Optimization of Activation Conditions on Bentonite Clay for the Bleaching of Sesame Oil Using Response Surface Methodology (RSM)

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Abstract

Bentonite is specialized clay composed mainly of the clay mineral montmorillinite and formed by the alteration of volcanic ash. Bentonite is used a number of industrial application due to its excellent adsorption and absorption properties. In this research work, activation of bentonite was carried out by using sulphuric acid under different conditions of acid concentration, activation time and activation temperature. Optimization of activation conditions were conducted by using response surface methodology (RSM). The conditions were 1, 1.5 and 2 M of H_2SO_4 concentration (x_1), 3, 4 and 5hr activation time (x_2), and 90, 100 and 110 ˚C activation temperatures (x_3). The quality of the second order polynomial model was confirmed the coefficient of determination, (R^2=96.0%). Box-Behnken experimental design indicated that the model can significantly ($p < 0.05$) express more than 80 % (> 0.80) of the response variation. The prepared activated clay was used in the bleaching of sesame oil. The color changes of sesame oil before and after bleaching with the prepared activated clay was measured by using Lovibond Tintometer PFXi-195/2 model which can output CIE LAB L*a*b* color system. Then, the bleaching efficiency of activated clay was determined. The optimum activation condition for maximum bleaching efficiency is 1.5M H_2SO_4 concentration, 4hr activation time and 100˚C activation temperature and the maximum bleaching efficiency is 64.22%.

Key words: Bentonite Clay, Activation, Bleaching, Sesame Oil, Response Surface Methodology

Introduction

Clay, the basic clay mineral, is montmorillonite, or smectite, is generally called bentonite. Bentonite is the clay generated frequently from the alteration of volcanic ash. Depending on the nature of their genesis, bentonites contain a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite and gypsum. All bentonites contain a percentage of other minerals; aluminium oxide, potassium oxide, magnesium oxide, to a name percentage of sand and silt (http://www.britannica.com/ EB checked/ topic/120723/ clay-mineral).

The chemical and mineralogical structures of the bentonites, which are activated by heating in strong acids, undergo considerable transformation. Acid activated bentonites are used as

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adsorbents in the bleaching of edible oil, in the carbonless copy paper, and heterogeneous catalysts. The surface activity and porous structure of bentonite can change into the desire extent by acid activation. Acid activation enhances the decolorizing power of some montmorillonite clay (http://www.sub-chemic.com).

In order to optimize the activation conditions, Response Surface Methodology (RSM) has been widely used. The bleaching efficiencies of activated clay was influenced by multiple parameters such as H_2SO_4 concentration, activation time and activation temperature. In this methodology, mathematical and statistical techniques are combined for designing experiments, building models, evaluating the effects of factors and searching optimum conditions of factors for desirable responses. The most common designs, such as Central Composite Design (CCD) and Box-Behnken Design (BBD), principal RSM have been widely used in various experiments. It has been successfully reported that RSM using Box-Behnken Design can be used to optimize the activation condition. In present study, bleaching efficiency of activated clay was considered as response value while H_2SO_4 concentration, activation time and activation temperature were considered for optimization parameters. Box-Behnken design was employed to optimize the process parameters from the bleaching efficiencies of activated clay on sesame oil. The experiments were done in triplicate. The results are given as standard deviation (SD). One-way Analysis of Variance (ANOVA) was used for comparison of more than two means. A difference was considered statistically significant when $p < 0.05$. (Barberousse H., & Blecker, C.,et al.,2009).

Sesame oil is an edible vegetable oil that is derived from sesame seeds that are small, yellowish-brown seeds. Sesame oil has a distinct nutty, flavourful taste and may be considered a healthier alternative to other vegetable oil because of its anti-inflammatory properties. Sesame oil is high in nutrients such as magnesium, zinc, copper, calcium and manganese. All of these nutrients improve bone health and density.

