

Response surface optimization of pigments removal from palm oil using activated Karaworo clay

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Abstract

In the present study, response surface methodology was deployed to optimize the removal of pigments from palm oil using activated Karaworo clay. Process variables considered for the optimization exercise include bleaching time, bleaching temperature, clay dosage and particle size while the bleaching efficiency was the response variable. A total of 30 bleaching experiments were carried out based on the conditions obtained by the central composite design of response surface methodology. The analysis of variance (ANOVA) and other statistical tests showed that a second order polynomial regression equation was suitable for fitting the experimental data. The experimental confirmation tests showed a correlation between the predicted and experimental responses ($R^2 = 0.9757$). The optimum conditions for the process parameters were obtained as: bleaching time of 2.47 hours, bleaching temperature of 124.67°C, clay dosage of 3.26 g and particle size of 0.15 mm. Under these conditions, about 71.65% pigments were removed.

Keywords: response surface methodology, bleaching, clay, pigment, optimization

1. Introduction

Palm oil is a flesh fruit fat with a unique orange-red colour, due to its high content of carotenoids. Raw palm oil, in addition to carotenoid pigments content, contains impurities like free fatty acid, fiber particles and chlorophyll (Egbuna, 2014) [8]. Other impurities are phosphatides, trace metals, traces of soap and peroxides. It is desirable to remove colour pigments from oil not only prior to use but also after use, thereby enabling re-using or recycling the oil (Aishat *et al.*, 2015) [2].

Clay minerals differ in their chemical composition and this leads to disparity in their mineralogical properties that include: layer charge, cation exchange capacity, adsorption capacity, and morphology (Stuedel *et al.*, 2009) [16]. Due to the large chemical composition variability, clay minerals are used in different industrial applications such as ceramics, food, chemical and paper minerals. Sometimes, the clay minerals are used in their natural state and at other times after some specific modification (Komadel *et al.*, 1996) [12]. One of such modification methods is acid treatment. Acid activation of clay mineral has been investigated for years by many researchers (Steduel *et al.*, 2009; Abdul-Latif and Weaver, 1969; Bonilla *et al.*, 1981; Cetisli and Gedikbey, 1990) [1, 5, 6].

Different types of acid treatment have been described in the literature, varying from each other by the nature of the acid used, temperature, and intensity and time of the attack. Many researchers have reported that the solids obtained, which are impure silica gels, keep the fibrous structure of the original clay mineral (Bonilla *et al.*, 1981; Gonzalez *et al.*, 1984) [5, 11]. This treatment modifies the surfaces of the clay minerals by disaggregation of particles, possible elimination of mineral impurities, and removal of metal-exchange cations (Vicente-Rodriguez *et al.*, 1994a, 1994b) [17, 18].

The most viable use of acid-activated clay minerals is bleaching or decolouration of oils (Srasra *et al.*, 1989) [15]

and in general in the field of adsorption and catalysis (Fahn and Fenderl, 1983; Mokaya and Jones, 1995) [13]. Acid treated clay minerals are commercially used for the bleaching or decolourizing of oils because they exhibit wide range of chemical and physical properties depending on the degree of activation (Boki *et al.*, 1992) [4].

The response surface methodology (RSM) model has been known as a powerful tool for optimization in several fields such as chemical engineering process and chemical analysis among many other applications (Esonye *et al.*, 2019) [9]. The most popular RSM is the central composite design (CCD). A CCD has three groups of design points: (i) two-level factorial or fractional factorial design points, (ii) axial points (star points), and (iii) center points. CCDs are designed to estimate the coefficients of a quadratic model. All point descriptions are in terms of coded value of the factors (Savic *et al.*, 2012) [14].

It was the purpose of this research to optimize the removal of colour pigments from palm oil using response surface methodology. The process parameters employed include bleaching temperature, bleaching time, clay dosage and particle size

2. Materials and methods

2.1. Materials

The clay sample used in this research was sourced from Karaworo town (Lat: 7°15'N; Long 6°50' E) in Kogi 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 prepare it for grinding. The clay sample was then pulverized and sieved to a particle of 300µm. 50g of the clay sample was mixed with 250ml 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 and 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).

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

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

2.3 Design of Experiment

The process variables that influence the removal of pigments from palm oil were investigated using RSM combined with five-level, four-factor factorial design as established by Design Expert software 10.0 trial version (Stat-Ease Inc., Minneapolis, USA). The process variables were bleaching time, bleaching temperature, clay dosage and particle size. The response variable was chosen as bleaching efficiency. The factor levels were coded as $-\alpha$, -1 , 0 , $+1$ and $+\alpha$. The range and levels are shown in Table 1.

