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Erratum: Application of Response Surface Methodology for Optimizing Oil Extraction Yield From Tropical Almond Seed

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The numberof Authors in this paper is wrongly typesetted as three, instead of two, in pages 330 – 336 in the vol. 30 issue of the Journal of NAMP. The entire pages of the article is therefore reproduced as it ought to appear.

Abstract

This study investigated the optimum processing conditions which give the maximum yield of oil extracted from tropical almond seed by the use of response surface methodology (RSM). The factors investigated were solvent concentration (50 – 100% v/v), extraction temperature (84 -100^{o}C) and processing time (60 – 120 min). Central composite design (CCD) was explored to get the optimum conditions for the extraction of the almond seed oil via soxhlet extraction. Solvent concentration, extraction time and one factor interaction term of the concentration exhibited significant effects on the yield of almond seed oil with coefficient of determination (R^2) of 0.9504. The model adequacy was further checked using the adjusted R^2 which gave a value of 0.9058. Optimum conditions for extraction, ascertained by RSM were 89% solvent concentration, 90^{o}C extraction temperature and 107 min extraction time. The calculated predicted results were close to the experimental results which further validate the developed mathematical model.

1.0 Introduction

The tropical almond (*Terminalia catappa* L.**)** tree is a popular tree in Nigeria. This tree grows to a height of about 30 to 55 feet. It is a deciduous tree and it forms a symmetrical upright shape with horizontal branches often reaching to about 35 feet in width. The almond tree produces the sea almond fruit locally called "ebelebo" in the southern part of Nigeria. In some part of the country it is also called 'fruit". This fruit is ellipsoid in shape and have a bluntly pointed apex. The ripened fruit which is often yellowish in colour contains a hard shell that covers the edible seed. The mesocarp is edible and often eaten by children as snacks while often neglecting the edible seeds [1]. This fruit has been found to be nutritional [2]. The almond seed is reported to contain about 41.4 – 51.4% oil of which about 66.7 – 69.7 % were poly-monounsaturated (oleic) as reported by Moayedi *et al.* [3]. The only polyunsaturated fatty acid was linoleic acid which range from about 18.2% to 23% for different varieties of almond seed oil.

Extraction of oil from almond seed has been successfully carried out with hexane as extracting solvent by several researchers [3 – 5]. The work carried out by Ogunsuyi and Daramola [4] using hexane as extracting solvent gave an extraction yield of 47%. Although, the use of hexane as an extracting solvent gives a better extraction yield compared to when aqueous solvents are used, hexane on the other hand can be emitted during the extraction process and recovery of the oil or solvent. Emission of this solvent has been identified as an air pollutant as it reacts with other pollutants to produce ozone. As a result of this, alternative solvents to hexane are being considered as an extracting solvent. Organic solvents such as methanol and ethanol have been identified as a possible replacement to hexane. Ethanol is one of the most promising solvent to use as an extracting solvent. Apart from the fact that it is obtained from non-petroleum matter, it can be produced from a variety of biological materials using simple technology [6, 7]. The use of ethanol as solvent will eliminate toxicity problems. The quality of the oil in terms of low acid value has also been observed by Liauw *et al*. [8] when ethanol is used for extraction.

The aim of this work therefore is to optimize the extraction of oil from almond seed using aqueous ethanol as an extraction solvent. In carrying out the optimization, response surface methodology (RSM) was applied. Response surface methodology (RSM) is an effective statistical technique that has been applied by several authors for optimization of a process when the independent variables have a combined effect on the desired response [9 – 13].

RSM is often used in processes when a particular response variable depends on several other variables. Several multiple independent variables affect the response factor (extraction yield) during extraction. The amount of oil extracted from a

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sample has been found to depend on the solvent concentration, temperature of extraction, particle size of sample and extraction time. RSM has the added advantage that it can be used in testing multiple process factors and also their interactive effects on the response. It also developed a mathematical model that can adequately describe the overall process [12].