Bleaching of fat and oil is a process whereby the clay adsorbent is mixed intimately with the oil under specified conditions to remove unwanted color bodies and other contaminants. Bleaching earth is the most important agent for decolorizing of degummed and alkali refined oils by adsorption (http://www.en.wikipedia.org/wiki/Bentonite). Efficiency of bleaching earth depends on selecting the right grade and proper blends of basic raw material bentonite, obtained from various mine (http://www.ieport.com). In this study, emphasis was placed on using bentonite clay as an adsorbent in removing undesirable matter from edible sesame oil. The objectives of this research would comprise to produce acid activated clay (bleaching clay) as an adsorbent for bleaching of sesame oil, to investigate the effects of acid concentration, contact time and temperature during acid activation, to study the utilization of activated clay.

Materials and Methods

Collection and Preparation of Sample

Bentonite clay sample was collected from Mogyotwin area, Tada-U Township, Mandalay Division and seasame oil was obtained from Gwegone Village, Tada-U Township, Mandalay Division.

Bentonite clay lump samples were dried under the sun drying at the temperature of 36°-40°C for about two days. The dried samples were then ground into fine powder by using grinder. Then it was sieved with vibrating sieve shaker of 200 mesh screen to obtain powder form.

Activation of Bentonite Clay by Sulphuric Acid

In this activation process, different concentration of H_2SO_4, activation time and activation temperature were tested. 50g of prepared bentonite clay (-200 mesh) and 200 ml of sulphuric acid solution were added in round bottomed flask. Acid treatment was carried out at 100 ˚C and 1M H_2SO_4 with different activation time (3, 4, 5 hr) at 450 rpm under reflux by mechanical stirring. Activation was repeated as describe above but at varying activation temperature, (90, 100, 110˚C) and at different acid concentration (1, 1.5, 2M). After activation, the clay was washed several times with deionized water followed by decanting until the discard water became neutral. Then, the clay was filtered off by a Buchner funnel. After that the clay was dried in an oven at 60˚C. After drying, the clay was ground and sifted by 200 mesh sieve.

Bleaching of Sesame Oil by Activated Bentonite Clay

50 ml of sesame oil was poured in 500 ml beaker and heated to 90˚C. Then, 5% (W/V) activated clay was added to the heated oil. The mixture of oil and clay was stirred mechanically for 30 minutes at constant rate of 300 rpm.

After 30 minutes, the mixture was filtered using a Buchner funnel. Most of the coloring matter was left in the filter cake. The activity of activated clay was known from the color changes of before and after bleaching. The color of resultant clear oil was measured in Lovinbond Tintometer PFXi-195/2 model which can output CIE LAB L*a*b* colour system, and total colour changes ΔE were calculated as follows:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

Where, ΔE = Total colour difference

ΔL^*,Δa^*,Δb^* = colour difference between final and initial point

The color changes of sesame oil before and after bleaching was shown in Figure (1).The bleaching efficiencies of activated clay on sesame oil was calculated according to the following equation and the results were shown in Table (2).

$$\textbf{Bleaching Efficiency}(\%) = \frac{\textbf{Colour Difference before Bleaching} - \textbf{Colour Difference after Bleaching}}{\textbf{Colour Difference before Bleaching}} \times \mathbf{100}$$

Experimental Design

The activation procedure of the experiment in a Box-Behnken Design was set as follows. Three factors including H_2SO_4 concentration (x_1), activation time (x_2) and activation temperature (x_3) were chosen. The bleaching efficiencies of activated clay (y) were determined using optimization method (Table 1). Each experiment was carried out in triplicate.

Table(1). Coded and Actual Levels of Three Variables

Variables	Factors	Coded levels of variables		
		-1	0	1
Concentration of H_2SO_4(M)	x_1	1	1.5	2
Activation Time (hr)	x_2	3	4	5
Activation Temperature (˚C)	x_3	90	100	110

A Box-Behnken experimental design was used to optimize three independent variables, (x_1), (x_2) and (x_3). Three levels of each variable were coded as -1, 0 and 1 as shown in Table (1). The experimental design consists of 12 factorial experiments and three replicates of the central point given in Table (2). Bleaching efficiency of activated clay on sesame oil was selected as the responses for the combination of the independent variables using Lovinbond Tintometer of CIE LAB L*a*b* colour system. Experiment runs were randomized, to minimize the effects of unexpected variability in the observed responses.

A second-order polynomial regression model was used to express the yield as a function of independent variable as follows.

