

Original Research Article

Optimization of Solvent Extraction of *Parinari polyandra* Benth Seed Oil Using Response Surface Methodology

ABSTRACT

Parinari polyandra B. seed is a potential source of oil with relatively high oil yield. Optimizing the extraction process of the oil will enhance its economic and industrial relevance, providing useful information for would be investors.

Aims: This work is aimed at extracting oil from the seeds of *Parinari polyandra* B. by using solvent extraction method. The process was optimized by using response surface methodology to determine the effect of four sets of parameters corresponding to optimum oil yield.

Methodology: Parinari oil was extracted using n-hexane and petroleum ether as solvents, Central Composite Design was used in the design of the 32 extraction experimental runs. The effects of solvent residence time (A), temperature (B), solid/solvent ratio (C) and solvent types (D) on the yield of parinari seed oil was studied using response surface methodology..

Results: The optimal yield of 64% was obtained at temperature of 60°C, residence time of 4 hours, solid/solvent ratio of 0.05g/ml using n-hexane as solvent. The physicochemical characteristics of the extracted *Parinari polyandra* oil compared well with literature values. Extraction temperature was found to have the most significant effect on the oil yield followed by residence time, solid/solvent ratio and solvent type.

Conclusion: The optimal yield of 64% was obtained at temperature of 60°C, residence time of 4 hours, solid/solvent ratio of 0.05g/ml using n-hexane as solvent. The physicochemical characteristics of the extracted *Parinari polyandra* oil compared well with literature values. Extraction temperature was found to have the most significant effect on the oil yield followed by residence time, solid/solvent ratio and solvent type.

Keywords: *Parinari polyandra* B., extraction, optimization, response surface methodology

1. INTRODUCTION

There is a pressing need to search for more seed oils that can be used as raw materials for industrial application and establish new pathways from potential oil producing seeds [1]. It is pertinent to expand the present vegetable oil feedstock especially in Africa where there is the need to replace industrial seed oils that constitute food sources with non-edible ones [2]. The replacement is necessary to reduce the problem of competition between industrial and food utilization of the same oil (such as soya oil). *Parinari polyandra* Benth is one of the available tropical seed producing plants in West Africa which are potential oil crops to serve as replacement feedstock for the chemical industries waiting to be harnessed [3].

Parinari polyandra B. plant is a savannah plant available in West Africa belonging to the family Rosaceae [4], It has a tree of about 8m high, glossy leaves that are elliptical and usually rounded at both ends. The deep red (Fig.1) or blackish purple colour (based on the variety) smooth fruits are about 2.5cm long. The

fruits have yellow white (Fig.1) endosperm with thick seed coats containing the oily mass. The variety and season of harvest of fresh seed kernel affects the oil yield giving a range of yields between 31-60% oil [5].

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32 Figure 1: Freshly harvested *Parinari Polyandra* fruits and seeds

33 The plant has been mainly used for medicinal purposes [6] for fertility improvement and to relieve
34 painful and inflammatory conditions [7]. Some species of *Parinari* have been used as herbal treatment for
35 diabetics [8]. The coconut water extract of *Parinari polyandra* seeds was reported to possess anti-diabetic
36 property [6]. The phytochemical components of the plant extracts include flavonoids, tannins, saponin and
37 glycosides [7, 9] though the active component responsible for the cure of diabetics is yet to be identified [6].
38 The administration of the ethanolic extract with *spondias mombin* in alloxan-induced diabetic rats was
39 reported by Emeka *et al.* [10] to promote desirable reduction on glucose and total protein levels of the rats.
40 Abolaji *et al.* reported the crude fibre, moisture content, total ash, total fat, total protein, total carbohydrate
41 and phosphorus of the *Parinari polyandra* fruit as $4.21 \pm 1.10\%$, $30.65 \pm 5.02\%$, $2.53 \pm 1.20\%$, $0.53 \pm 0.15\%$,
42 $7.09 \pm 0.20\%$, $54.27 \pm 3.20\%$, and $0.690 \pm 0.10\%$ respectively [9].

