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Comparative study of Response Surface Methodology (RSM) and Artificial Neural Network (ANN) on Oil Extraction from *Citrus sinensis* Oilseed and Its Quality Characterization

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Abstract In this work, optimization of oil extraction from the *Citrussinensis* (*C. sinensis*) oilseed was carried out. The physiochemical properties of the seed oil were determined for its aptness for industrial application. This was with a view to add value to *C. sinensis* oil and finding environmentally friendly alternative to conventional oil.

C. sinensis oilseed was obtained from the fruit garden market in Port Harcourt, River State. Nigeria. The seeds were washed to remove dirt, after which the seeds were sun dried until a constant weight was obtained. The dried seeds were de-husked, winnowed, and further sun dried for two days before milling. The oil was extracted using solvent extraction method (n-hexane). For the optimization of the oil extraction, a three-level-three-factors response surface methodology (RSM) and artificial neural network (ANN) were employed. Seventeen (17) experimental runs were generated and were carried out. Independent factor considered were powder weight, solvent volume and extraction time. The physiochemical and other parameters (cetane number, API, aniline point among others) properties were determined using standard methods.

Results showed the that experimental *C. sinensis* oil yield (CSOY) of 52.64 (% w/w) was obtained, but RSM predicted CSOY of 50.240 (% w/w), validated as 49.98 (% w/w) at powder weight of 40 g, solvent volume of 180 ml and extraction time of 40 min. ANN predicted CSOY of 51.720 (% w/w), validated as 50.85 (% w/w) at powder weight of 43 g, solvent volume of 202 ml and extraction time of 41 min. Physicochemical analysis of *CSOY* showed the oil to be golden yellowish in colour with specific gravity of 0.9200. The moisture content of 0.0134%, refractive index of 1.5019, FFA of 2.23 which corresponds to acid value of 4.46 mg KOH/g, the saponification value of the oil was 77.14 mg KOH/g while peroxide value of 17.00 was obtained. The iodine value of 78.1 g I_2 /100 g with cetane number of 99.48 was obtained for the oil. Higher heating value of the oil was 45.10 MJ/kg. The API gravity of 22.3 and high aniline point of 557.31 of the oil shows that *C. sinensis* oil is of a better diesel oil. Gas chromatography analysis to determine the free fatty acid of the oil showed the oil to be unsaturated (60.13%).

Hence, the study concluded that *C. sinensis* oils could serve as feedstock for animals and as lubricant for Industrial purposes.

Keywords *C. sinensis* oil, optimization, response surface methodology, artificial neural network, physicochemical properties, free fatty acid.

Introduction

With the recent increase in the consumption of seedoil and the development of biofuel Industries, there is need for utilization of biomass wastes (wood crops, seaweed, animal waste, skin, pulp, seeds etc.) that occurs in most

agricultural processes [1]. It is almost a known fact that the worldwide seed oil production will face an increasing demand in the next thirty years and beyond [2]. However, oil has been extracted from different seeds, fruits and nuts in commercial quantity and they have been used in cooking, soap making, cosmetics, paints, nutritional supplements, detergents and also as an ingredient in other food [3]. Some of these oils extracted from seeds, nuts and fruits can be used to replace certain petroleum based lubricants and fuels, as a matter of fact, vegetable oil has been used in production of biodiesel and it has found a market niche because its use has reduced some noxious exhaust emissions [4]. Reports have shown that various research works have been carried out on extraction of oil from seeds and they include; extraction of vegetable oils ground seeds using percolation method [2], solvent extraction of oil from soursop oil seeds and its quality characterization [1], extraction of seed oil from date palm seeds [5], extraction of oils from rubber [6], extraction of oil from shea seeds of the shea tree leaves[7], extraction of oil from soybeans [8], extraction of oil from patchouli [9-10]Sorrel (*Hibiscus sabdariffa*) seed oil extraction optimization and quality characterization, an optimization approach to oil, extraction from *Chrysophyllum albidium* oil seeds and its quality characterization [11], to mention but a few. Furthermore, orange fruit is a potential source for production of essential oil.

The orange fruit just like the grape fruits and lime belongs to the *citrus specie* from the *Rutacae* family, it is one amongst other fruit crops that is consumed in commercial quantity as fresh fruit or as a juice and this is due to its high vitamin C content[12]. There are different varieties of orange fruits but they are generally classified as either sweet orange (*citrus sinensis*) or bitter orange (*citrus aurantium*). *Citrus fruits* are cholesterol and sodium free, they have high ascorbic and folic acid content, they also consist of potassium, calcium, thiamine, niacin, vitamin B6, magnesium and copper, and all of these constituents contributes to the nutritional value of the fruit [13].Research has also shown that the nutritional value of orange goes beyond the juice, the peelis known to be a good antioxidant that helps in preventing cardiovascular and other diseases [14]. The orange seed like other part of the fruit also has its nutritional benefits and the oil produced from the seed has a high degree of unsaturation, high level of acid with the presence of palmitic, stearic and oleic acid and also the presence of reasonable amount of free fatty acid was also observed [15].This oil can be obtained from the seed via extraction.