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i{}^2 + \sum_{i=1}^{2} \sum_{j=1+1}^{3} \beta_{ij} X_i X_j + \varepsilon$$

When y represents the response variables antioxidant activities, β_0 is the model constant, βi, βii, βij are the linear, quadratic and interactive coefficients, respectively, x_1, x_2, x_3 were levels of the independent variables and ε is the error.

Analysis of the Box-Behnken design data was carried out by using Minitab software (Version 14). Additional confirmation experiments were subsequently conducted to verify the validity of the statistical experimental design.

Results and Discussion

In this research work, the activation of bentonite clay was done by using sulphuric acid. The activated conditions for bleaching efficiencies of activated clay on sesame oil were optimized through RSM approach (Box-Behnken Design). The coded and actual levels of the three variables in Table (1) were chosen to optimize the bleaching efficiencies. Each experiment was carried out in triplicate. From the results of a single factor, the maximum bleaching efficiencies of each factor was defined as the center of domain (x_0). The actual level of -1, 0 and 1 were calculated as described in experimental part. Table (2) also represents the treatments with coded levels of variables and experimental results of bleaching efficiencies of activated clay in sesame oil. The treatments with coded levels ranged from 25.79 ±0.162 %to 64.22±0.083 %. The highest value (64.23±0.083) % was obtained under experiment condition of 1.5M H_2SO_4 concentration, 4hr activation time and 100 ˚C activation temperature.

By applying multiple regression analysis on the experimental data, the response variable (bleaching efficiency) and the test variables are related by the following polynomial equation (in terms of coded factors).

y=64.22-1.905Concentration+0.6237Time-1.0312Temperature+6.9625Concentration*Time +2.595Time*Temperature-7.417Concentration*Temperature-2.950Time*Time-9.427 Concentration*Concentration -20.635 Temperature* Temperature

The analysis of variance (ANOVA) for the regression equation by Minitab 14 Software is presented in Table (3). The quality of fit to the second-order polynomial models was confirmed based on the coefficient of determination, R^2=96.0% (0.96). The result indicated that models can significantly ($p < 0.05$) express more than 80 % (> 0.80) of the response variation. The lack of fit ($p < 0.05$) was significant, suggesting that the model was suitable to represent the actual situation, reflecting the relationship between the bleaching efficiencies and activation parameters. In addition, the obtained regression equation can predict well the activation condition for high bleaching efficiencies. The terms of square (p = 0.001), interaction (p= 0.026) and regression model (p=0.005) indicating that the relationship between response and the test variable were significant as shown in Table (3).

Three-dimensional response surface plots and two-dimensional contour plots are presented in Figure 2 (A-C). These types of plots reflect the effects of two factors on the response at a constant agitation (450 rpm).

In Figure 2 (A), at the beginning of activation time, bleaching efficiency of activated clay increase as decrease acid concentration but after 4hr the efficiency increase with acid concentration. According to Figure 2 (B), the highest bleaching efficiency of activated clay is observed at mid-level of H_2SO_4 concentration and activation temperature, further increase of acid concentration with temperature significantly decreases the efficiency. In Figure 2(C), the optimum condition is observed at middle level of activation temperature and activation time. By applying the increased temperature with longer time, the bleaching efficiency will also decrease. The effect of temperature and H_2SO_4 concentration has a more significant effect on the bleaching efficiency than activation time.

Natural bentonite clays have little natural bleaching power. By treatment with mineral acid, adsorbed alkali metals are removed, aluminium and ferric salts are washed out, silica to alumina ratio are increased to about 5:1 to more than 9:1 and swelling is almost completely eliminated(http://www.aquatechnologies.com/info-activated-clay.htm). The removal of the more soluble constituents has increased the specific surface of the clay by the formation of pores. In the activation of clay with acid, the clay is reduced to a fine state of division. Reducing the particle size also increase the reactivity of solids. Grinding of the treated clay is a much easier process than untreated clay. The highest bleaching efficiency in present study (64.22±0.083%) is found in agreement with commercial bleaching earth (china) (66.92%) (Than Than Kyi (2010), "Study on Bentonite Clays from Different Localities in upper Myanmar", Ph.D (Dissertation)).