In this present work, RSM using a central composite design (CCD) was employed which was aim at developing a mathematical model to optimize and study the effect of aqueous solvent concentration, extraction temperature and time on the yield of oil from tropical almond seed. The CCD is an experimental design which is not only effective and efficient but it is also an economical, since the number of experiments that are required for optimization is reduced.

2.0 Materials and Methods

2.1 Materials

Dried almond fruits were collected from the vicinities of the Faculty of Engineering and the Faculty of Social and Management Sciences of the University of Benin, Benin City, Nigeria. Analytical grade ethanol (99.5%) was purchased from Winteck Nigeria Limited, while distilled water was obtained from Department of Chemistry, University of Benin, Nigeria.

2.2 Extraction of Almond Seed Oil

The seeds of the almond fruits were removed from their shells after cracking with a small wooden pestle and a mortal. The skins and other impurities were removed from the seeds after which they were washed with water and sun dried. The dried clean seeds were ground in a locally fabricated grinding machine. The ground seeds were fractionated and the particles that passed through the 50-mesh size were retained for use in the extraction process.

For the extraction process, a known mass of the ground almond seeds were put in a thimble which was then placed in the soxhlet apparatus. Extraction was thereafter carried out using solvent concentration at different volume percentage concentration as solvent while varying also the extraction temperatures and the time for extraction. After the extraction process, the ethanol was removed from the extracts using a rotary evaporator (Heidolph, Laborota 4001, Viertrieb, Germany) which was connected to a vacuum pump (Heidolph, Rotavac, Viertrieb, Germany).

2.3 Experimental Procedure and Design

A known mass of the ground almond seed was placed in the soxhlet apparatus and extraction was carried out using the various concentrations of ethanol. The values obtained for the various independent variables were used for each runs of the extraction. In this study, response surface methodology (RSM) was used to estimate the effect of the independent variables (solvent concentration, X_1; extraction temperature ^{o}C X_2, and Time min. X_3) on the response (extraction yield (%)). The yield obtained from the extraction process was calculated as

$$\text{Yield of oil (Y)} = \frac{\text{mass of extracted oil}}{\text{mass of ground almond seed}} \times 100 \qquad (1)$$

The actual levels of the independent variables are listed in Table 1. The experimental design for the extraction was carried out using a central composite design (CCD). A 2^3 full-factorial CCD for three independent variables was employed which gave a total number of 20 experiments (2^n + 2n + 6) where n represents the number of independent variables. The experiments consists of eight factorial points, six axial points at a distance $\pm$ 1.682 from the centre and six replicates at the centre point to evaluate the pure error.

Table 1: Independent variables and their levels for the central composite design

Variable	Symbol	Range and their levels					
		-1.682	$-1.$	$0 + 1$	$+1.682$		
Solvent concentration (v/v%)	X_1		50	60	7590	100	
Extraction temperature (^{o}C)	X_2		80	84	90	96	100
Time (min)	X_3		60	72	90	108	120

2.4 Statistical Analysis

The experimental data obtained from the use of the CCD were analyzed by RSM using the second order to describe the relationship between the predicted response variable (Extraction yield) and the independent variables of the process. The regression coefficient of the second order multiple regression model were determined using the data obtained from the central composite design employed for the optimization of the extraction variables as shown in Eq. (2).

$$Y_{\text{yield}} = b_o + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} {X_i}^2 + \sum_{i} \sum_{<j=2}^{n} b_{ij} X_i X_j + e \qquad (2)$$

Where Y_{yield} is the predicted response (extraction yield), b_o, b_i, b_{ii}, b_{ij} are intercept, linear, quadratic and interaction constant coefficient respectively; n is the number of independent variables studied and optimized in the experimental work. X_i, X_j are the actual independent variables, while e is the error term. The RSM was applied to the experimental data using a commercial statistical package, Design-Expert version 6.0.8 (Statease Inc., Minneapolis). The experiments were carried out in random in order to minimize the effects of explained variability in the observed responses due to extraneous factors. Coefficient of determination (R^2) and analysis of variance (ANOVA) were used to evaluate the quality of the model. The mathematical model was considered when the satisfactory when the ANOVA data showed a high level of statistical significance. Response surfaces were developed using the fitted quadratic polynomial equation obtained from regression analysis by holding one of the independent variable constant and changing the other two variables.