The key processing step in the recovery of oil from seeds, nuts and fruits is the extraction process [16].Mechanical pressing method of extraction is known as the simplest but not so efficient method because an extraction medium is not required [17].Ultrasonic extraction method is the method that uses ultrasonic wave also known as acoustic wave with the frequency between 20 kHz and 10 kHz, this wave form bubbles that produces force to penetrate into the cells of the plants and this affects the mass transfer [9]. Supercritical fluid extraction method (SFE) is the process of separating one component from another (the matrix) using supercritical fluids as the extracting solvent, Carbon dioxide (CO_2) is known to be the most used supercritical fluid, sometimes modified by co-solvents such as ethanol or methanol [18]. Aqueous enzymatic oil extraction involves grinding (wet or dry) of the oil-bearing sample, mixing of sample with an aqueous solution, incubating the sample with enzyme which helps to hydrolyze the structural components and help in releasing of oil, separating the sample into liquid and solid phases by centrifugation or filtration and recovery of oil from liquid phase[19]. Soxhlet Extraction which is also known as solvent extraction is one of the oldest and traditional means of extraction of oil from seeds but it is said to be hazardous due to the use of organic solvent used for extraction [20]. The edible oil industries are constantly in search for an alternative replacement of hazardous organic solvents that can be used for extraction [21], this organic solvent must have no potential health risk and the technique must be suitable and environmentally friendly. In recent times, this solvent extraction step has been modified by adding a pre-pressing step which helps in improving the permeability of the solids for the liquid in order to increase its efficiency [22]. The solvent extraction method is therefore suitable for oil extraction for oilseeds with low oil content [23], oilseed with high oil content and oilseed with medium oil content [24]. Nevertheless, modeling and optimization of the oil extracted from the seeds can improve the yield and its characteristics qualities.

Meanwhile, different tools can be employed in modeling and optimization of experimental data for oil extraction. Such tools includesResponse Surface Methodology (RSM), Artificial Neural Network (ANN) design, Arena,

Matlab, Minitab Response Surface (MRS), to mention but a few. Integrated method on the other hand is the combination of two or more of the above mentioned experimental design software's. Although, different researchers have reported the use of one or more software's [25-32]. However, the use of integrated software's such as fussy logic, factorial design, particle swamp, statistical method, wavelet transform, wavelet coherence, expert system and genetic algorithms, in modeling and optimization has received little or no attention from the researchers. Its main advantage is the ability to compare statistically various results obtained from each of the above mentioned software and eliminate the disadvantages of using single ones. Hence, this work engaged the use of integrated software in modeling and optimization of oil extraction from *C. sinensis* seeds. To determine the qualities and potential of the extracted oil, physicochemical analysis of the oil was carried out.

Materials and Method

C. Sinensis seed preparation

The *C. Sinensis* seeds were gotten from Local market in Port Harcourt, Rivers State, Nigeria. The seeds were washed to remove dirt, after which the seeds were sun dried until a constant weight was obtained. The dried seeds were de-husked, winnowed, and further sun dried for two days before milling. The milled *C. sinensis* powder was stored in a clean container for further processes.

Oil extraction procedure

The method used by Okunola and Adepoju [33], was employed in this study but with little modification. Four-phased 500 ml Soxhlet extractor and n-hexane as the solvent were used for this study. The apparatus was initially charged with a known mass of *C. Sinensis* powder placed in a thimble. A round bottom flask filled with a known volume of n-hexane was connected, a condenser was fixed, the inlet and outlet water streams were connected and the taps turned on, retort stands were used to hold them in place. A temperature controlled four-faced heating mantle was used as a heating medium to carry out the extraction process. At the end of this experiment, the solvent was distilled and the percentage of *C. sinensis* oil yield (CSOY) was determined using Eqn. (1).

$$CSOY(\%\, w/w) = \frac{weight\ in\ gram\ of\ extracted\ C.sinensis\ \text{oil}}{weight\ in\ gram\ of C.sinensis\ powder\ sample} \qquad (1)$$

Modeling of experimental design for oil extraction from *C. sinensis* seed powder

A three-level-three factor Central Composite Design (CCD) from response surface methodology (RSM) was employed for the modeling of *C. sinensis* seed powder oilseed extraction. The CCD generated twenty (20) experimental runs, and was carried out. The selected independent variable factors considered were: extraction time (min): X_1; solvent volume (ml): X_2. powder weight (g): X_3, respectively. Table 1 shows the coded independent variables levels considered for this experiment. The percentage CSOY results were inserted in the software's and RSM and ANN statistically optimized the variable conditions. The integrated software's (RSM and ANN) produced predicted yields and the residual values. The modeling equation in terms of the variables considered (X_1, X_2, X_3), the response (Y_F) and the error (ε) value is expressed in Eqn. (2).

$$Y_F = \rho_0 + \sum_{i=1}^{k} \rho_i X_i + \sum_{i=1}^{k} \rho_{ii} X_i^2 + \sum_{i<j}^{k} \rho_{ij} X_i X_j + \varepsilon \qquad (2)$$

Table 1: Variables factors considered for *C. sirensis* oil extraction

Variable	Symbol	Coded factor levels		
		-1	**0**	**+1**
Extraction time (min)	X_1	40	50	60
Solvent volume (ml)	X_2	180	200	220
Powder weight (g)	X_3	40	45	50

Physicochemical properties of *C. sinensis* oil

Determination of moisture content [34]