A total of 30 runs were carried out to optimize the process variables and experiments were performed according to the actual experimental design matrix shown in Table 2. The experiments were performed randomly to avoid systemic error. The results were analyzed using the analysis of variance (ANOVA), model summary statistics 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.

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^{n-1} \sum_{j=2}^n \beta_{ij} x_i x_j + \sum_{i=1}^n \beta_{ii} x_i^2 + \epsilon \tag{2}$$

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 i th linear coefficient of the input variable x_i , β_{ii} is the i th 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 Karaworo clay after activation with hydrochloric acid.

Independent variables	Symbol	Range and Levels				
		-a	-1	0	+1	+a
Bleaching Temperature (°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

Table 2: Experimental design/plan for adsorption/bleaching studies of Karaworo 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	150	-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 Karaworo clay shows that Alumina (Al₂O₃), Iron Oxide (Fe₂O₃) and Silicon Oxide (SiO₂) are present in major quantities while other components are present in trace amounts. The following compositions were obtained: Al₂O₃ (14.1%), SiO₃ (57.00%), Fe₂O₃ (8.643%), SO₃ (0.05%), CaO (0.20%), TiO₂ (2.70%), V₂O₅ (0.29%), Cr₂O₃ (0.10%), Mn₂O₃ (0.01%), P₂O₅ (0.30%), NiO (0.19%), CuO (0.045%), ZnO (0.03%), MoO₃ (0.20%), Rh₂O₃ (1.11%), Re₂O₇ (0.20%) and IrO₂ (0.22%).

3.1.2 FTIR analysis

The FTIR spectra of Karaworo clay is shown in Figure 1.

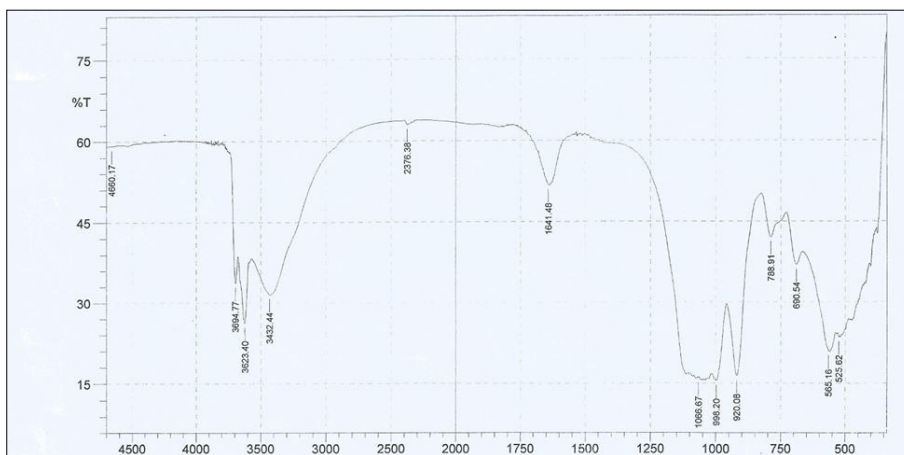


Fig 1: FTIR spectrum of Karaworo clay

The result showed the functional groups present in the clay. The band at 525.62 cm⁻¹ is attributed to C-C=O bend and C-I stretch while the band at 565.16 cm⁻¹ is attributed to Si-O-Al stretch. The band at 690.54 cm⁻¹ is attributed to C-S stretch and CH out-of-phase deformation while the band at 788.91 is attributed to Si-C stretch and Si-O bend. The band at 920.08 cm⁻¹ is attributed to Al-O-Si stretch while the band at 998.20 cm⁻¹ is attributed to Si-O-Si stretch. The band at 1066.67 cm⁻¹ is attributed to Si-O-Si anti-symmetrical stretch while the band at 1641.48 cm⁻¹ is attributed to C=N, C=O and Al-O-H stretches while the band at 2376.38 cm⁻¹ is also attributed to Al-O-Si stretch. The bands at 3623.40 cm⁻¹ and 3694.77 cm⁻¹ are attributed to OH stretch for dilute solution.

3.2 Statistical Analysis

The bleaching efficiency (BE) of acid activated Karaworo clay was optimized statistically using the response surface methodology (RSM). The data generated from the central composite design was analyzed using the Design Expert software 10.0 Trial Version. Mathematical relationship between the dependent variables and the independent variable was evaluated using the software. The second order polynomial regression equation that fitted the data is shown in Equation 3.

$$BE (\%) = 52.41 + 6.17*A + 5.37*B - 0.23*C + 6.32*D - 2.61*AB - 0.031*AC + 0.34*AD - 0.32*BC + 0.20*BD - 0.78*CD - 0.88*A^2 + 1.76*B^2 + 1.20*C^2 - 0.74*D^2 \quad (3)$$