3.0 Results and Discussion

3.1 Optimization of Extraction Parameters by Response Surface Methodology

3.1.1 Model Fitting and ANOVAL

The relationship between the response (oil yield) and the three independent extraction variables (solvent concentration, temperature and time) was evaluated by using response surface methodology (RSM). Twenty experiments with different experimental parameters, ranges and levels of independent variables were performed in duplicates and the mean values were reported as experimental yield value as shown in Table 2. The response obtained in Table 2 with the three independent variables was correlated with the three independent variables using the second order polynomial equation (Eq. (2)).

The following equation (Eq. (3)) in terms of the actual factor was generated to predict the oil yield from almond seed.

$$Y_{\text{yield}} = -205.993 + 1.315X_1 + 3.132X_2 + 0.397X_3$$
$$-6.410 \times 10^{-3}{X_1}^2 - 0.014{X_2}^2 - 9.327 \times 10^{-4}{X_3}^2$$
$$-3.588 \times 10^{-3}X_1X_2 + 1.560 \times 10^{-3}X_1X_3 - 3.300 \times 10^{-3}X_2X_3 \quad (3)$$

Where X_1, X_2 and X_3 are the solvent concentration (v/v%), extraction temperature (^{O}C) and time (min) respectively. In order to evaluate the analysis of variance (ANOVA) and to check the adequacy of the model obtained, statistical analysis was performed. The results for the ANOVA for the second order response surface model are shown in Table 3. The model F-value of 21.3 with the very low probability value (< 0.0001) is an indication of the significance of the fitted model. Each term in the model was also checked for its significance.

Table 2: Experimental design for the extraction of almond seed oil

Standard	Solvent concentration v/v %	Temperature ^{o}C	Time min	Yield (%) Experimental	Predicted
1	60	84	72	8.02	7.70
2	90	84	72	12.67	12.63
3	60	95	72	10.25	9.92
4	90	95	72	14.57	13.57
5	60	84	108	8.56	9.31
6	90	84	108	15.83	15.92
7	60	96	108	10.34	10.14
8	90	96	108	15.38	15.46
9	50	90	90	5.73	5.67
10	1	90	90	13.89	14.29
11	75	80	90	12.34	11.94
12	75	100	90	12.67	13.42
13	75	90	60	10.87	11.75
14	75	90	120	15.23	14.69
15	75	90	90	12.45	14.06
16	75	90	90	14.38	14.06
17	75	90	90	14.52	14.06
18	75	90	90	14.67	14.06
19	75	90	90	14.42	14.06
20	75	90	90	13.98	14.06

Table 3: Analysis of variance (ANOVA) for response surface quadratic model

Source	Sum of squares	Degree of freedom	Mean squares	F value	Prob. value
Model significant	137.93	9	15.33	21.3	<0.0001
A	89.72	1	89.72	124.71	<0.0001
B	2.65	1	2.65	3.68	0.0839
C	10.43	1	10.4314.49	0.0034	
A^2	29.98	1	29.98	41.67	<0.0001
B^2	3.45	1	3.454.80	0.0533	
C^2	1.27	1	1.27	1.76	0.2136
AB	0.82	1	0.82	1.14	0.3110
AC	1.39	1	1.39	1.94	0.1940
BC	0.98	1	0.98	1.36	0.2702
Residual	7.19		10		0.72
Lack of Fit not significant	3.78	5	0.76	1.11	0.4568
Pure Error	3.41	5	0.68		
Cor Total	145.12	19			
CV = 6.76%	R^2 = 0.9504	Adj R^2 = 0.9058		Pred R^2 = 0.7635	