5 g of the oil was weighed and poured into a moisture dish of 5 cm diameter and 2 cm depth covered with a tight-fitted-slip-over, and was placed inside an oven operating at a temperature of 125 ^{o}C, pressure of 95 mmHg, and the

readings were taken at 30 min intervals until a constant weight was achieved. The percentage moisture content was calculated based on Eqn. (3).

$$\%\ Moisture\ content = \frac{Initial\ weight\ of\ oil - final\ weight\ of\ oil}{Initial\ weight\ of\ oil} \quad (3)$$

Determination of Acid Value [34]

The acid value of the oil was determined by dissolving 5 g in a hot mixture of diethyl ether (95% v/v) and ethanol (1:1) in a 250 ml reactor, the hot solution was neutralized with 0.1 M KOH solution using two drops of phenolphthalein as indicator. The acid value of the oil was computed based on Eqn. (4)

$$Acid\ Value = \frac{VXNX\ 282}{W} X\ 100 \quad (4)$$

Where: V = volume of KOH used during titration, N = Normality of KOH, and W = Weight of oil.

Determination of FFA of oil

The FFA of oil was computed using Eqn. (5)

$$FFA = \frac{Acid\ value\ of\ oil}{2} \quad (5)$$

Determination of Iodine Value (Wij's Method)

0.26 g of the oil was dissolved in 10 ml cyclohexane and 20 ml of Wij's solution was added in a stopper flask, the stopper flask was allowed to stand in a dark cupboardfor 30 min at room temperature. Then, 20 ml of 10% KI solution was added to the mixture. The resulting mixture was titrated with 0.1 M $Na_2S_2O_3$ using starch as the indicator. The iodine value was then computed using Eqn. (6)

$$Iodine\ Value = \frac{(B - S) \times N\ \times 12.69}{weight\ of\ the\ oil} \quad (6)$$

Where: N = Concentration of $Na_2S_2O_3$ used; B = Volume of $Na_2S_2O_3$ used for blank

S = Volume of $Na_2S_2O_3$ used for determination

Determination of Specific Gravity

The specific gravity of the oil sample was measured using the specific gravity bottle. The bottle was washed and dried and filled with water, weighed on a weighing balanceand the measurement was recorded as W_w.The bottle was emptied and properly dried before it was filled with oil and also weighed on a weighing balance and the measurement was recorded as W_o. The specific gravity was computed based on Eqn. (7).

$$Specific\ gravity = \frac{W_o}{W_w} \quad (7)$$

Determination of peroxide value [34]

2 g of the oil was weighed into a 250 ml flask, 40 ml of the solvent mixture of trichloromethane and water-free-acetic-acid in ratio 1:2 was added. 2 g of KI powder was also added. The mixture was rapidly boiled in a water bath at a temperature of 70^{o}C for 1 min. The boiled mixture was added to the flask containing 40 ml of already prepared 5% KI and the resulting mixture was washed thrice with 50 ml of distilled water into the flask. The content of the flask was titrated with 0.004 M $Na_2S_2O_3$ solution using starch as the indicator. The peroxide value was computed based on Eqn. (8).

$$Peroxide\ value\ (meqO_2/kg\ oil) = \frac{V_{Na_2S_2O_3} X\ N_{Na_2S_2O_3}}{Weight\ of\ oil} \quad (8)$$

Determination of saponification value

25 ml of 0.1 M ethanolic KI was added to 2 g of the oil sample in a reactor flask. The mixture was constantly stirred and was boiled for 60 min in a water bath, a reflux condenser was placed on top of the flask containing the mixture in other to achieve a uniform temperature. Two drops of phenolphthalein served as an indicator was added to the warmed soap solution and it was titrated against 0.5 M HCl. The saponification value was computed based on Eqn. (9).

$$S.V\ \left(mg\frac{KOH}{g}oil\right) = 28.05X\frac{V_{HCl\ blank}\ -V_{0.5\ M\ HCl}}{Weight\ of\ oil\ in\ g}(9)$$

Determination of refractive index

A digital refractometer was used in determining the refractive index of the oil sample. Water at room temperature was circulated round the glass slide to keep the temperature uniform and also to normalize the refractometer. A syringe and needle was used to put few drops of oil into the glass slide of the refractometer and the reading was recorded. This was done twice and the average value of refractive index was taken as the refractive index of oil.

Determination of Cetane Number (ASTM D2015)

Cetane number of the oil was computed based on Eqn. (10)

$$\text{Cetane No} = 46.3 + \frac{5458}{saponification\ \ value} - 0.225\ Iodine\ Value \quad (10)$$

Determination of API (American Petroleum Institute) gravity

API gravity of the oil was computed based on Eqn. (11)

$$API\ gravity = \frac{141.5}{Specificgravity} - 131.5 \quad (11)$$

Determination of Diesel Index

Diesel index of the oil was computed based on Eqn. (12)

$$Diesel\ index = \frac{cetane\ number - 10}{0.72} \quad (12)$$

Determination of Aniline Point

Aniline point of the oil was computed based on Eqn. (13)

$$Aniline\ point = \frac{diesel\ index\ \times 100}{API} \quad (13)$$

Determination of Higher Heating Value (HHV) (ASTM D2015)

HHV of the oil was computed based on Eqn. (14)

$$HHV\left(\frac{MJ}{kg}\right) = 49.43[0.041(saponification\ value) + 0.015(iodine\ value)] \quad (14)$$