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 factors, respectively. Positive sign in front of the terms indicates synergistic effect; where 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 test statistics. The significance of the model was tested using the analysis of variance (ANOVA) shown in Table 3. And from

the statistics test, the regression coefficient ($R^2 = 0.9757$) is high, and the adjusted R^2 (0.9530) is in close agreement with the predicted R^2 (0.8994) value as shown in Table 4. A model is considered significant if the p-value (significance probability value) is less than 0.05. From the p-values presented in Table 3, it can be seen that the linear terms A, B and D, interaction term AB, and the quadratic term B^2 are significant model terms. Based on this, the insignificant terms of the model are removed and model reduces to Equation 4.

$$BE (\%) = 52.41 + 6.17*A + 5.37*B + 6.32*D - 2.61*AB + 1.76*B^2 \tag{4}$$

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

$$BE (\%) = 22.02609 + 0.22321*Bleaching\ Time + 0.059953*Bleaching\ Temp. + 42.27923* Particle\ Size - 9.95871E-004*Bleaching\ Time*Bleaching\ Temp. + 1.43615E-003* -Bleaching\ Temp.^2 \tag{5}$$

Table 3: ANOVA for the quadratic model.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	2313.48	14	165.25	43.04	< 0.0001	Significant
A-Bleaching Time	761.71	1	761.71	198.38	< 0.0001	
B-Bleaching Temp	577.44	1	577.44	150.39	< 0.0001	
C-Dosage	1.02	1	1.02	0.27	0.6130	
D-Particle Size	798.47	1	798.47	207.96	< 0.0001	
AB	109.34	1	109.34	28.48	< 0.0001	
AC	0.015	1	0.015	3.921E-003	0.9509	
AD	1.80	1	1.80	0.47	0.5039	
BC	1.67	1	1.67	0.44	0.5190	
BD	0.61	1	0.61	0.16	0.6959	
CD	9.81	1	9.81	2.55	0.1309	
A ²	7.25	1	7.25	1.89	0.1896	
B ²	28.89	1	28.89	7.52	0.0151	
C ²	13.37	1	13.37	3.48	0.0817	
D ²	5.16	1	5.16	1.34	0.2644	
Residual	57.59	15	3.84			
Lack of Fit	44.93	10	4.49	1.77	0.2737	not significant
Pure Error	12.66	5	2.53			
Cor Total	2371.08	29				

The Model F-value of 43.04 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. The "Lack of Fit F-value" of 1.77 implies the Lack of Fit is not significant relative to the pure error. There is a 27.37% 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.

The coefficient of variation (CV) value of 3.68 illustrate that the model can be considered reasonably reproducible (Chen and Chen, 2011) [7]. The signal to noise ratio which is given as the value of the adequate precision is 27.426 as shown in Table 4. 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 4: Summary of regression values.

Std. Dev.	1.96	R-Squared	0.9757
Mean	53.29	Adj R-Squared	0.9530
C.V%	3.68	Pred. R-Squared	0.8994
PRESS	238.57	Adeq. Precision	27.426

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) [3].

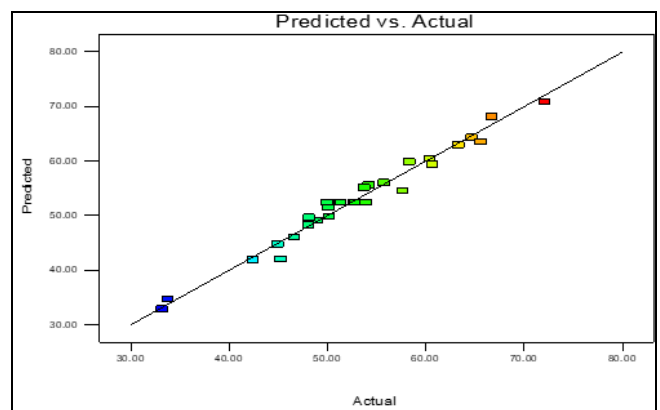


Fig 1: Plot of predicted values versus the actual experimental values.

3.3 Response Surface Plots

The interactive effects of process variables on the removal of pigments from palm oil using activated Karaworo clay are shown in 3-dimensional response surface plots depicted in Figures 2 (a-d). The response variable which is the bleaching efficiency was plotted against two factors while keeping other factors at their central level. The interactive effect of bleaching time and particle size is positive as shown in Figure 2a and Equation 2. This implies that increasing both variables simultaneously will have a

positive impact on the bleaching efficiency. Figure 2b shows the response surface plot of clay dosage and bleaching time. The result as shown in Equation 2 indicates a negative influence on the bleaching efficiency. The interactive effect of particle size and bleaching temperature

is shown in Figure 2c and it indicates a positive influence on the bleaching efficiency while the interactive effect of particle size and dosage had a negative simultaneous effect on the bleaching efficiency.