Value of Prob > 0.05 is an indication that the model term is significant. From the ANOVA results the model term wish are quite significant are the solvent concentration (X_1), time (X_3) and solvent concentration factor interaction term (${X_1}^2$). While for Prob > 0.10 is an indication of the insignificance of the model. The adequacy of the model was further checked. There was an insignificant lack of fit. According to Montgomery [14], the lack of fit is an indication of the failure for the model representing the experimental data at which points not included in the regression or variations in the models cannot be accounted for by random errors. It therefore implies that if there is a significant lack of fit, the model should be discarded. From the model results (Table 3) the "lack of fit F-value" of 1.11 implies that it is not significant relative to pure error. There is a 45.68% chance that "lack of fit F-value" this large could occur due to noise. The coefficient of variation (CV) obtained from ANOVA was 6.76%. A CV of more than 10% is an indication that the variation in the mean value is high and does not satisfactory develop an adequate response model [15]. Generally, the CV should not be greater than 10% [15].

The suitability of the model was also tested using the coefficient of determination (R^2). The coefficient of determination (R^2) is the proportion of variation in the response that is attributed to the model. For a good fitted model, R^2 should not be less than 80%. R^2 values that are close to unity signify the suitability of the fitting empirical model to the actual value. From the analyses, the R^2 value was 0.95. A large value of R^2 does not always imply the adequacy of the model. Thus, the adjusted R^2 of over 90% is more appropriate to evaluate the model adequacy [9]. The adjusted R^2 value was 90.58% which further validates the model adequacy.Figure 1 shows the plot of the response predicted from the empirical model and the actual values obtained from experiment. Most of the data points on this plot lie close to the straight line with some points above and below the line.

The data was also analyzed to check the normality of the residuals. The normal probability curve in Figure 2 shows the normal distribution of the residuals. The residuals give the difference between the observed value of a response measurement and the value that is fitted under the theorized model [11].

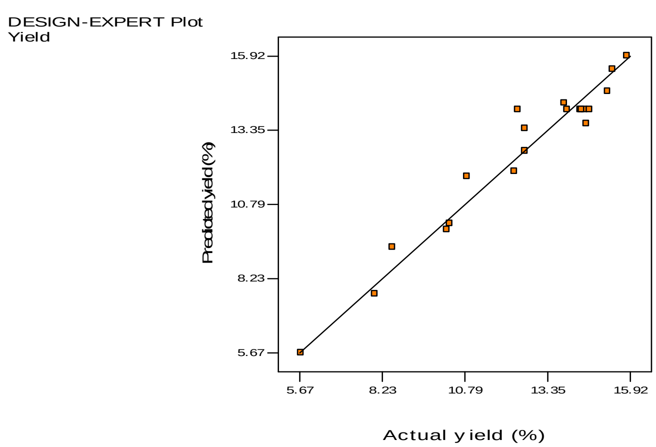

Figure1: Comparison between predicted and experimental values of yield

A closer examination of this plot shows that most of the data points on this plot are close to the line, having some points scattered. This was expected with normal data. From the observed distribution, it could thus be concluded that the data was normally distributed