Determination of Barrel per metric ton (BPMT)

BPMT of the oil was computed based on Eqn. (15)

$$BPMT = \frac{1}{\left[\left[\frac{141.5}{(API + 131.5)}\right]X0.159\right]} \quad (15)$$

Analysis of the *C. sinensis*oil using GCMS

An aligent 1909IS-433HP-5MS system was used to carry out the gas chromatography mass spectroscopy analysis. The system was programmed as follows: Column Elite-1 fused silica capillary column (30 mm×250 µm×0.25 µm) composed of 5 % phenyl methyl silox, operating in Electron multipliers volts 1329.412 eV; 99.99 % of Helium was

used as the carrier gas at a constant flow of 1.5 mL/min and an injection volume of 1 µl was employed in a split ratio of 10:1; injector temperature of 150 ◦C, Ion-source temperature 250 ◦C. The oven temperature was programmed from 35 ◦C (it was isothermal for 5 minutes), with an increase of 4 ◦C/min, to 150 ◦C, for 2 min, then 20 ◦C/min to 250 ◦C. Mass spectra were taken at an average velocity of 44.297 cm/sec; a hold up time of 1.1287 min, pressure of 11.604 psi and frequency of 50 Hz. The total running time for the gas chromatography was 45 min.

Results and Discussion

Optimization of *C. sinensis* oil extraction by RSM and ANN

In a bid to optimize oil extraction from *C. sinensis* seed, a new trial version of Design Expert dx 10.0.3.1 and Neuralpower 21365 were employed. Central Composite Design (CCD) under Response surface Methodology (RSM) was chosen and 20 experimental runs was generated and were carried out. Table 2 show the experimental results of *C. sinensis* oil yield (CSOY), the predicted yield and the residual values by RSM and ANN. From the table,

Table 2: Experimental Data for Experimental CSOY, Predicted (RSM &ANN) and Residue Values (RSM & ANN)

Std run	X_1	X_2	X_3	CSOY (%w/w)	Predicted		Residual	
					RSM	ANN	RSM	ANN
1	-1	-1	-1	50.20	50.24	50.2	-0.037	3.9274E-5
2	1	-1	-1	48.65	48.51	48.65	0.14	8.9471E-5
3	-1	1	-1	48.55	48.14	48.552	0.41	0.0015318
4	1	1	-1	50.30	50.59	50.3	-0.29	9.9895E-5
5	-1	-1	1	52.64	52.30	52.64	0.34	4.7205E-5
6	1	-1	1	48.54	48.91	48.54	-0.37	9.4007E-6
7	-1	1	1	48.61	48.71	48.609	-0.10	0.0010992
8	1	1	1	49.58	49.50	49.58	0.081	0.00011279
9	-2	0	0	50.00	50.34	50.00	-0.34	5.9564E-5
10	-2	0	0	49.83	49.55	49.83	0.28	1.4146E-5
11	0	-2	0	49.90	49.92	49.9	-0.024	5.2526E-6
12	0	-2	0	48.62	48.66	48.62	-0.037	0.00030703
13	0	0	-2	48.92	49.03	48.92	-0.11	0.00045599
14	0	0	-2	49.90	49.85	49.9	0.051	3.5915E-6
15	0	0	0	48.54	48.69	48.688	-0.15	0.14846
16	0	0	0	48.60	48.69	48.688	-0.087	0.088462
17	0	0	0	48.61	48.69	48.688	-0.077	0.078462
18	0	0	0	48.64	48.69	48.688	-0.047	0.048462
19	0	0	0	48.64	48.69	48.688	-0.047	0.048462
20	0	0	0	49.10	48.69	48.688	0.41	0.41154

The 20 runs consists of 8 factorial points, 6 axial points and 6 central points

It was observed that the highest experimental CSOY was 52.64 (%w/w) at extraction time of 40 min: X_1, solvent volume of 180 ml: X_2 and powder weight 50 g: X_3, respectively. However, the RSM and ANN predicted values at the variable conditions were 52.30 (%w/w) and 52.64 (%w/w), respectively. The lowest yield was obtained as 48.14 (%w/w) at extraction time of 40 min: X_1, solvent volume of 220 ml: X_2 and powder weight 40 g: X_3, respectively. The results were statistically optimised using the two software's. Table 3 shows the results of test of significance (TS) for every regression coefficient. The significance of regression was evaluated by F-value and p-values using Fischer's and null-hypothesis tests. P-value lesser than 0.05 indicate model terms to be significant, in this case, all p-

values were found significant and it were fit for the suitable representation of the relationships among the variable factors consider during the design ($X_{1,}X_2$ and X_3). However, the model interaction of

Table 3: Test of Significance for Every Regression Coefficient

Source	Sum of squares	df	Mean Square	F-value	p-value
X_1	0.76	1	0.76	7.85	0.0187
X_2	1.94	1	1.94	20.08	0.0012
X_3	0.81	1	0.81	8.36	0.0161
X_1X_2	8.76	1	8.76	90.82	<0.0001
X_1X_3	1.39	1	1.39	14.38	0.0035
X_2X_3	1.12	1	1.12	11.59	0.0067
X_1^2	2.86	1	2.86	29.62	0.0003
X_2^2	0.66	1	0.66	6.82	0.0260
X_3^2	1.02	1	1.02	10.63	0.0086