Figure.1. Sesame Oil Before and After Bleaching with Prepared Activated Clay

Table (2) Experimental Designs Using Box-Behnken Design and Results

Run Order	Natural Variables			Coded Variables			Bleaching Efficiencies of Activated Clay on Sesame Oil (%)
	Concentration of H_2SO_4 (M)	Activation Time (hr)	Activation Temperature (˚C)	x_1	x_2	x_3	
1.	1.5	3	110	0	-1	1	33.31±0.098
2.	1	4	110	-1	0	1	45.38±2.577
3.	2	4	110	1	0	1	27.69±0.137
4.	1.5	3	90	0	-1	-1	47.38±0.235
5.	1.5	4	100	0	0	0	64.22±0.083
6.	1	4	90	-1	0	-1	25.79±0.162
7.	1.5	4	100	0	0	0	64.22±0.083
8.	1.5	5	90	0	1	-1	42.77±0.286
9.	2	3	100	1	-1	0	41.54±0.267
10.	1	3	100	-1	-1	0	60.23±0.22
11.	1.5	5	110	0	1	1	39.08±6.718
12.	1	5	100	-1	1	0	48.22±0.158
13.	2	5	100	1	1	0	57.38±0.049
14.	2	4	90	1	0	-1	37.77±0.1092
15.	1.5	4	100	0	0	0	64.22±0.083

Table (3) Analysis of Variance (ANOVA) for the Regression Equation

SD	SS	DF	MS	F value	P value	S
Model	2284.49	9	253.832	13.27	0.005	*
Linear	40.65	3	13.551	0.71	0.587	-
Square	1802.91	3	600.971	31.41	0.001	*
Interaction	440.92	3	146.973	7.68	0.026	*
Residual Error	95.67	5	19.134	-	-	-
Lack-of-Fit	95.67	3	31.891	*	*	-
Pure Error	0.00	2	0.000	-	-	-
Total	2380.16	14	-	-	-	-

Note: SD= source of deviation, SS= sum of square, DF= degree of freedom, MS= mean square, S= significant, p* = 0.05

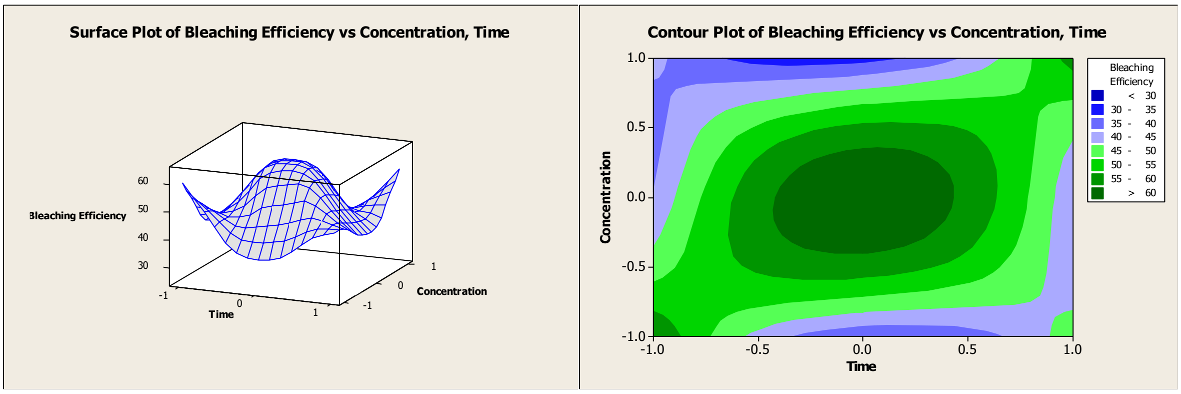


Figure (2-A) Three-dimensional Response Surface Plot and Two-dimensional Contour Plot of Bleaching Efficiency of Activated Clay, Response Surface Plot of H_2SO_4 Concentration (x_1) Vs Activation Time (x_2)