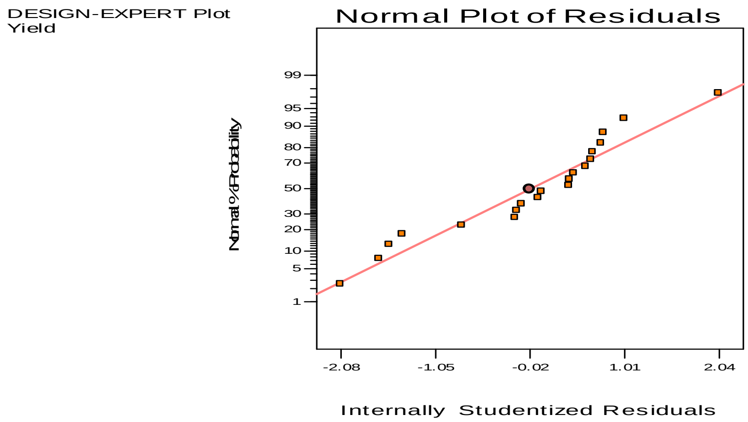

Figure2: Normal probability plots of studentized residuals

3.1.2 Influence of Parameters on Extraction Yield

Figures 3 – 5 shows the relationship between the independent variable (yield) and the independent variables (solvent concentration, temperature and time) which are represented in a three-dimensional (3-D) plot of the response surface and counter plots that are generated by the model. The data were generated by keeping one of the independent variable at a constant (central) level and varying the other two within their experimental range.
The variation in the yield of oil obtained with extraction temperature and solvent concentration at constant time (90 min) is shown in both the 3-D and the counter plots as seen in Figure 3.
From the 3-D plot, the yield increases exponentially with temperature and solvent concentration. Comparing the two variables, the effect of temperature on the yield of oil is minute when compared to the solvent effect on the oil yield.

From the counter plot in Figure 3, it can be seen that when extraction time is extending beyond 90 min at constant solvent concentration, there is no much effect on the oil extraction from almond seed.
The effect of varying solvent concentration and the time for extraction on the yield of oil at constant temperature of 90^{o}C can be seen in both the 3-D surface and counter plots of Figure 4. From the 3-D plot, the extraction yield increases as both the solvent concentration and the time for extraction is increased. It was also observed that when the time is fixed at 72 min and increasing the solvent concentration from 60 – 90%, the extraction yield increases from 9.33 to 13.61%. On the other hand, increasing extraction time from 72 – 108 min at a fixed solvent concentration at 60%, the extraction increases from 9.33% to 10.2%

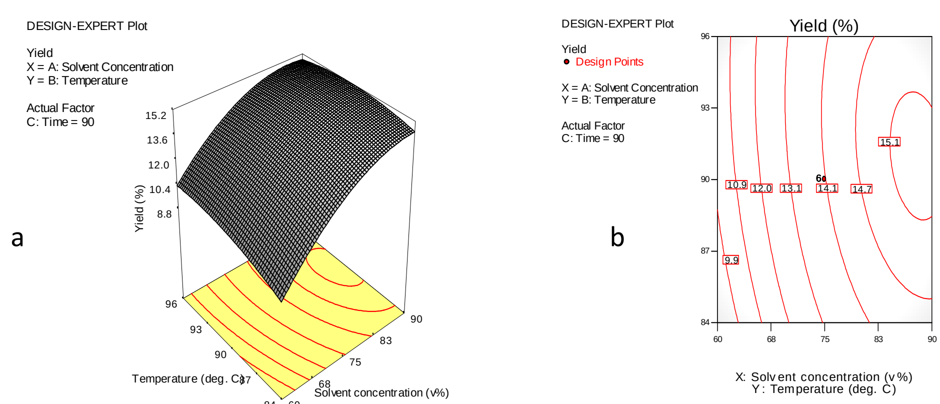

Figure 3: (a) Response surface plot (3D) and (b) counter plot showing the effect of solvent concentration and extraction temperature on the extraction yield at constant time of 90 min.

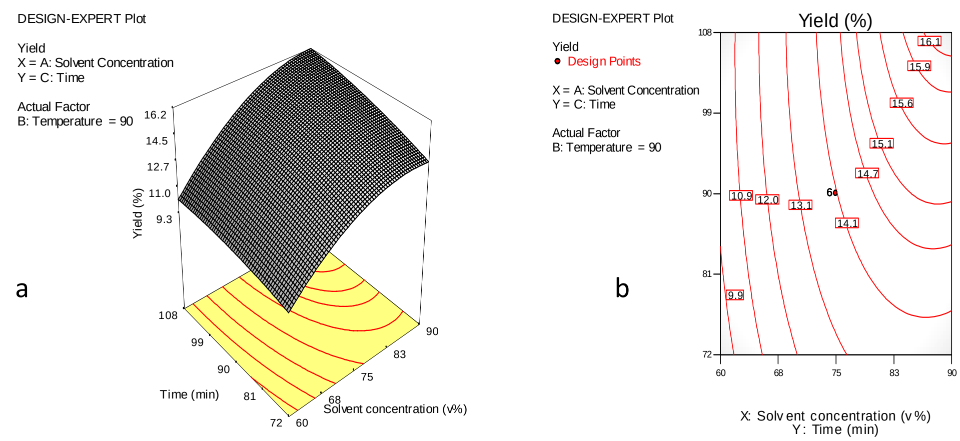

Figure 4: (a) Response surface plot (3D) and (b) counter plot showing the effect of solvent concentration and time on the extraction yield at constant temperature of 90°C