43 However, less research has been done on *Parinari* seed oil. One of the few available works on the seed oil
44 includes Olatunji *et al.*'s report on the protein and triacylglycerol contents of *Parinari polyandra* seed oil.
45 They were stated as 18.33% and 31.1% respectively [11]. *parinari* seed oil yield varies between 31 and
46 60% depending on the season of harvest [11]. The oil was reported as non-edible because of its relatively
47 high concentration of eleostearic acid [6]. Similarly, the oil of *parinari* seed was extracted and refined using
48 the methods of degumming, neutralization and bleaching by Odetoye *et al.* [5]. An earlier work also
49 indicated *parinari* oil as a potential feedstock for alkyd resin production [3].

50 *Parinari* seeds oil has not been well-harnessed possibly because of lack of adequate information on the
51 extraction [3,11]. Presently, available information on *parinari* oil extraction is scanty. There is no published
52 research work on the optimization of the extraction process of *Parinari* seed oil [3]. Such information will be
53 useful in establishing *Parinari* seeds as an industrial feedstock. Therefore, this study is aimed at
54 investigating the effects of some process parameters on the extraction process of *Parinari polyandra* Benth
55 seeds oil.

56 Response surface methodology has been regarded as an effective tool in the optimization of several
57 chemical processes [12-15]. The choice of central composite design (CCD) was based on its economical
58 advantage of the reduction in the number of required experimental runs to obtain statistically acceptable
59 result [12].

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63 2. MATERIAL AND METHODS

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65 2.1. Materials

The Parinari fruits were harvested from trees in Ilorin, Kwara State, Nigeria in the month of November. The seeds of parinari were obtained by cutting fresh but tough fruits with a knife into halves to release the whitish coloured oily seed kernel from the woody endocarp. The parinari seeds were further cleaned by hand-picking the dirt. Then the yield of seeds from the fruits harvested was calculated thus:

$$\frac{\text{Weight of seeds obtained} \times 100}{\text{Weight of fruits harvested}} = \% \text{ yield} \quad (1)$$

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The seeds were dried at room temperature for 10 days. The dried seeds have a light brown colouration. After drying, the dried seeds were crushed by pounding with laboratory mortar and pestle and sieved to obtain a mean particle size of about 2mm. The n-Hexane and the petroleum ether (60 - 80°C) used for the extraction process were commercially obtained from BDH Chemicals.

75 2.2. Methods

76 2.2.1. Moisture content determination

The moisture content was determined using the method of Akpan *et al.* [16]. 50g of the cleaned sample was weighed and dried in an oven at 80°C. Weight was taken after every 2 hours. The procedure was repeated until a constant weight was obtained. After 2 hours, the sample was removed from the oven and placed in the desiccator for thirty minutes to cool. It was then removed and re-weighed.

$$\% \text{ Moisture content} = \frac{w_1 - w_2}{w_1} \times 100 \quad (2)$$

where w_1 = Original weight of the sample before drying;

w_2 = Constant Weight of the sample after drying.

The moisture content was calculated on a wet basis.

85 2.2.2. Experimental design

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The experiment was designed using Design-Expert version 6.0.8. (Stat-Ease Inc, Minneapolis, U.S.A.). The experimental design was based on a five level, three (numeric) factor CCD with one categorical factor was generated using the parameters presented in Table 1. Time, temperature and solid/solvent ratio were the numeric factors coded as A, B, C respectively. The categorical factor, solvent type, was coded as D.

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Table 1: Experimental Design Summary

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	Time	hrs	Numeric	2	6	-1	1
B	Temperature	deg C	Numeric	60	70	-1	1
C	Solid/solvent ratio	g/ml	Numeric	0.03	0.09	-1	1
D	Solvent types		Categorical	n-Hexane	Pet ether		

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94 2.2.3. Oil extraction

Thirty-two (32) extraction experiments with different combinations of time, temperature and solvent types were performed. The extraction of the oils was carried out with soxhlet apparatus of 250cm³ capacity using n-hexane and petroleum ether (fraction 60 – 80°C). The soxhlet thimble was charged with between 5 – 15g ground seeds of 2mm mean particle size and extracted with the solvents according to the experimental design. 200ml of solvent [9] was poured into a round bottom flask. Then, Xg of the sample (as specified in the design) was placed in the thimble and inserted in the soxhlet extractor. The heating mantle was pre-set

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to the design temperature. As the solvent boiled, the vapour rose through the vertical tube into the condenser at the top. The liquid condensate dripped into the thimble, which contained the solid sample to be extracted. The extract seeped through the pores of the thimble and filled the siphon tube, where it flowed back down into the round bottom flask. This was allowed to continue for the specified time after which the solid sample in the thimble was removed. The solvent was recovered and the oil obtained weighed. The experiment was repeated for other parameters.