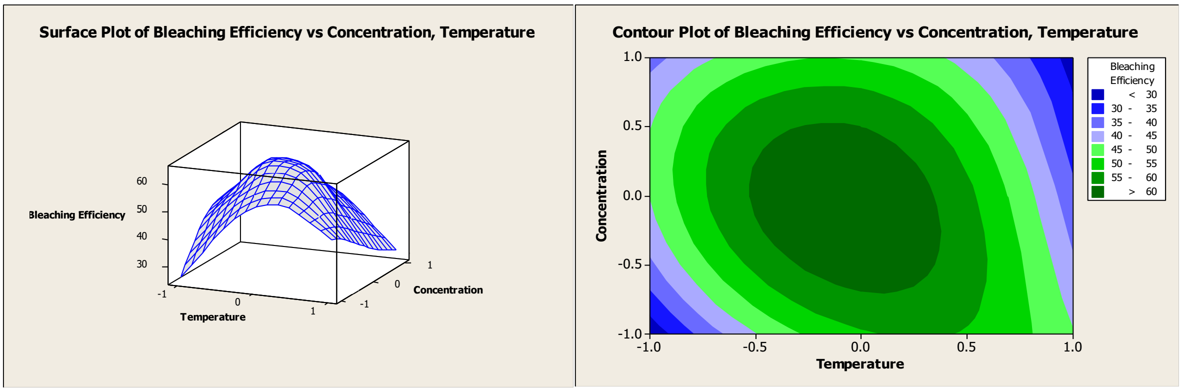
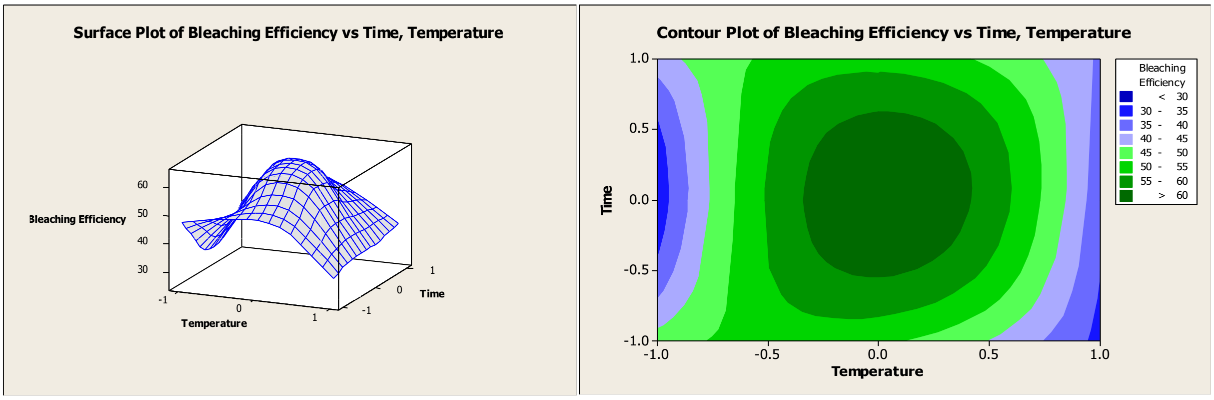


Figure (2-B) Three-dimensional Response Surface Plot and Two-dimensional Contour Plot of Bleaching Efficiency of Activated Clay, Response Surface Plot of H_2SO_4 Concentration (x_1) Vs Activation Temperature (x_3)



Figure(2-C) Three-dimensional Response Surface Plot and Two-dimensional Contour Plot of Bleaching Efficiency of Activated Clay, Response Surface Plot of Activation Time (x_2) Vs Activation Temperature (x_3)

Conclusion

The Response Surface Methodology (RSM) was used to optimize the activation condition for bleaching efficiency of activated clay on sesame oil using Box-Benken Design. According to the ANOVA analysis, the optimal condition was 1.5 M H_2SO_4 concentration, 4hr activation time and 100 ˚C activation temperature. Moreover, p-value is less than the significant level. Therefore, it can be concluded that there is a statistically significant association between response variables and the terms. Conventional acid activation in this study has produced the activated clay having high bleaching efficiency. Despite being natural resources in Myanmar would produce in the refining of edible oil processing, the enormous availability of acid activated clay could be beneficial for the production of value added products in line with green technology.

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