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Optimization of Activation Model of Clay from Enugu State for the Bleaching Crude Palm Oil

Echegi Christian Uche
Department of Chemical Engineering,
Institute of Management and Technology, Enugu, Nigeria.
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Abstract

In this study, response surface methodology was used to study the optimization of bleaching of palm oil using local clay from Enugu State of Nigeria. The clay was subjected to acid activation using HNO_3 and H_2SO_4 as activating agents. The interaction effects of the process variables on bleaching performance of Palm Oil by activated clay samples were investigated using Design Expert Software. The experimental results of adsorption process showed that all the linear effects of independent variables of dosage, time and temperature investigated were highly significant as well as their interactive effects. The optimum conditions for the maximum adsorption efficiency of 84.13% and 86.25% for the two clay samples were obtained at temperature of 50^0C, clay dosage of 3.0g and time of 30 minutes. The model predicted R^2 is in a reasonable agreement with the adjusted value while a high determination coefficient of greater than 98% was recorded. This study shows that Eha-Ndiagu clay is a classified highly rated adsorbent whose adsorptive potentials can be maximized under optimum process conditions.

Keywords: *Clay, Acid-activation, Palm Oil, Optimization, Bleaching*

Introduction

Clay is a type of fine grained natural soil consisting of hydrous alumino-silicate minerals with particles that are within the range of 2μm in nominal spherical diameter. Clay is abound in all parts of the globe but the mineralogical and chemical composition which comprise montmorrilonite, kaolinite, illite, chlorite, attapulgite etc. vary across geographical locations of source [Echegi, Eze et al 2013]. Clay and clay products are of great significant to humanity due to their natural characteristics for domestic and industrial utilizations. Some of the essential attributes of this adsorbent in the sourcing and modification processes to the desired form include high cost effectiveness and environmental friendliness.

Due to extremely small particle size, clay exhibits a large surface area per unit mass [Javed et al, 2018; Echegi, 2019]. It possesses surface charges that attract negative and positive ions and water. The attraction (adsorption) of ions such as Ca^{2+}, Mg^{2+}, K^+, etc on the surface of colloidal clay and humus is not as exciting as the exchange of these ions for other ions in soil solution. The intimate contact between clay solution ions and adsorbed ions makes such exchange possible [Bello et al, 2018]. However, like other raw materials, clay has to undergo appropriate physical and chemical treatments such as activation, ion exchange and heating in other to promote surface properties and optimizes its industrial potentials.

Activation of clay involves the treatment of clay precursor with activating agent such as acid, alkali etc and subjecting the mixture to process variables of time, temperature and varying concentration of activating agent, particle sizes, among others. In acid activation, the clay is stripped off octahedral ions such as Fe, Al, Mg, K and removes tetrahedral ions from clay minerals due to the isomorphous substitution in the crystal lattice (Abdelfattah et, 2018]. Jeldi and Co-workers (Jeldi et al, 2018), stated that the acid attack may lead to progressive dissolution and leaching out of the organic matter on the crystal lattice resulting in increased porosity and surface acidity. For a specific mode of activation, the efficacy of the activated clay is a function of interactive dictation of the above enumerated process variables of activation [Echegi et al, 2023].

There are numerous applications of activated clay ranging from bleaching of vegetable oils, metal extraction and refining, remediation of soil, production of sugar, refining of petroleum products, purification of water to catalyst and catalytic supports in process industries [Echegi, 2019]. Bleaching of palm oil (PO) is an adsorption process which improves colours, flavour, taste and stability of the residual oil. In adsorption, the coloured pigments of carotenoid, chlorphyll, xanthophyll, tocophenrol, etc are adsorbed onto the pore sites of the clay adsorbent and thus allowing the pure and colourless oil to separate out into a distinct phase. The adsorptive capacity of any adsorbent is a function of specific surface area, surface charge, porosity and pore size distribution among others.

Crude palm oil bleaching using activated clay has been reported by many researchers [Hauwa et al 2021]. From their reports, it was observed that the clay source/location is a significant factor to the variation of bleaching performance of adsorbates. Further observation reveals that for a particular mode of clay activation, the overriding parameters for sorbate bleaching efficiency are temperature, contact time and adsorbent dosage. Optimization of the process variables in bleaching process is viable through application of statistical experimental design techniques in adsorption process development that results in improved product yields and reduced contact time and overall costs [Wuraola et al, 2019].

