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Yield, quality, kinetics and thermodynamics studies on extraction of *Thevetia peruviana* oil from its oil bearing seeds

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The present research shows possibility of extracting *Thevetia peruviana* oil from its oil bearing seeds by cold and soxhlet extraction methods, using petroleum ether as extracting solvent at room temperature and 40 to 60°C respectively. Characterisation of the oil showed that the percentage oil yield, acid value, saponification value and viscosity increased as temperature of soxhlet extraction increased, while the specific gravity and iodine value of the extracted oil decreased at high temperature of extraction in soxhlet extraction method. Cold extraction showed improved quality and oil yield, in comparison with oil obtained from soxhlet extraction method. The kinetics of the oil extracted from soxhlet extraction method was derived from mass transfer rate equation and was found to fit well with only pseudo-second order kinetic of volumetric mass transfer rate coefficient 0.04 h^{-1}. The thermodynamics study of the extracted oil showed that ∆H and ∆S were positive while ∆G was negative, indicating that *T. peruviana* oil extraction process was endothermic, spontaneous and irreversible with exception to extraction at 40 and 45°C.

Key words: Extraction, irreversible, kinetic, thermodynamic, quality.

INTRODUCTION

There are two varieties of the oleander plant; both belong to order *apocynales* of *apocyanaceae* family (Sahoo et al., 2009). One with yellow flowers is called yellow oleander (*Thevetia peruviana*), and the other with purple flowers is known as nerium oleander (*Thevetia nerrifolia*) (Usman et al., 2009). *T. peruviana* is a native of tropical America; especially Mexico, Brazil and West Indies and has naturalized in tropical regions worldwide. In the native countries it is believed to be more than 2000 years old and known as yellow oleander, gum bush or milk bush, exile tree, olomi ojo in India, Cabalonga in Puerto Rico, Ahanai in Guyana and Yoruba in Nigeria respectively (Sahoo et al., 2009). In Nigeria, *T. peruviana* has been grown for over fifty years as an ornamental plant in homes, schools and churches (Usman et al., 2009; Ibiyemi et al., 2002), flowers and fruits all year

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round, providing steady supply of seeds from fruits of between 400 to 800 per annum depending on the rainfall pattern and plant age (Usman et al., 2009; Balusamy and Manrappan, 2007), each of the fruits contains between one to four seeds of oil content 60 to 65% in its kernel (Mohibbe et al., 2005). Despite the fact that there is high level of oil in the seed, it remains non–edible because of the presence of cardiac glycoside (toxins) (Usman et al., 2009), as a result of this, *T. peruviana* oil is not used as food but used in industrial production of insecticides, lubricant, bio-diesel, soap, cosmetics, paints, polyol etc (Kareru et al., 2010). The three common methods by which *T. peruviana* oil is extracted from its oil bearing seeds are; mechanical pressing, supercritical fluid extraction and solvent extraction (Liauw et al., 2008). Industrial extraction of the oil from its seeds is commonly done by mechanical pressing, but the oil obtained from this method usually contain a high percentage of water, metal content and its turbid nature result in low market price (Adeeko and Ajibola, 1990). Highly purified oil is obtained from supercritical fluid extraction method, but has a demerit of high operating cost (Mongkholkhajornsilp et al., 2005). Solvent extraction method gives higher percentage yield and less turbid oil than mechanical extraction and a low operating cost in relation to supercritical fluid extraction method (Herodez et al., 2003; Khraisha, 2002). In this research, we used soxhlet and cold extraction (both are solvent extraction) methods to extract *T. peruviana* oil from its oil bearing seeds using petroleum ether as extracting solvent. The effect of temperature on extracted oil was studied; kinetics and thermodynamics of the soxhlet extraction process were also investigated.

MATERIALS AND METHODS

Raw material

T. peruviana seeds were collected from Aule in Akure south local government area of Ondo state, Nigeria in March 2012.

Pre-treatment of material

Seed coats were removed from seeds using hammer, before sun drying for 15 days to obtain moisture free seeds. After sun drying, dirt-like particles were removed from the seeds and the seeds were oven dried at 60°C for 5 h before they were ground with blender. *T. peruviana* oil was extracted from a known weight of its oil bearing seeds using two different solvent extraction methods, which are cold and soxhlet extraction method.

Cold extraction method

A known weight of ground seeds was tightened in a filter cloth before immersing in a metal container containing petroleum ether as extracting solvent with liquor ratio 1:5 and extraction was carried out at room temperature for 7 days. At the end of the extraction time, the extracted oil-solvent mixture was collected, distilled and evaporated to obtain solvent-free oil. The obtained solvent-free oil was weighed to calculate the percentage yield.