2.2.4. Oil yield determination

The oil yield (OY % by wt) was determined by using the equation 3 [17]:

$$OY = 100 \left(\frac{M_o}{M_s} \right) \quad (3)$$

where

M_o is the mass of oil extracted in grams,

M_s is the mass of the Parinari seed in grams.

2.2.5. Physicochemical analysis

The iodine, saponification and the acid values of the extracted oil were determined using the AOCS official method [18].

2.2.6. Optimization of the extraction parameters

The optimization of the extraction parameters was carried out for the maximal extraction of *Parinari* oil using central composite design (CCD) method. Multiple regression analysis of the experimental data was done using Design Expert software 6.0.8. The independent and the dependent variables were fitted to the second-order model equation. The fitted quadratic response model is represented as

$$Y = \beta_o + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j}^k \sum_{j=2}^k \beta_{ij} x_i x_j \quad (4)$$

Y is the response variable (oil yield), x_i, x_j are the coded variables, $\beta_o, \beta_i, \beta_{jj}, \beta_{ij}$ are intercept, linear, interactive and quadratic coefficients respectively, k is the number of factor studied and e represents random error. The goodness of fit of the regression equation Y was evaluated by the coefficient of determination (R^2) and the coefficient of relation (R). Statistical testing of the model was done in the form analysis of variance (ANOVA), which is required to test the significance and adequacy of the model.

3. RESULTS AND DISCUSSION

3.1. Oil yield

The moisture content of the fresh seed kernel was obtained on a wet basis as 0.96%. The values obtained for the oil yields are as given in Table 2 showing the values obtained for various experimental runs. The maximum oil yield of 64% was obtained for parinari seeds as the yield ranged from 31.7 to 64%. This maximal yield value obtained is slightly higher than that presented by Olatunji *et al.* [11] and Motojesi *et al.* [19] (60.7%). The varying oil yield values presented in Table 2 are indications that parinari seed extraction process condition/parameters considerably affect the oil yield..

3.2. Optimization of the Extraction Process Parameters

Multiple regression analysis of the experimental data using Design Expert 6.0.8. software gave the following second order polynomial equations in terms of coded factors:

$$Y = 52.50 + 2.79A - 2.84B - 2.0C + 0.56D - 13.25A^2 + 7.16B^2 + 3.65C^2 + 4.99AB - 2.62AC - 0.83AD + 2.14BC + 3.30BD + 0.21CD$$

Considering the solvent types:

156 For n-hexane: $Y_h = +1475.07131 - 1.53683A - 41.29352B - 1578.22070C - 3.31192A^2 + 0.28622B^2 +$
 157 $5836.28560C^2 + 0.49944AB - 52.36250AC + 17.14500BC$
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159 **Table 2: Oil yields obtained**
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Run	A:Time (hrs)	B:Temperature (°C)	C:Solid/solvent ratio (g/ml)	D:Solvent type	Oil yield (%)
1	4	65	0.05	Pet ether	50
2	6	70	0.03	Pet ether	61.7
3	6	70	0.07	n-Hexane	45
4	4	65	0.09	n-Hexane	58.3
5	4	65	0.05	n-Hexane	52
6	4	65	0.05	Pet ether	50
7	2	70	0.07	n-Hexane	34.29
8	4	65	0.05	n-Hexane	57
9	4	65	0.05	n-Hexane	57
10	2	70	0.03	n-Hexane	31.7
11	2	70	0.03	Pet ether	41.7
12	4	65	0.05	n-Hexane	57
13	4	60	0.05	Pet ether	61
14	4	65	0.05	n- Hexane	57
15	2	60	0.07	Pet ether	51.4
16	4	65	0.09	Pet ether	60.5
17	4	65	0.05	Pet ether	50
18	2	60	0.03	n-Hexane	53.3
19	2	70	0.07	Pet ether	50
20	6	60	0.03	Pet ether	55
21	4	65	0.05	Pet ether	50
22	6	70	0.03	n-Hexane	53.3
23	6	60	0.07	n-Hexane	45.7
24	2	60	0.07	n-Hexane	55.7
25	4	60	0.05	n-Hexane	64
26	4	65	0.05	n-Hexane	50
27	6	60	0.07	Pet ether	42.1
28	6	70	0.07	Pet ether	60
29	4	65	0.05	Pet ether	50
30	2	60	0.03	Pet ether	60
31	4	65	0.05	Pet ether	50
32	6	60	0.03	n-Hexane	60