The conventional and statistical methods of studying a process by one factor at a time method in which other process variables are maintained constant does not represent and predict the actual combined effects of all the parameters involved [Nwabanne and Ekwu, 2013]. This age-long method of assessment which is time consuming and unreliable, requires in addition a large number of experiments to determine the optimum level of performance. The actual solution involves the collective optimization of all the contending variables by statistical experimental design such as response surface methodology (RSM).

RSM is based on polynomial surface analysis which lies on the collection of mathematical and statistical techniques for the modeling and analysis in which a response of interest is a function of several variables [Wuraola et al, 2019]. The main objective of the RSM is to optimize the innate interactive effects of each of the variables acting together of a given process. In this work, the RSM is used to optimize the bleaching process variables of temperature, clay dosage and contact time toward obtaining optimum conditions of palm bleaching using Design Expert Software to design the experiment. The main aim of this work is to exploit and harness the industrial potentials of the locally bound clay in Enugu State to the benefit of humanity.

Materials and Method

Materials: The materials and reagents used in this experiment include; clay sourced from Eha-Ndiagu and Palm oil obtained from Eke Ede-Oballa market square in Nsukka Local Government Area of Enugu State, Nigeria. Others are HNO_3, H_2SO_4, KOH, HCl, C_2H_5OH (Ethanol), Na_2SO_3. The equipment includes Sieve, magnetic stirrer, weighing balance, conical flask, UV-spectrophotometer, etc.

Experimental Procedures

Clay Activation using Nitric acid (HNO_3) and Sulphuric acid (H_2SO_4). The clay was pulverized, pre-treated and then activated as follows: After clay had been dried, it was ground to powder form using pestle and mortar. The powdered clay was sieved using 0.075mm to a very fine particle. This was done repeatedly to get 500g of the sieved fine particles.

50g of clay sample was put in a beaker in which 250ml of 1.0M HNO_3 was added to it. The mixture was heated for 1 hour at a temperature of 95^0C on a magnetic stirrer. After 1 hour, the mixture was washed several times with distilled water, so as to drive off the acid completely and later it was tested with a blue litmus paper for confirmation. The resulting slurry was filtered, the filtrate dried and ground to powder form and stored in air-tight can. Similarly, the same procedure was carried out using 1.0M H_2SO_4.

Bleaching Process

In the bleaching processes, interactive effects of temperature, time and dosage on the bleaching efficiency (BE) were monitored. It was carried out in batches, in which different masses of activated clay was added to 50ml of degummed palm oil at various temperature and time, on a magnetic stirrer with stirring rate of 500 rpm. For each bleaching process, the beached oil was filtered with filter paper and the bleached oil stored in a sample bottle. 0.1g of each crude oil and bleached oil were taken differently and mixed with 7.5ml of n-Hexane in different beakers and the colour monitored with UV-spectrophotometer at a wavelength of 450nm. The percent bleaching efficiency (% B.E) is obtained from the equation below.

$$\%\ \text{B.E} = \frac{A_0 - A_f}{A_0} \times \frac{100}{1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

A_0 = initial adsorbance before the bleaching

A_f = final absorbance after the bleaching

Experimental design and optimization

The experimental design and statistical analysis were carried out according to response surface analysis method using Design Expert 7.0.0 (stat. Ease Inc., Minneapolis MN, USA) trial version software. Historical data design (HDD) was employed for the optimization of the bleached palm oil by the combined effects of three independent variables of temperature, time and dosage of clay on the bleaching performance. The statistical analysis was carried out using Analysis of Variance (ANOVA), regression analysis and response surface plots of the interactive effect of the above independent variables to evaluate the optimum conditions for the bleaching process.