Soxhlet extraction method

A known weight of ground seeds was placed in the thimble of the soxhlet apparatus, while petroleum ether (extracting solvent) was placed in a 500 ml round bottom flask and extraction was carried out with liquor ratio 1:5 at 40, 45, 50, 55 and 60°C for 4 h each. At every hour interval, the extracted oil-solvent mixture was collected, distilled and evaporated to obtain solvent-free oil. The obtained solvent-free oil was weighed to calculate the percentage yield.

Extraction kinetics and thermodynamics

Mass transfer kinetic model was used to study the extraction process, since there was no reaction between the extracting solvent (petroleum ether) and Thevetia peruviana oil (Liauw et al., 2008). The affinity of the oil for the extracting solvent from the oil bearing seeds was determined using Van't Hoff model, as described by Baba et al. (2011)

Physico-chemical properties of the oil

The physico-chemical properties, like acid value (Cd 3a- 63), specific gravity (Ta 1b-64), saponification value (Cd 3–25), iodine value (Cd 1–25), peroxide value Cd 8 –53, refractive index Cc 7 – 25 (09), and viscosity was measured using Abe viscometer at room temperature (Firestone, 2009).

RESULTS AND DISCUSSION

Physicochemical properties of extracted oil

The effect of extraction temperature on physico-chemical properties of *T. peruviana* oil is shown in Table 1. In soxhlet extraction method, higher extraction yield was achieved at higher temperature, which reduced the oil viscosity thereby releasing oil from intact cells and also reduced moisture in the cells. This observation agreed with the findings of Liauw and co workers in extraction of neem oil using n-hexane and ethanol (Liauw et al., 2008). This high percentage yield shows that *T. peruviana* oil has a good potential in the production of oleochemical that can serve as an alternative substitute to high cost ever depleting, non-biodegradable, non-renewable petrochemical resource as concluded by Odeomelam (2005), in proximate composition and selected physicochemical properties of African oil bean (Odeomelam, 2005). In contrary to soxhlet extraction, cold extraction (at room temperature) method gave a better oil yield in comparison with yield from soxhlet extraction as shown in Table 1.

The quality of the extracted *T. peruviana* oil decreased with increase in temperature. This is shown in Table 1, where the acid, free fatty acid, saponification, peroxide value, viscosity and refractive index increased as extraction temperature increased, while the specific gravity and iodine value decreased as the extraction temperature increased, these observations agreed with

Table 1. Physicochemical properties of cold and soxhlet extracted *T. peruviana* oil at different temperature.

Extraction temperature (°C)	Room temp.	40.0	45.0	50.0	55.0	60.0
Oil yield (%)	63.5	45.9	50.1	54.8	58.1	62.2
Moisture content (%)	0.10	0.09	0.09	0.09	0.08	0.08
Specific gravity (g/dm^3)	0.922	0.921	0.918	0.916	0.912	0.908
Acid value (mgKOH/g)	7.50	7.80	7.90	8.10	8.30	8.30
Free fatty acid (mgKOH/g)	3.75	3.90	3.95	4.05	4.15	4.15
Saponification value (mgKOH/g)	162.43	169.73	174.36	179.46	183.65	186.25
Peroxide value (mg/Kg)	3.52	4.03	4.04	4.06	4.10	4.12
Iodine value (g/100g)	106.00	92.42	88.56	85.25	82.08	79.21
Refractive index	1.440	1.442	1.442	1.444	1.447	1.448
Viscosity (mPa. s)	154.88	162.92	169.28	171.84	177.06	185.50

Khraisha (2002), in retorting of oil shale followed by solvent extraction of spent shale: experiment and kinetic analysis (Khraisha, 2002).

Acid value is an indication of level of free fatty acid formed from hydrolytic decomposition of glycerides to free fatty acid (Abayeh et al., 2011), that was been accelerated by increased in *T. peruviana* oil extraction temperature as shown in Table 1. Increase in level of free fatty acid caused by increase in extraction temperature was an indication of reduction in quality of the oil in terms of edibility (Adelaja, 2006). The acid values obtained showed that *T. peruviana* oil is good as starting material for production of paints and varnishes according to the findings made by Abayeh et al. (2011), in quality characteristics of pumpkin seed oil (Abayeh et al., 2011).

Average molecular weight of the oil is indicated by saponification value, increase in saponification value with temperature of extraction (Table 1) showed that as temperature of extraction increased, the average molecular weight of the oil reduced, due to breaking down of oil to higher proportion of lower molecular weight fatty acid. The saponification value of *Thevetia peruviana* (Table 1), showed that the oil is an effective raw material in the soap industry in disagreement with Akanni et al. (2005), in physicochemical properties of some non-conventional oil seeds (Akanni et al., 2005).