X_1X_2 with f-value 90.82, p-value < 0.0001, is highly significant than all other counterpart shown in Table 4 is the analysis of the variance of regression equation model. The F-value predicts the quality of the entire model considering all design factors at a time whereas the p-value is the probability of the factors having very little or insignificant effect on the response. Larger F-value signifies better fit of the RSM model to the experimental data [35]. According to Datta and Kumar [36], F-value with low p-value indicates the high significance of the regression model. However, the p-value should be lower than 0.05 for the model to be statistically significant [37].The model F-value of 21.65 implies the model was significant (p-value < 0.0001) and the data obtained fitted best to the chosen quadratic model with mean 49.32 and standard deviation of 0.31, respectively. The coefficient of determination (R^2) was 95.09% and this shows a greaterreliability between the experimental CSOY and predicted values. The adjusted R^2 called (R^2Adj.) was 90.67% and the p-value of lack of fit was not significant (>0.05).On the other hand, ANN shows better results in terms of R^2= 99.463% and adjusted R^2Adj. = 98.93 % with mean 0.09444 and standard deviation 2.899, respectively. Analysis of variance of regression equation model is

Table 4: Analysis of Variance (ANOVA) of Regression Equation

Source	Sum of squares	df	Mean Square	F-value	p-value
Model	18.66	9	2.07	21.51	< 0.0001
Residual	0.96	10	0.096	-	-
Lack of Fit	0.75	5	0.15	3.59	0.0935
Pure Error	0.21	5	0.042	-	-
Cor Total	19.63	19	-	-	
R-Sq = 91.09%, R-Sq(adj) = 90.67%, RSM; R-Sq = 99.463%, R-Sq(adj) = 98.93%, ANN					

As shown in Table 5, the variance inflation factor (VIF = 1.00) shows that centre points were orthogonal variable factors considered. The expression of optimized mathematical relationship between the response (CSOY) and variables ($X_{1,}X_2$ and X_3) considered expressed in Eqn. (16).

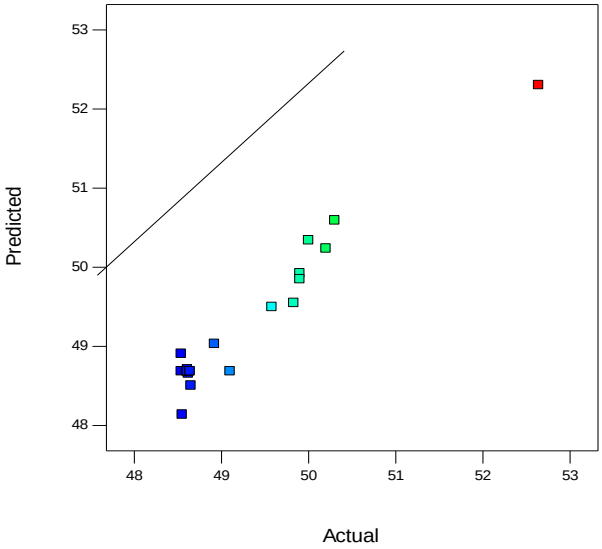
$$CSOY\ \%(w/w) = 48.69 - 0.24X_1 - 0.3X_2 + 0.24X_3 + 1.05X_1X_2 - 0.42X_1X_3 - 0.37X_2X_3 + 0.45X_1^2 + 0.21X_2^2 + 0.27X_3^2 \quad (16)$$

Table 5: Regression Coefficients and Significance of Response Surface Quadratic

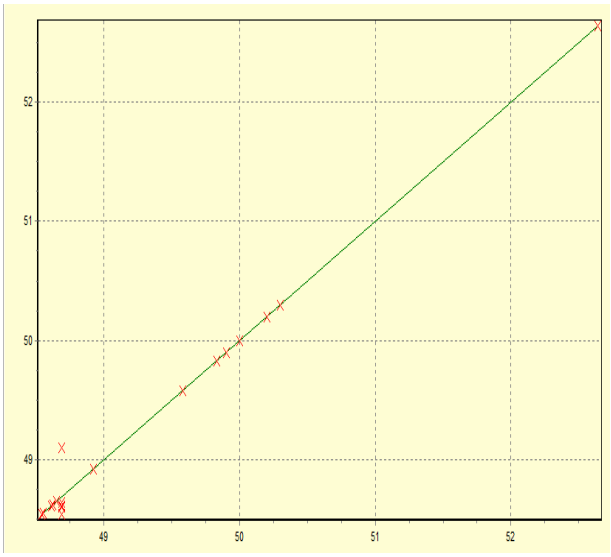
Factor	Coefficient Estimate	df	Standard Error	95%CI Low	95%CI High	VIF
Intercept	48.69	1	0.13	48.40	48.97	-
X_1	-0.24	1	0.084	-0.42	-0.048	1.00
X_2	-0.38	1	0.084	-0.56	-0.19	1.00
X_3	0.24	1	0.084	0.056	0.43	1.00
X_1X_2	1.05	1	0.11	0.80	1.29	1.00

X_1X_3	-0.42	1	0.11	-0.66	-0.17	1.00
X_2X_3	-0.37	1	0.11	-0.62	-0.13	1.00
X_1^2	0.45	1	0.082	0.26	0.63	1.02
X_2^2	0.21	1	0.082	0.031	0.40	1.02
X_3^2	0.27	1	0.082	0.084	0.45	1.02

The method to visualize the relationship between the experimental variables considered and the responses is depicted by graphical means. Fig. 1 shows the plot of predicted against the actual CSOY. It was observed that the ANN plot fit in perfectly than the RSM plot.