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162 For Petroleum Ether: $Y_p = 1392.83869 - 2.36871 A - 39.97273B - 1561.53642C - 3.31192A^2 + 0.28622B^2 +$
 163 $5836.28560C^2 + 0.49944AB - 52.36250AC + 17.14500BC$
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where Y is the response variable in terms of % Parinari oil extraction yield, Y_h is the response variable in terms of % *Parinari polyandra* oil extraction yield when n-hexane was used, Y_p is the response variable in terms of % Parinari oil extraction yield when petroleum ether was used, while A, B, C, D were the coded values of the independent variables i.e. time, temperature, solid/solvent ratio and solvent types respectively.

3.2. Statistical analysis

Statistical testing of the model was done in the form analysis of variance (ANOVA), which is required to test the significance and adequacy of the model. The coefficient of determination (R^2) for Parinari oil extraction was determined to be 0.8374. This value indicates that the response model can explain 83.74% of the total variability in the responses. The coefficient of correlation (R) for the oil extraction was determined to be 0.9151. The summary of the analysis of variance (ANOVA) obtained from the Design-Expert software corresponding to equation Y for % oil yield oil is shown in Table 3. The independent and the dependent variables were fitted to the second-order model equation. The goodness of fit of the regression equation Y was evaluated by the coefficient of determination (R^2) and the coefficient of relation (R).

Table 3: Analysis of Variance (ANOVA) table for the effect of time and temperature on % oil yield

Source	Sum of Squares	Degree of Freedom	Mean square	F value	P value (Probability) P>F
Model	1504.4	13	115.72	7.13	<0.0001 significant
Residual	292.01	18	16.22		
Total	1796.41	31			

The ANOVA results of the regression model corresponding to quadratic equation Y for the % oil yield demonstrates that the model is highly significant, as it is evident from the calculated F-value (=7.13) and a very low probability value (probability (P)>F=0.0001) which is less than 0.05. The adequate precision value is greater than 4 ($P_{ad} = 10.8$) indicating an adequate signal to noise ratio of the model. The analysis indicates that the main linear interaction effects are due to the coded terms A, B, corresponding to time, temperature indicating that time and temperature are significant model terms. The linear interaction effects between the factors time and temperature (AB) time and solid/solvent ratio (AC) and temperature and solvent types (BD) are also significant. The quadratic effects of time (A^2) and solid/solvent ratio (C^2) are both significant. The ANOVA results however, indicated that the terms C, D, AD, BC, CD, B^2 are insignificant.

