the bleaching efficiency. The interactive effect of bleaching temperature and particle size as well as clay dosage and particle size are shown in Figures 2e and 2f, respectively. The results show that the bleaching temperature and particle size had positive simultaneous influence on the bleaching efficiency while the clay dosage and particle size had negative simultaneous influence on the bleaching efficiency.

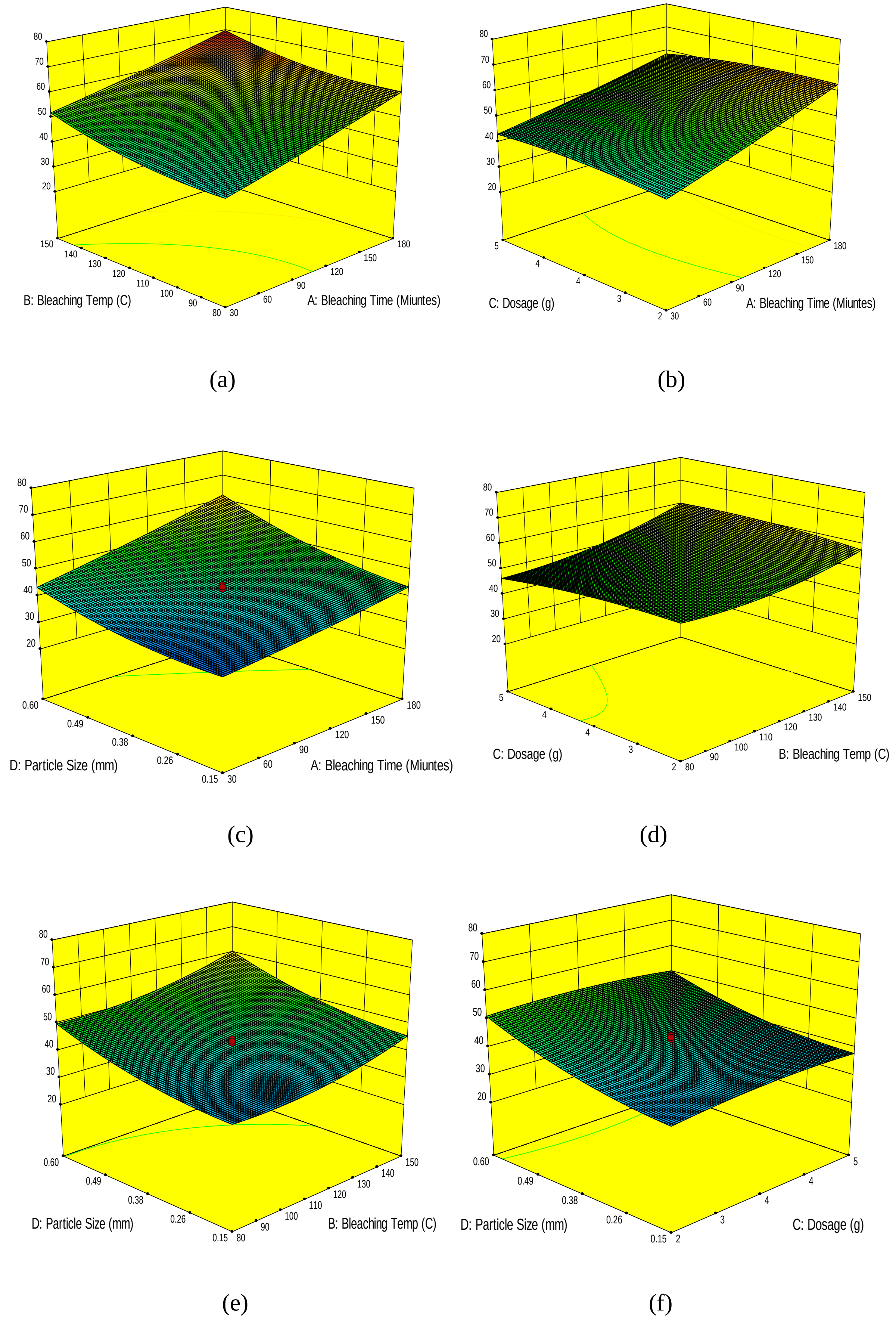

Figure 2: *Response surface plots for the bleaching of palm oil using Ibusa clay.*

3.4 Numerical Optimization

The main objective of this study was to determine optimum conditions for the bleaching of palm oil using activated Ibusa clay. The optimization exercise was carried out separately using the optimization tool of design expert software. Optimum conditions of 111.07°C bleaching temperature, 2.30 hours bleaching time, 3.16 g clay dosage and 0.16 mm particle size were obtained. At the above conditions, the predicted bleaching efficiency was 75.34 %, which was in good agreement with the experimental value of 75.12 %.

4. CONCLUSION

The optimum bleaching conditions of kaolinite from Ibusa have been studied. Response surface methodology was employed to study the effect of process parameters on the bleaching of palm oil. A five-level four-factor central composite rotatable design was successfully deployed for the experimental design. The good correlation between the experimental and predicted response showed that the regression model was adequate in explaining the experimental data. The interactive effects of the process variables were found to be positive except for the simultaneous effects of bleaching time and clay dosage as well as particle size and clay dosage. An optimum bleaching efficiency of 75.34% was recorded at a bleaching temperature of 111.07°C, bleaching time of 2.30 hours, clay dosage of 3.16 g and particle size of 0.16 mm. This study shows that the central composite design of response surface methodology is a good technique for analyzing the effect the effect of the process parameters studied on the response factor by reducing the number of experiments in the bleaching process to a great extent. This study also showed that Ibusa kaolinite can serve as an effective adsorbent for palm oil bleaching when properly optimized.

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