Result and Analysis

Analysis of variance (ANOVA)

In Tables 1 and 2, the model F-values of 74.51 and 120.01 for HNO_3 and H_2SO_4 respectively show that the models are significant. There is only a 0.01% chance that a model "F-Value", this large could occur due to noise. P-values less than 0.500 indicate model terms are significant. For HNO_3 as recorded in Table 1 - A, B, C, AB, BC, A^2, B^2 and D^2 are significant model terms while for H_2SO_4 in Table 2 – A, B, AB, AC, BC, A^2, B^2 and C^2 are revealed to have exhibited significance of the model terms. The model presented high determination coefficient $R^2 > 0.98$ indicating that above 98% of the variability was obtaining for both activating agents.

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	3812.69	9	423.63	74.51	< 0.0001	Significant
A-Dosage	545.23	1	545.23	95.89	< 0.0001	
B-Temperature	45.03	1	45.03	7.92	0.0183	
C-Time	276.26	1	276.26	48.59	< 0.0001	
AB	0.0078	1	0.0078	0.0014	0.9712	
AC	0.7626	1	0.7626	0.1341	0.7218	
BC	34.57	1	34.57	6.08	0.0333	
A^2	633.16	1	633.16	111.36	< 0.0001	
B^2	62.14	1	62.14	10.93	0.0079	
C^2	162.36	1	162.36	28.55	0.0003	
Residual	56.86	10	5.69			
Lack of Fit	56.86	5	11.37			
Pure Error	0.0000	5	0.0000			
Cor Total	3869.55	19				
Std. Dev.	2.38		R^2		0.9853	
Mean	69.84		Adjusted R^2		0.9721	
C.V. %	3.41		Predicted R^2		0.8898	
			Adeq Precision		24.0626	

Table 1: ANOVA for Quadratic model of HNO_3 Treated Clay Bleaching efficiency

Source	**Sum of Squares**	**Df**	**Mean Square**	**F-value**	**p-value**	
Model	4141.89	9	460.21	120.01	< 0.0001	significant
A-Dosage	657.88	1	657.88	171.56	< 0.0001	
B-Temperature	22.44	1	22.44	5.85	0.0361	
C-Time	358.80	1	358.80	93.57	< 0.0001	
AB	4.84	1	4.84	1.26	0.2877	
AC	7.07	1	7.07	1.84	0.2044	
BC	63.84	1	63.84	16.65	0.0022	
A^2	642.10	1	642.10	167.44	< 0.0001	
B^2	72.24	1	72.24	18.84	0.0015	

C^2	167.12	1	167.12	43.58	< 0.0001	
Residual	38.35	10	3.83			
Lack of Fit	38.35	5	7.67			
Pure Error	0.0000	5	0.0000			
Cor Total	4180.24	19				
Std. Dev.	1.96		R^2		0.9908	
Mean	71.75		Adjusted R^2		0.9826	
C.V. %	2.73		Predicted R^2		0.9219	
			Adeq Precision		32.7488	

Table 2: ANOVA for Quadratic model of H_2SO_4 Treated Clay Bleaching Efficiency

The predicted R^2 of 0.8898 is in reasonable agreement with the adjusted R^2 of 0.972, that is, the difference is less than 0.2. A similar observation was obtained in Table 2 for the activating agent of H_2SO_4. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratios of 24.063 and 32.749 indicate adequate sign for both of them. This model can be used to navigate the design space.

Regression Model Equation

Based on the experimental design and the results obtained, the second order response functions representing Y is the response for the bleaching performance of HNO_3 activated clay sample expressed as:

$$Y = 83.65 + 7.38A + 2.12B + 5.26C - 0.0313AB - 0.3088AC - 2.08BC - 15.17A^2 - 4.75B^2 - 7.68C^2 \quad \ldots\ldots (2)$$

In this equation, A, B, & C are the coded values for the independent variables of clay dosage (g), temperature (^0C) and time (mins) respectively. While for H_2SO_4 counterpart, the response function as obtained is expressed as:

$$Y = 85.85 + 8.11A + 1.50B + 5.99C - 0.7775AB - 0.9400AC - 2.82BC - 15.28A^2 - 5.13B^2 - 7.80A \quad \ldots\ldots (3)$$

From both equations (2) and (3), the coded variable of dosage has the highest effect on the bleaching performance with coefficient of 7.38 and 8.11 for HNO_3 and H_2SO_4 activated clay samples respectively. This is followed by the coded value of variable of contact time while that of temperature took the rear. The coded equation is useful for identifying the relative impact of the factors by comparing the factor co-efficient. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor.