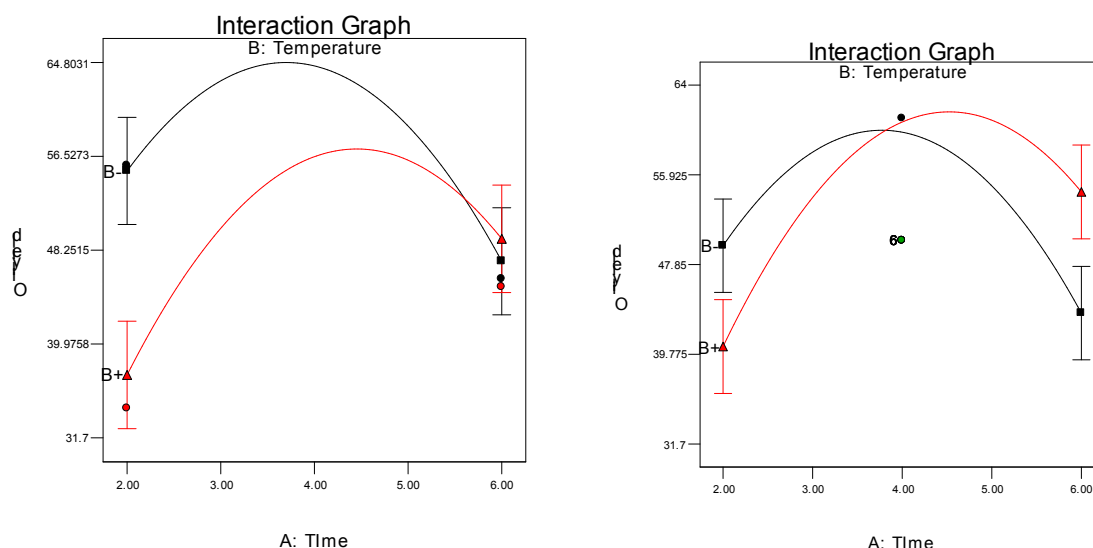
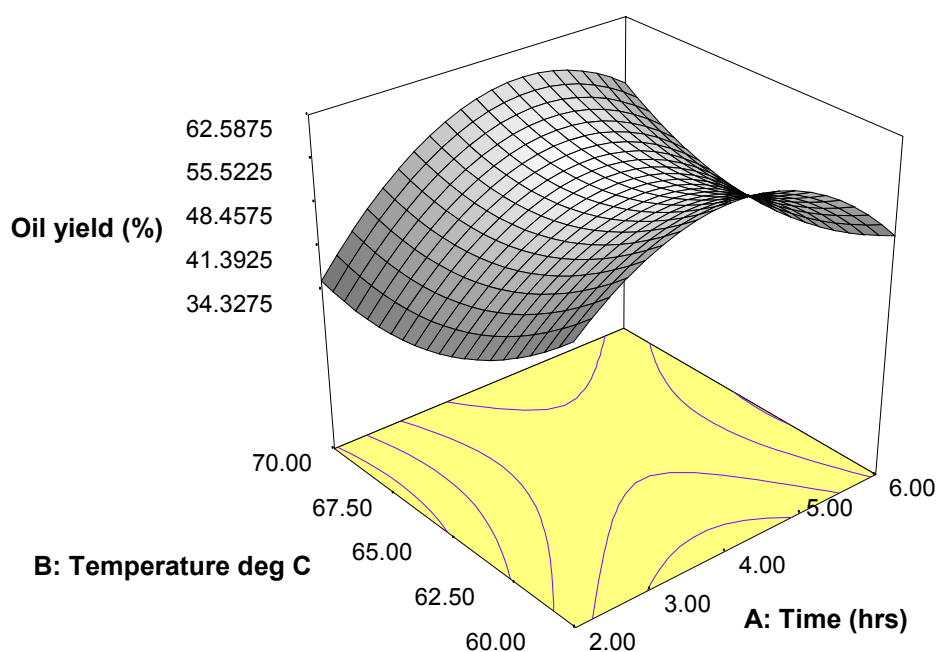


Figure 2: Interaction of time and temperature for n-hexane and petroleum ether respectively at 60 and 70°C.

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For the chosen model equations Y_h and Y_p , the contour plots illustrate the two dimensional relationship for the effects of temperature and time respectively on oil yield, the effects of extraction time and temperature on oil yield is displayed for both solvents. From the the n-hexane solvent plot, the oil yield tends to be more favourable with the temperature at 60 °C then further decrease with increasing time while petroleum ether tend to favour higher yield with increasing time for 70°C. Figure 2 indicates that relatively higher yields were obtained using n-hexane solvent at 60°C compared to petroleum ether in which higher yield was obtained at 70°C. This relatively lower temperature advantage of n-hexane may be indicative of a more economical solvent when considering heating among other requirements.