RSM



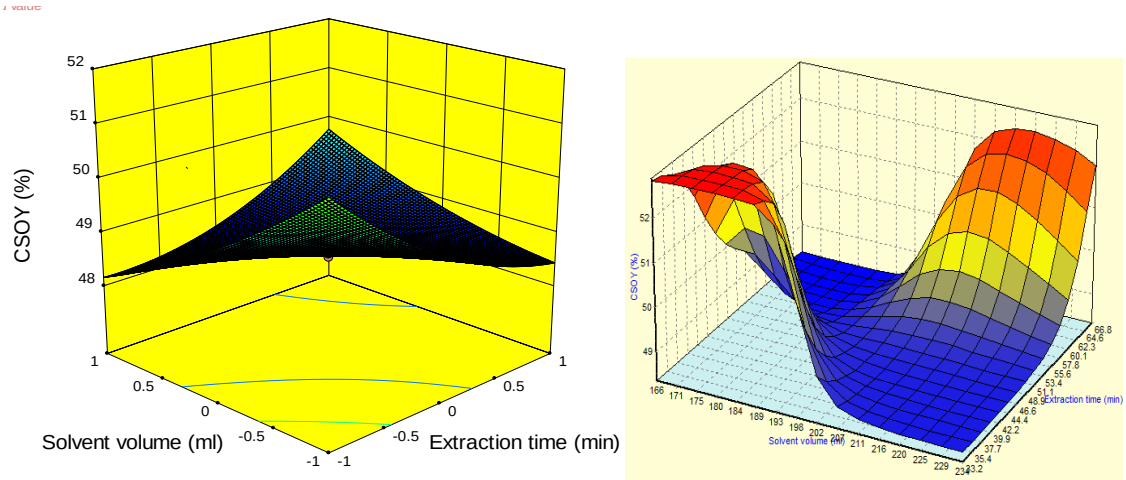
ANN

Figure 1: Plots of Predicted Vs. Actual

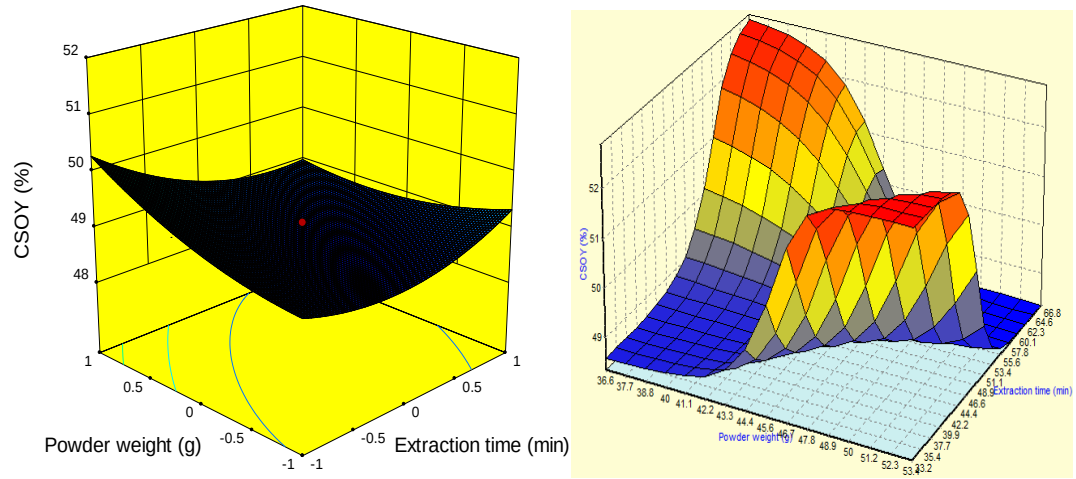
The 3-D's surface plots for CSOY for RSM and ANNare shown in Fig. 2. The result in Fig. 2(a) shows that low extraction time and high solvent volume favors the CSOY while decreasing in extraction time and solvent volume leads to low CSOY. The result also shows that low extraction time and high solvent volume gave a better CSOY. Fig. 2(b) shows the 3-D's plots representing the effect of extraction time, sample weight and their reciprocal

interaction on CSOY while keeping solvent volume constant at zero level. The lowest CSOY was observed at the lowest powder weight and lowest extraction time. There was no significant yield when the lowest powder weight was combined with the highest extraction time. However, the highest CSOY was observed at the highest powder weight and lowest extraction time. Fig. 2(c) shows the 3-D's plots representing the effect of solvent volume, solvent weight and their reciprocal interaction on oil yield while extraction time constant at zero level. Lowest CSOY was recorded at the highest powder weight and mid solvent. An increase in CSOY was observed at lowest powder weight and highest solvent volume. Highest CSOY was also observed at lowest powder weight and high solvent volume. Fig. 3 shows the important variable contribution by ANN, it was observed that solvent volume is of high importance than the extraction time and powder weight.