Oxidative stability of the oil can be determined by its peroxide value, in this extraction process, peroxide value increased with increase in temperature and as a result, the quality of the oil reduced with increase in temperature of extraction, because those extracted at higher temperature are liable to go rancid faster than the one extracted at room temperature of 30°C. The peroxide value obtained in this extraction process is lower than the value between 20 to 40 mg/g at which oil becomes unstable with offensive odour in storage (Jauro et al., 2011), this mean that *Thevetia peruviana* oil extracted at room temperature (cold extraction) is more stable than those extracted at higher temperature (soxhlet extraction) and all of them not easily deteriorate in storage according to Jauro et al. (2011), in extraction and characterisation of *Pentaclethra macrophylla* seed oil (Jauro et al., 2011).

Viscosity, specific gravity and refractive index of the extracted oil fall within the range of other non-conventional oil and their values increased as extraction temperature increased, with exception to specific gravity (Table 1), this agreed with a report on extraction of oil from water melon seed and analysis (Sodeke, 2005).

The iodine value is a measure of unsaturation of triglyceride oil (Gunstone, 2004) and the values obtained in this study ranges from 79.2 to 106.0 g of I_2/100 g. Table 1 showed that iodine value of extracted *T. peruviana* oil decreased with increase in temperature of extraction process. Hence, the oil became less reactive, this is because increase in temperature initiated the breakdown of C = C unsaturation of the oil to C – C saturated carbon chain. The iodine value of *T. peruviana* oil reported here is within the range of semi drying oil, this showed that it is a potential raw material in paint, lacquer, resin, polyol, grease, lubricating oil and diesel production as stated in the findings made by Eromosele et al. (1998), in studies on seeds and seed oils (Eromosele et al., 1998).

Extraction kinetics

The *T. peruviana* oil and the extracting solvent (petroleum ether) are organic materials, this natural similarity made it possible for the oil to migrate into the solvent from the cake cementing it to the ground seeds. Since there was no reaction between the extracted oil and the extracting solvent, the obtained experimental data in soxhlet extraction method were treated using mass transfer kinetic model (Liauw et al., 2008).

The first kinetic model

The first kinetic model named pseudo first-order kinetic assumed that, the concentration of the extracted oil is directly proportional to the mass transfer rate; represented

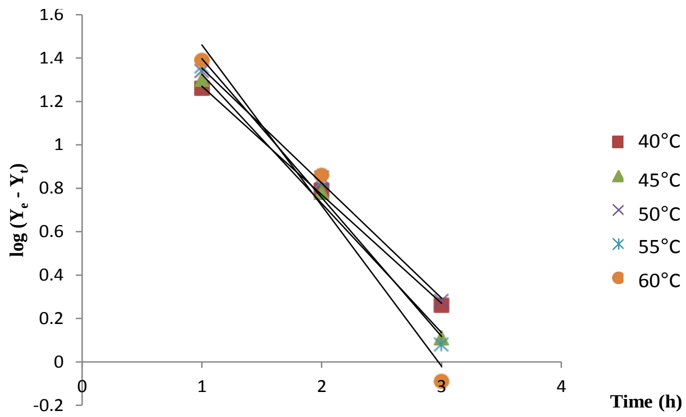

Figure 1. Graph of pseudo first-order kinetic.

Table 2. Intercept and slope of pseudo first-order graph.

Temp. (K)	Intercept (log)	Slope (h^{-1})
313	1.785	-0.566
318	1.900	-0.609
323	1.915	-0.683
328	2.060	-0.691
333	2.125	-0.718

mathematically as follows:

$$dW_e/dt = K.A (C_e – C_t) \quad (1)$$

Where, dW_e/dt is the mass transfer rate of *T. peruviana* oil (g/h), C_e and C_t are the concentration of *T. peruviana* oil in organic solvent at equilibrium (g/L) and at time t (h) respectively, K is mass transfer rate coefficient (h^{-1}) and A is the surface area (m^2) for mass transfer process.
In the batch extraction process carried out, the volume of the extracting solvent was assumed to be constant, therefore;

$$dW_e/dt = K. A/V (W_e - W_t) \quad (2)$$

$$dW_e/dt = K.a (W_e - W_t) \quad (3)$$

$$\int dW_e = K.a \int(W_e - W_t)\, dt \quad (4)$$

$$\ln W_e = \ln(W_e - W_t)\, K.a\, t + C \quad (5)$$

Where K.a is the volumetric mass transfer rate coefficient, while W_e and W_t are the mass of the *T. peruviana* oil in organic solvent at equilibrium (g) and at time t (g) respectively.