The variation of extraction yield with extraction temperature and extraction time at a fixed solvent concentration of 75% is shown in Figure. 5. It was observed that as the extraction time is kept constant 72 min and also increasing the extraction temperature from 84 – 96°C, there was an increase in extraction yield from 11.60 – 13.20%. When the temperature is kept constant at 84°C and increasing extraction time from 72 – 108 min, extraction yield increases from 11.60 – 14.0%. Thus, extraction time has more effect in increasing extraction yield compared to extraction temperature.

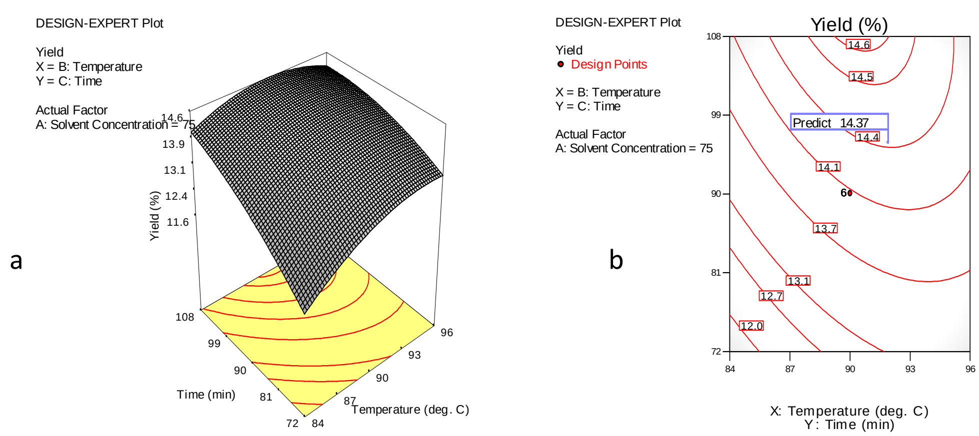

Figure 5: (a) Response surface plot (3D) and (b) counter plot showing the effect of extraction time and extraction temperature on the extraction yield at solvent concentration of 75%

3.1.3 Selection of Optimum Process Condition

The optimal values for the independent variables were obtained by solving the second order polynomial equation (Eq. (3)) using the software Design Expert 6.0.8. The optimum condition is tabulated in Table 4. The solution to the polynomial equation gave an extraction yield of 16.2%

Table 4: Predicted optimum values of the responses at optimum conditions

Factor	Low	High	Optimum
Solvent concentration (v/v%)	60	90	89
Temperature (°C)	84	96	90
Time (min)	72	108	107

3.1.4 Model verification

In order to verify the suitability of the model equation for predicting the optimum response value, extraction experiments were carried under these optima conditions and the results were compared with the predicted values obtained using the model equation. These experiments were conducted in triplicates and the mean value of the extraction yield was calculated to be 16.54%

4.0 Conclusion

The extraction of almond seed oil using soxhlet apparatus was optimized in this study. The three independent variables involved in the optimization were solvent concentration (v/v%), extraction temperature (^oC) and time (min). The effect of solvent concentration and time were found to be the most significant, whereas the extraction temperature above 90^oC has negligible effect on the extraction yield. The optimum conditions for oil extraction from the almond seed are solvent concentration (89%), extraction temperature (90^oC) and extraction time (107^oC). Under these conditions, the experimental yield obtained was found to be 16.54%, an error of 2.099% from the predicted value of 16.2%.

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