Modern Diagnostic Plots

The interactive effects of the process factors on bleaching efficiency of PO were investigated by plotting three dimensional surface curves against any two independent variables, while keeping other variable(s) at their central (0) mark. The 3D curves of the response and the contour plots from the interactions between the variables are contained in figures 1-6. Figures 1 and 4 represent the responses for the interactive factors of temperature and clay dosage for the two activated clay samples. The analysis reveals that the interactive effects of these two variables have positive influence on the bleaching capacity of clay on PO. For instance, in HNO_3 activated sample, it was observed that the bleaching efficiency increases with temperature and reaching the optimum value of above 84% at the temperature of 50^0C, but later decreases with further increase in temperature. This trend is in agreement with the reports of Wuraola et al, (2019) and Echegi and Co-workers, (2023). As remarked by Nwabanne et al, (2013), this effect may be as a result of oil viscosity which decreases with increasing temperature, leading to better dispersion of particles, improved clay oil interactions and flow ability.

In the same manner, the clay dosage analysis portrays another remarkable occurrence. In HNO_3 activated clay, the value of B.E obtained increases with the dosage and recording the optimum value at 3.0g from 1.0g. But as the dosage increases to 5.0g and beyond the down turn sets in and the value decreases progressively. This result appears obvious in view of oil retention which occurs at higher amount of clay dosage. The result from H_2SO_4 clay activated sample exhibited the same trend of occurrence.

Figures 2 and 5, show responses for the interaction of adsorbent dosage and contact time. It is observed that the higher values of B.E occurred at a higher time level and reaching optimum value of above 84% at the time (t) = 30 minutes. In the same vein, at higher values of dosage, the B.E increases progressively and recording the optimum at around 3.0g of clay dosage. In line with the reports of many researchers [Egbuna et al, 2015, Ikechukwu et al, 2020] it may be inferred that dosage is one of the most significant factor in the adsorption of coloured pigment from PO. This may be attributed to the enhanced adsorption capacity of clay whose surface characteristics of surface area, surface charge, active sites, porosity, etc are promoted by activation.