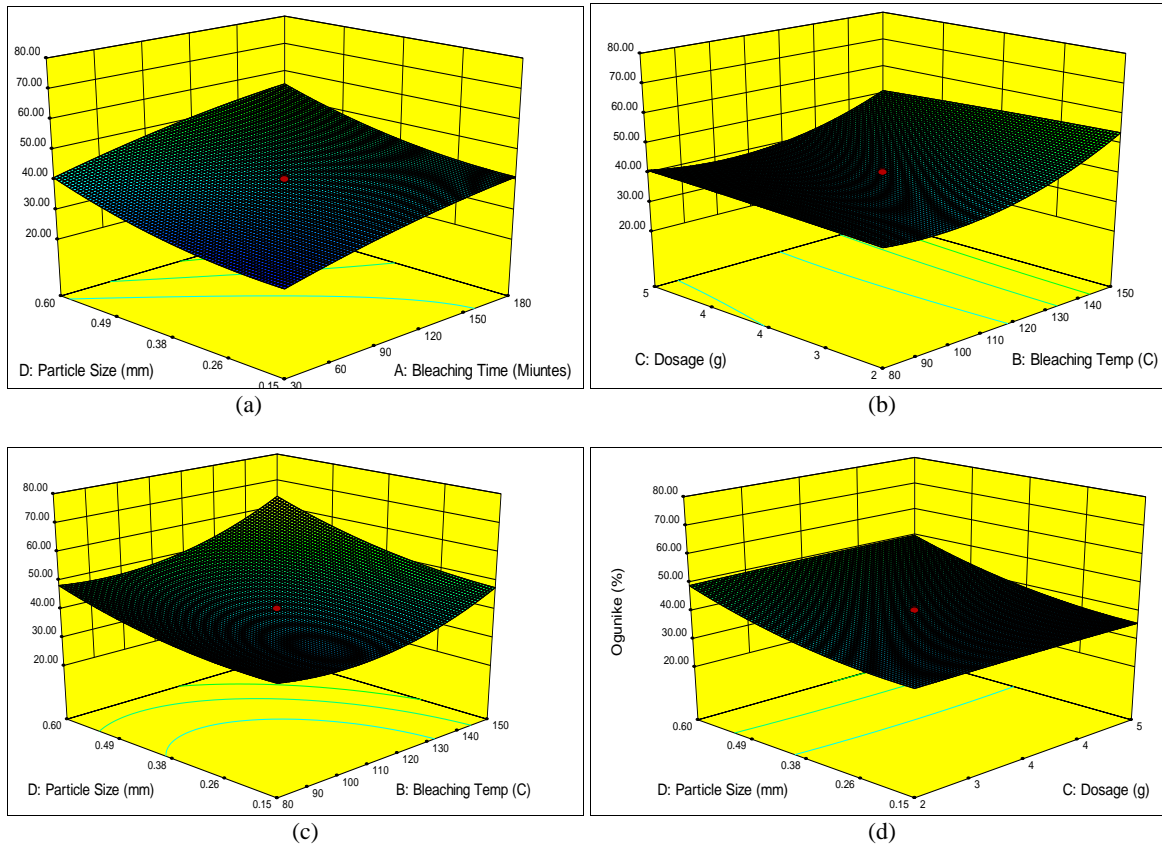


Fig 2: Response surface plots for pigments removal from palm oil using activated Karawor clay.

3.4 Numerical Optimization

This study was aimed at determining optimum conditions for the removal of pigments from palm oil using activated Karaworo clay. The numerical optimization tool of design expert software was utilized for the optimization exercise. The optimum conditions for the removal of 71.65% pigments from palm oil were obtained as follows: bleaching time of 2.47 hours, bleaching temperature of 124.67°C, clay dosage of 3.26 g and particle size of 0.15 mm. Confirmatory test carried out at these conditions gave a bleaching efficiency of 71.37%.

4. Conclusion

Response surface methodology was successfully deployed to determine optimum conditions for the removal of colour pigments from palm oil using activated Karaworo clay. Process parameters considered include bleaching time, bleaching temperature, clay dosage and particle size. From the model developed, the bleaching time, bleaching temperature and particle size gave positive correlation with the bleaching efficiency while clay dosage gave a negative correlation. Also, the interactive effects of bleaching time and particle size as well as bleaching temperature and particle size showed positive simultaneous influence on the bleaching efficiency. Based on the central composite rotatable design, the optimum conditions for the removal of pigments from palm oil are: bleaching time of 2.47 hours; bleaching temperature of 124.67°C; clay dosage of 3.26 g

and particle size of 0.15 mm.

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