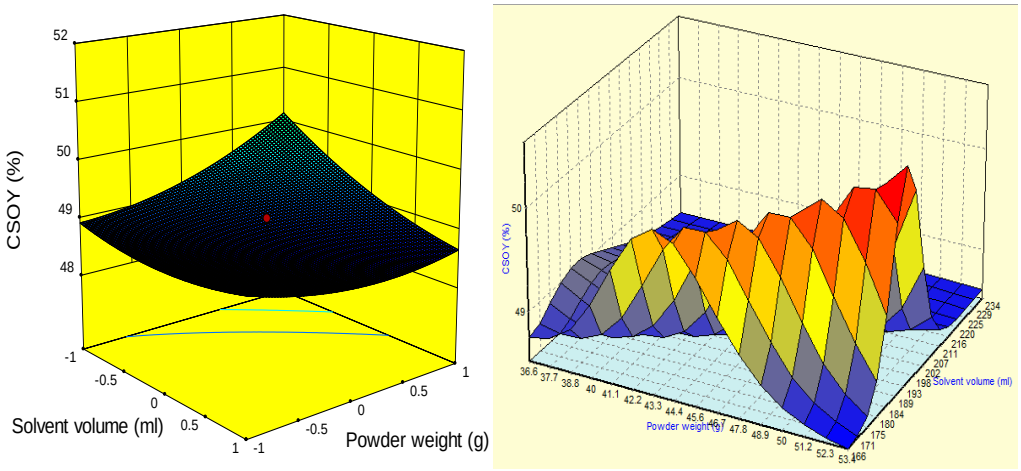
The RSM statistical model predicted CSOY of 50.240 (%w/w), at the following optimized conditions: powder weight of 40 g, solvent volume of 180 ml and extraction time of 40 min. Using these optimal factor values under experimental conditions, the experiment was validated in triplicates, an average content of 49.98 (% w/w) was achieved, and this value was well within the range predicted by the model. Similarly, the ANN statistical model predicted CSOY of 51.720 (% w/w), at the following optimized conditions: powder weight of 43 g, solvent volume of 202 ml and extraction time of 41 min. Using these optimal factor values under experimental conditions, the experiment was validated in triplicates, an average content of 50.85 (% w/w) was achieved, and this value was well within the range predicted by the model. This shows that ANN software prediction is far better than the RSM prediction.



(a)



(b)



(c)

Figure 2(a-c): 3-D's plots of RSM and ANN

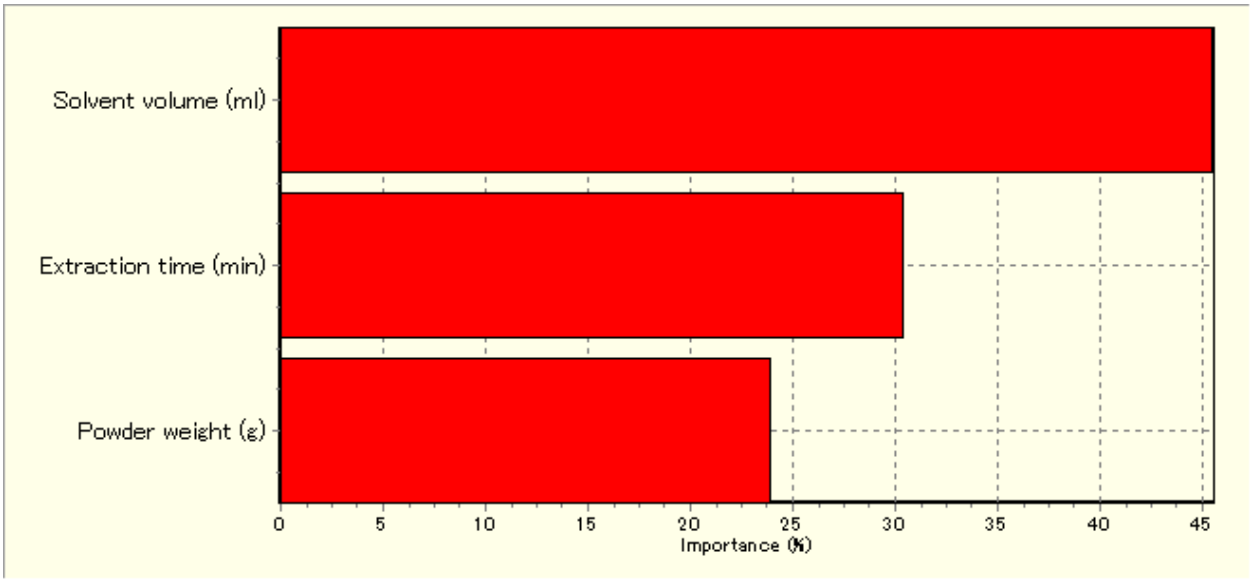


Figure 3: Level of importance

Quality characterization of CSOY

Physical properties of C. sinensis oil

The content and composition of the extracted oil must be subjected to physicochemical analysis in order to evaluate the quality of the oil. The result obtained from the physicochemical analysis is shown in Table 6. The CSOY was 54.65% which is higher than the 36.00% [15], 34.00% [38] and 43.10% [39], respectively. At room temperature, the extracted oil is golden yellowish in colour; the colour of this oil is due to the presence of chlorophyll pigment and carotene which is rich in vitamin A, hence, giving the oil a medicinal value [3].The brighter the colour of the oil the better the quality of the oil, the colour obtained in this study indicate good quality of the oil [40]. The moisture content of the oil was 0.0134% and this conforms to literature of standard oil. According to literature, low moisture content of oil indicates little or no impurity in the oil [41]. Hence, *C. sinensis* oil can be said to have lesser

impurities and with longer shelf life. The presence of linoleic acid makes the oil non-edible [15]. The refractive index of the oil sample indicates the level of oil purity, the refractive index of the *C. sinensis* oil was 1.5019 and it conforms to the refractive index in literature [3]. The specific gravity used to determine the weight of the oil in the case of heavy shipment or storage, the specific gravity obtained (0.92) is in line with what was reported by Ueno *et al* [42].