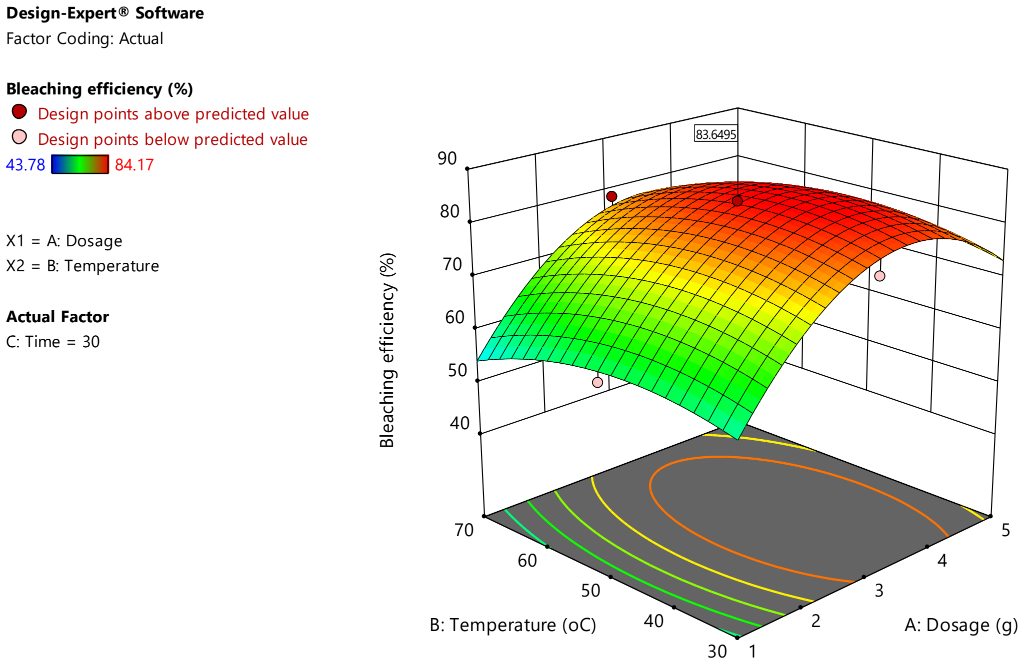

Figure 1

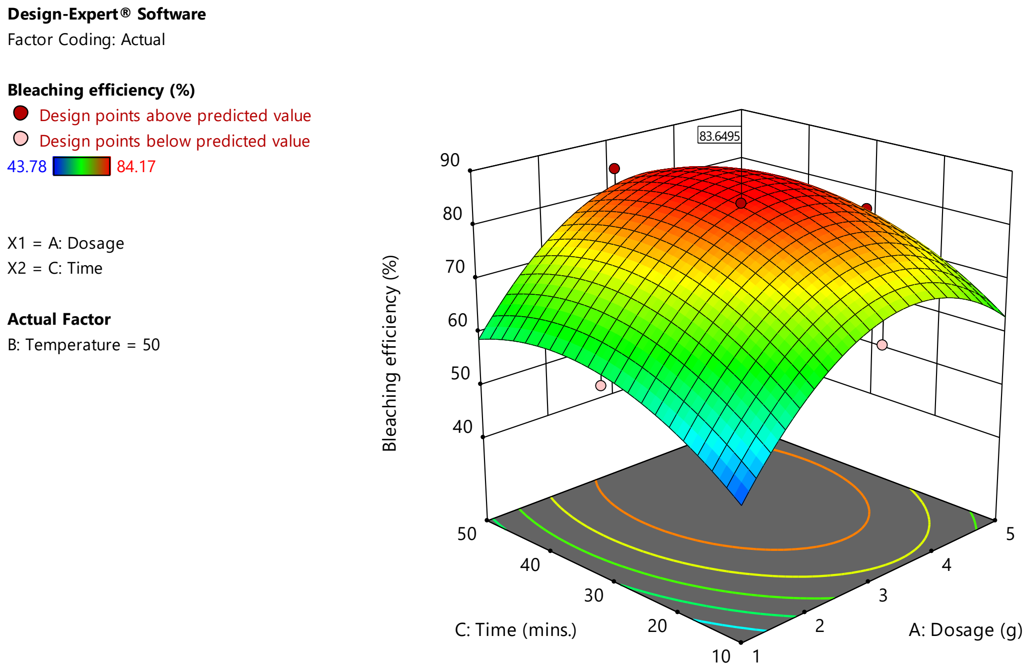

Figure 2

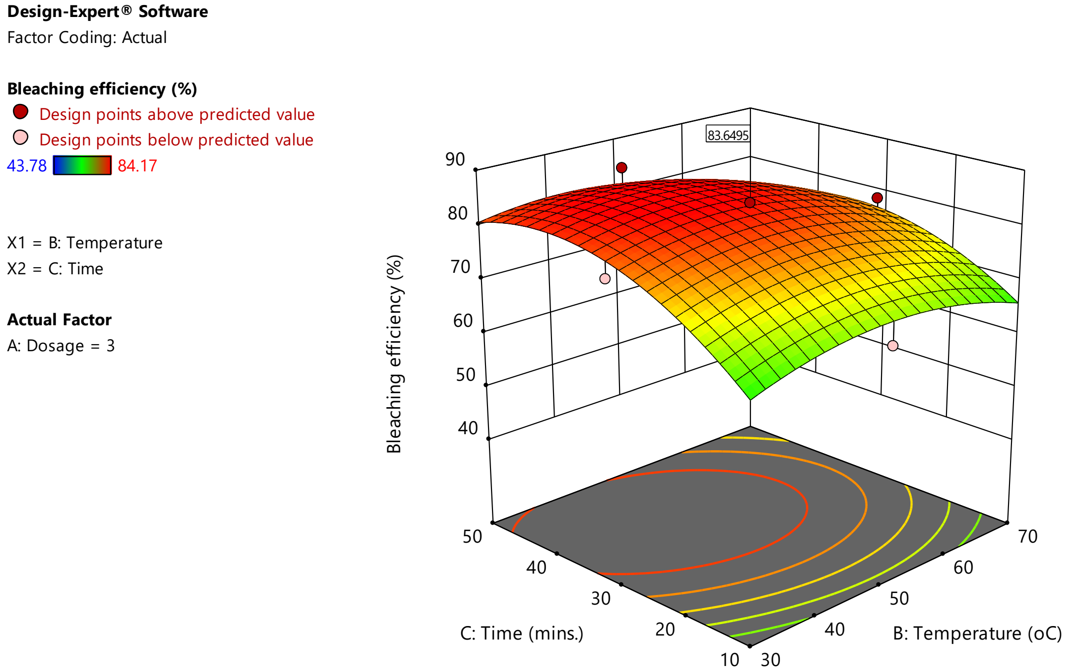

Figure 3

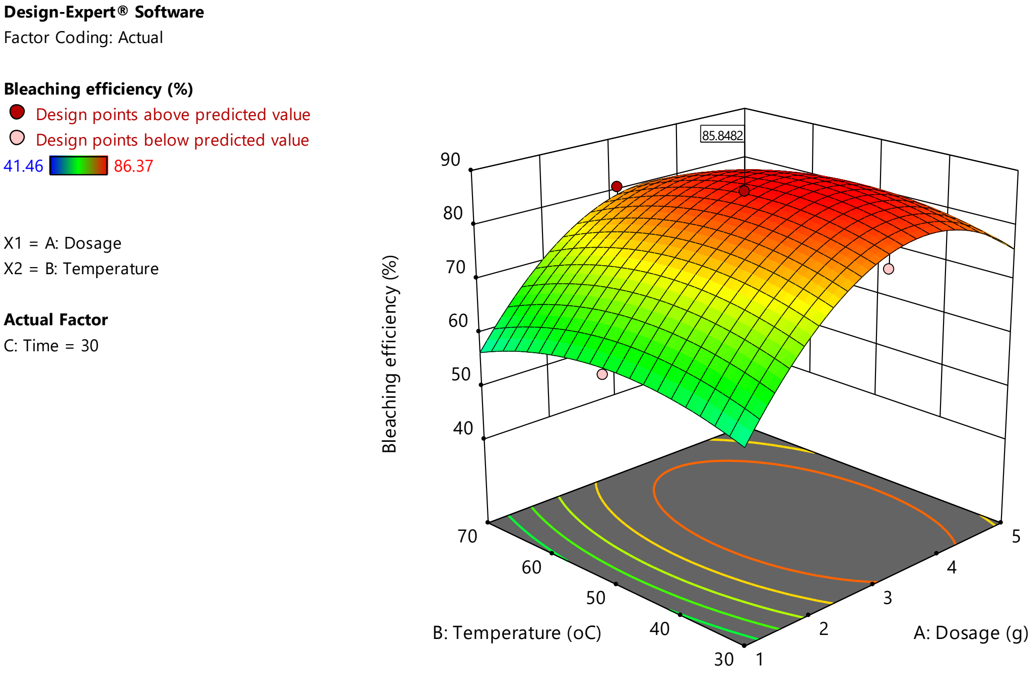

Figure 4

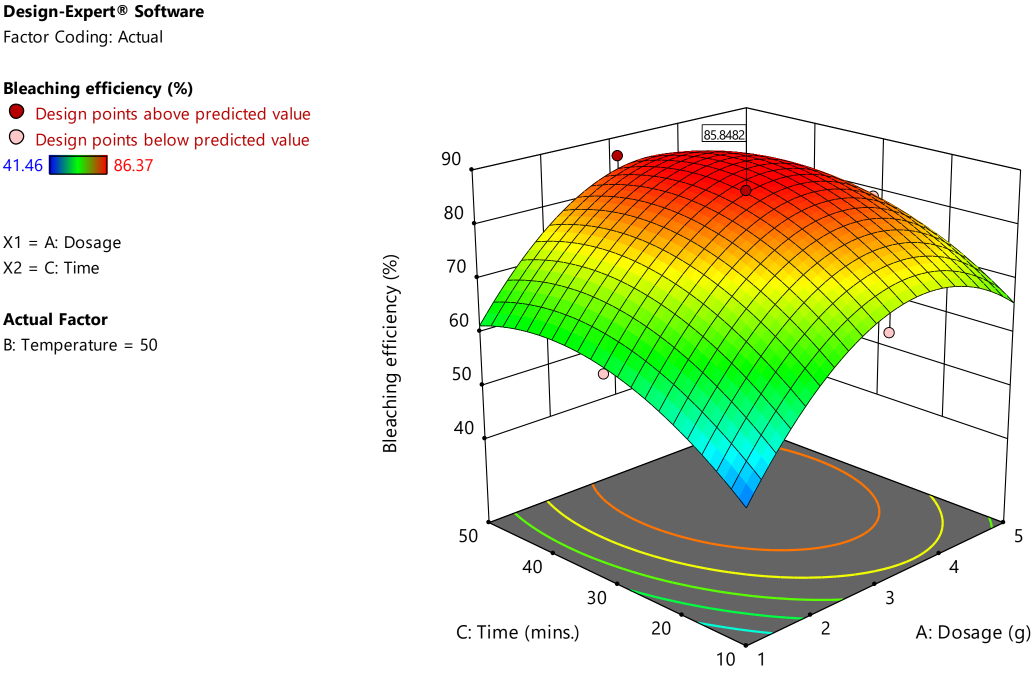

Figure 5

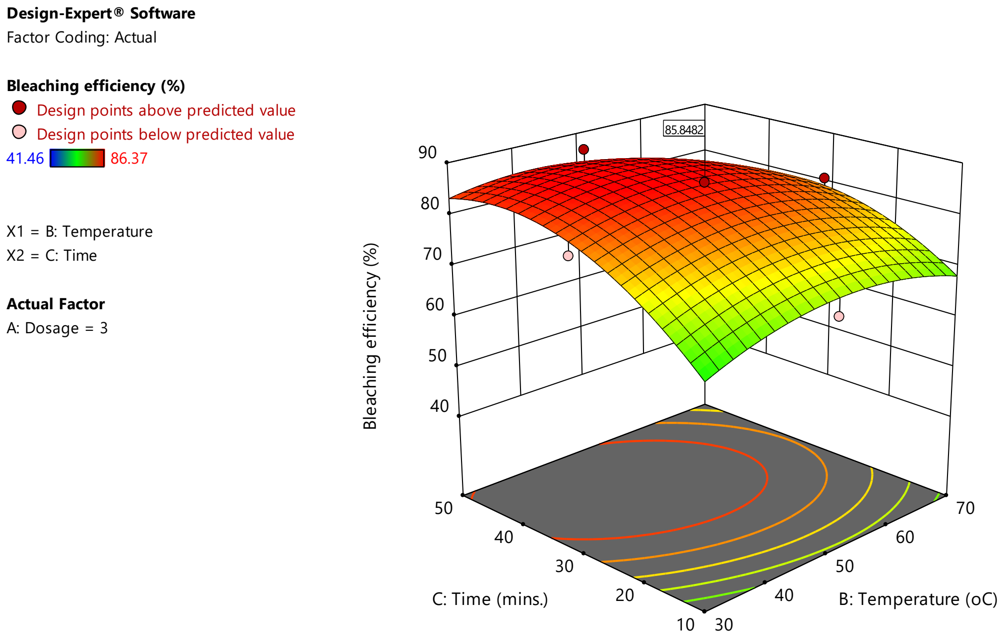

Figure 6

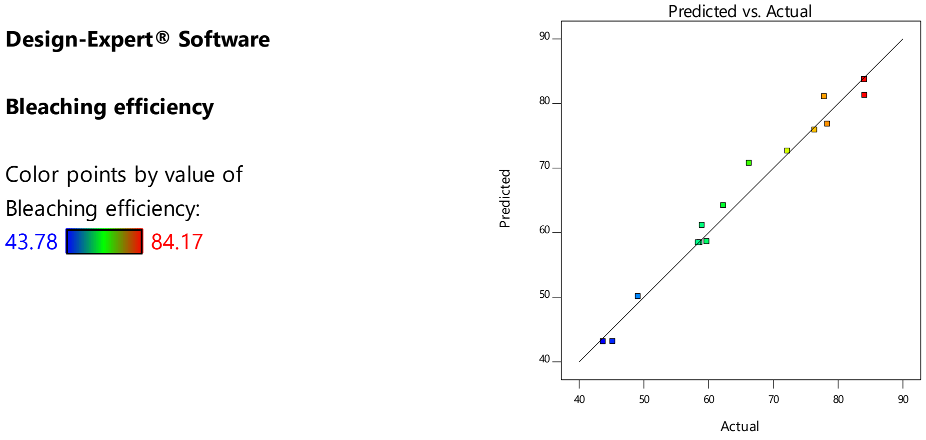

Figure 7

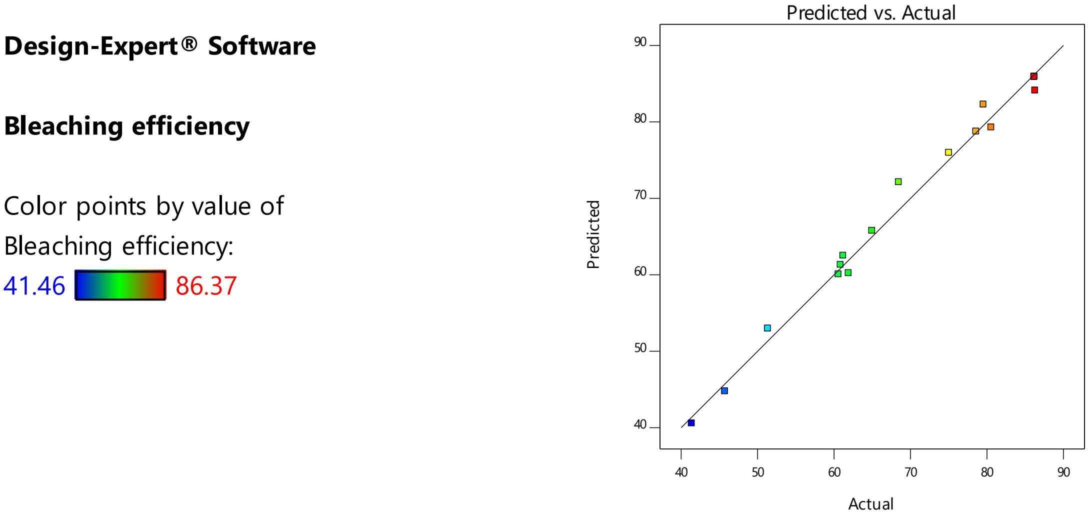

Figure 8

The surface response curves of the response (bleaching performance) against temperature and contact time at constant dosage are shown in figures 3 and 6. From the two contour plots, it