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209 Fig.3: 3D response surface plots showing effect of temperature, time and their interactive effect on oil yield
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211 The 3D response surface plot shown in Figure 3 indicates that the percentage oil yield increased as
212 temperature and time increased to the optimum conditions and then declined with a further increase of
213 these parameters (temperature and time). This trend is similar to what is observable in Figure 4, where the
214 percentage oil yield increased as solid/solvent and time increased to the optimum conditions and then
215 declined with the further increase of these parameters. This result indicates that the three numerical
216 variables (temperature, time and solid/solvent ratio) had mutually dependent influence on the percentage oil
217 yield. The optimum oil yield was found to be 64%. This was obtained when the extraction process
218 parameters of 4 hours, 60 C, 0.05 solid/solvent ratio and Hexane were used.
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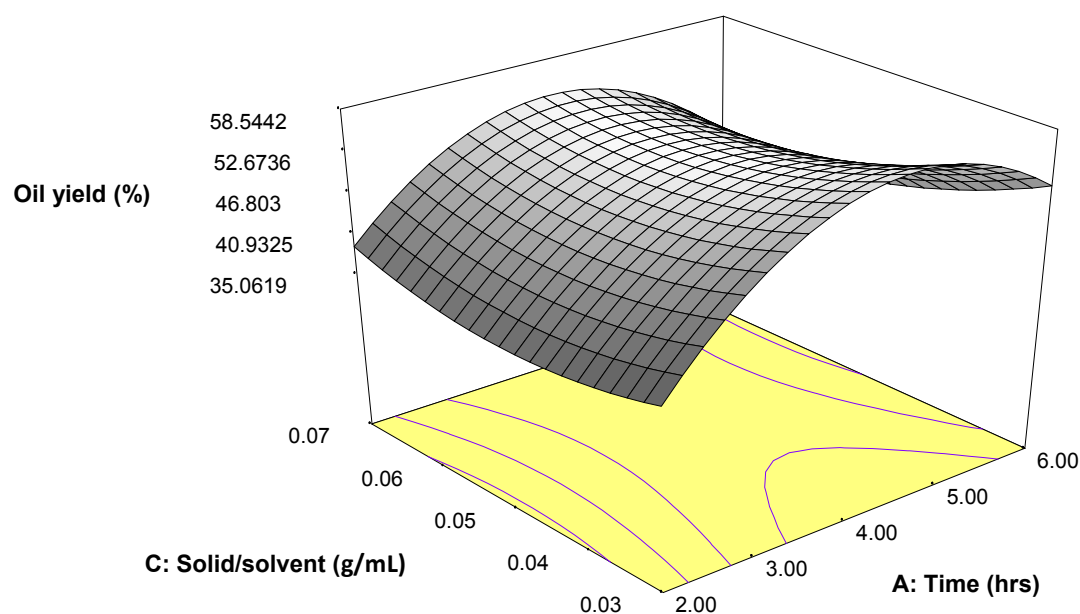


Fig. 4: 3D response surface plots showing effect of solid/solvent, time and their interactive effect on oil yield

3.3. Physicochemical characteristics of the extracted oil

The physico-chemical properties of the oil obtained at maximum yield are presented in Table 4. The results further suggest the use of the oil which is a drying oil for industrial reactions and for potential application as a drying oil in the paints industry based on the relatively high iodine value and refractive index indicating high level of unsaturation [3,5].

Table 4. The physico-chemical properties of oil obtained at maximum yield response

Physico chemical properties

Saponification value (mgKOHg^{-1})	241.9
Iodine value ($\text{Ig}/100\text{g oil}$)	170.2
Acid Value (mgKOHg^{-1})	3.61
Oil yield (%)	64
Viscosity (mPa s)	48.22
Refractive index (25°C)	1.4641
Specific gravity	0.887

4. CONCLUSION

Several parameters such as extraction time, extraction temperature, solid/solvent ratio and solvent type affecting solvent extraction of *Parinari polyandra* oil were investigated. Their effects on oil yield were clearly shown. This work has demonstrated the use of CCD based response surface methodology for determining the conditions leading to the optimum yield of *Parinari* seed oil extraction. The developed second order polynomial equations was suitably employed in *parinari* seed oil extraction process, where the analysis of the interactions of extraction time, temperature, solid/solvent ratio and solvent types (n-Hexane or

Petroleum ether) were considered. The optimal conditions were indicated as extraction time of 4 hours, extraction temperature of 60°C, solid/solvent ratio of 0.05g/ml using n-Hexane as the solvent. The physicochemical analysis of the extracted oil further suggests its potential application as a drying oil in the paints industry.

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