Chemical properties of C. sinensis oil

Table 6 also contained the chemical properties of the extracted oil. The acid value of 4.46 mg KOH/g obtained is lower than what was reported by [39], but in line with what was reported for most seed oil. The free fatty acid obtained was2.23; literature states that the maximum value for non-rancid acid is 5.00 hence this oil conveniently falls under the range of non-rancid acids [43].The peroxide value of 17.00 meq O_2/kg oil indicates that the oil has a high level of oxidative rancidity and little or no presence of oxidants [44]. The iodine value of 78.1 g I_2/100 g oil shows the moderate level of unsaturation of the oil and it places the oil between non-drying and semi-drying oil, hence this oil can be used in Industries as feed stocks.

Other properties C. sinensis oil

The higher heating value (HHV) determined for the oil in this study was 45.10 MJ/kg, which takes into account the latent heatof vaporization of water in the combustion products. Cetane number which is a measure of the fuel's ignition delay and combustion quality. The higher the cetane number, the shorter the delay interval and the greater the combustibility. Oil with low cetane number is difficult to start, hence it smokes. Standard minimum specification value of cetane number for biodiesel is within the range of 47-51 (ASTM D6751 and EN 14214). The value obtained in this study (99.48) is high. This observation may be attributed to the extraction method employed. The API (American Petroleum Institute) gravity is used in determining the weight of oil/petroleum in comparison with water. When the API gravity >31.1 (light oil), when the API gravity is within 22.3-31.1, (medium oil) and it is heavy oil when < 22.3. The API gravity in this study is 22.3 thus, falls under medium oil. The lower the aniline point the higher the content of the aromatic compounds in the oil. Hence a high aniline point makes the oil better diesel oil. The value of 557.31 obtained in this study shows that *C. sinensis* oil is of a better diesel oil.

Table 6: Qualities of *C. sirensis* as compared with other researched work

Properties	**This work**	**[15]**	**[40]**	**[39]**	**ASTM D6751**	**EN 14214**
Oil yield (%)	*54.65*	*36.00*	*43.10*	*34.00*	-	-
Physical state	Golden yellowish colour	Golden yellow colour	-	-	-	-
Acid value (mg KOH/g)	4.46	82 %	7.59	51.40	<0.80	0.5 max.
Free fatty acid (mg KOH/g)	2.23	-	-	25.70	<0.40	0.25 max.
Iodine value (mg I_2 /100 mg)	78.1	108	37.08	-	-	120 max.
Saponification value (mg KOH/g)	77.14	192.00	106.30	194.25	-	-
Viscosity	1357.00	-	-	-	-	-
Cetane number	99.48	-	-	-	47 min.	51 min.
Moisture content (wt. %)					<0.03	0.02
Specific gravity	0.92	0.92	-	-	0.86-0.90	0.85
Higher Heating Value (MJ/kg)	45.10	-	-	-	-	-
API	22.30	-	-	-	36.95	-
Diesel index	124.28	-	-	-	50.4	-
Aniline point (^oF)	557.31	-	-	-	331	-
Mean molecular mass	72.60	-	-	-	-	-
Peroxide Value	17.00	92.84	2.21	0.30	-	-

Barrel per metric ton (BPMT)	6.84	-	-	-	-	-

Gas Chromatograph Analysis of *C. sinensis*oil

GC-MS is one of the most recent technique of identifying the constituents of volatile matter, long and branched chain hydrocarbons, alcoholic acids, esters and other components [45]. The results pertaining to the analysis leads to the identification of the number of compounds from the GC fractions of *C. sinensis*oil. The analysis shows that the oil contained linoleic (34.01%), oleic (26.12%), linolenic (3.46%), palmitic (35.16%), stearic (1.02%) and other (0.23%) acids. It was observed that the oil contained substantial level of unsaturation (60.13%) which accounted for a low saponification value (77.14 mg KOH/g) and high iodine value (78.10 g I_2 /100 g).

Conclusion

This work demonstrated that the ANN software predicted better than RSM in modeling and optimization of oil extraction from *C. sinensis* seed. The RSM predicted CSOY of 50.240 (% w/w) and was validated as 49.98 (% w/w) at powder weight of 40 g, solvent volume of 180 ml and extraction time of 40 min. ANN predicted CSOY of 51.720 (% w/w) and was validated as50.85 (% w/w) at powder weight of 43 g, solvent volume of 202 ml and extraction time of 41 min. Fatty acid composition of the oil show that the oil is unsaturated (60.13%). Physicochemical analysis of *C. sinensis* oil showed that the oil is non-edible and could serve as raw materials in many Industries.

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