was observed that the bleaching performance increases with temperature and contact time. However, at a low contact time, the bleaching efficiency does not proceed to an appreciable level. Initially, it was slowly and later preceded with faster rate to an optimum, at a contact time of 30 minutes and thereafter decreases. A further increase in temperature and time beyond 50^0C and 30 minutes respectively, leads to reversal of trend in optimum point mark which invariably brings about a significant decrease of the bleaching efficiency. From the reported of Iloabachie et al, (2020), this result has confirmed that Eha-Ndiagu clay is montmorillonite whose activation process has factors of temperature, acid activating agent and time as their main determinants in the bleaching of vegetable oil.

Conclusion

In this work, RSM was successfully employed in the study of the optimization of process variables on the bleaching performance of PO using acid activated clay from Enugu State. The result shows that there was a high level of correlation between the predicted and observed response and this indicates that the regression model is adequate in explaining the variations in the experimental data. Among the process variables investigated, clay dosage is found to be most linear significant, followed by contact time and then, the temperature. The optimum conditions for the maximum adsorption efficiency of 84.13% and 86.25% for clay activated with HNO_3 and H_2SO_4 respectively were: dosage of 3.0g, time of 30 minutes and temperature of 50^0C. The study shows that Eha-Ndiagu clay from Enugu State has the required adsorptive potentials for high bleaching performance of vegetable oil under optimized process conditions.

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