At the beginning of the extraction process, time t = 0, the mass of *T. peruviana* oil in bulk liquid is zero, $W_e = 0$, therefore integration of Equation (5) gives:

$$\ln W_e = C \quad (6)$$

At any time t, W_e and W_t are the mass of the *T. peruviana* oil in organic solvent at equilibrium (g) and at time t (g) respectively. Therefore, Equations (5) and (6) become:

$$\ln (W_e - W_t) = \ln W_e - K.a (t) \quad (7)$$

Equation (7) can be rearranged so that it can be written in terms of percentage yield per mass of *T. peruviana* seed.

$$\log (Y_e - Y_t) = \log Y_e – K.a(t)/2.303 \quad (8)$$

Where Y_e and Y_t are the percentage yield of *T. peruviana* oil in bulk liquid at equilibrium and time t per mass of *T. peruviana* seed.

Therefore, a plot of log (Y_e - Y_t) against time t (Figure 1) is a linear graph with slope equal to volumetric mass transfer rate coefficient K.a (Table 2) and intercept equal to log of the percentage yield of *T. peruviana* oil in bulk liquid at equilibrium (log Y_e), that was used to determine $Y_{e(cal.)}$. Table 3 shows that pseudo first-order kinetic model did not fit the *T. peruviana* oil extraction kinetic process, because Y_e calculated >> Y_e experimental and at 55 and 60°C Y_e calculated > 100%. This indicates that another kinetic model is needed to treat the *T. peruviana* oil extraction experimental data.

The second kinetic model

The second kinetic model called pseudo second-order extraction kinetic states that the rate of *T. peruviana* oil extraction from its oil bearing seeds is directly proportional to the square of oil yield.

$$dW_e/dt = K (W_e - W_t)^2 \quad (9)$$

Where, K is the volumetric mass transfer rate coefficient (h^{-1}) of pseudo second-order extraction kinetic.
Integrating Equation (9) with boundary condition; time t = 0, the mass of *T. peruviana* oil in bulk liquid is zero, We = 0, at the beginning of the extraction process. This gives:

$$t/(W_e – W_t) = 1/W_e + Kt \quad (10)$$

Equation (10) can be rearranged so that it can be written in a linear form and in terms of percentage yield per mass of *T. peruviana* seed.

$$t/Y_t = 1/KY^2_e + t/Y_e \quad (11)$$

The slope and intercept (Table 4) of the plot of t/Y_t versus t (Figure 2) can be used to calculate the percentage oil

Table 3. Pseudo first-order volumetric mass transfer rate coefficient K.a and oil yield Y_e.

Temp. (K)	Intercept (log)	Slope (h^{-1})	
313	61.0	45.9	1.303
318	79.4	50.1	1.402
323	82.2	54.8	1.573
328	114.8	58.1	1.592
333	133.4	62.2	1.653

Table 4. Intercept and slope of pseudo second-order graph.

Temp. (K)	Intercept (h)	Slope
313	0.0120	0.022
318	0.0100	0.020
323	0.0090	0.018
328	0.0075	0.017
333	0.0063	0.016

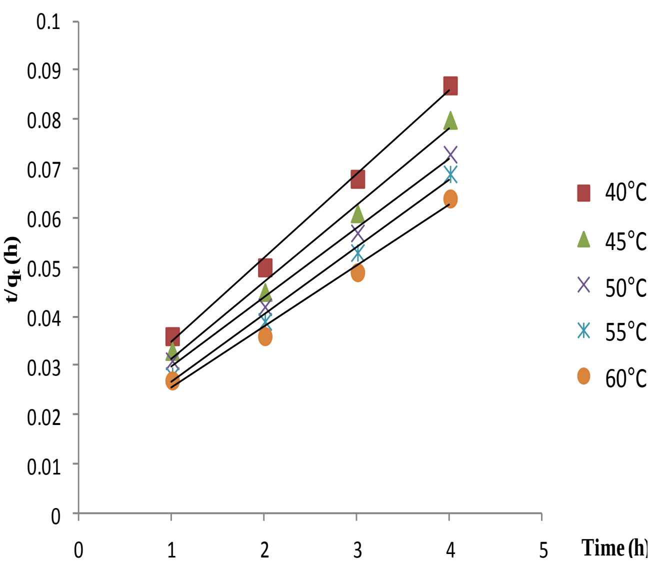

Figure 2. Pseudo second-order graph.

yield Y_e(cal) and pseudo second-order volumetric mass transfer rate coefficient K respectively. Table 5 shows that pseudo second-order kinetic model fitted the *T. peruviana* oil extraction kinetic process, because Y_e calculated ≈ Y_e experimental and volumetric mass transfer rate coefficient K ≈ 0.04 h^{-1} in all the extraction temperature.

Extraction thermodynamics

Thermodynamics parameters (ΔH, ΔS and ΔG) for extraction of *T. peruviana* oil from its oil bearing seeds using petroleum ether as extracting solvent in soxhlet extraction method can be determined using second law of thermodynamic equations.

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

$$\Delta G = -RT \ln K_o \quad (13)$$

Equating Equations (12) and (13) gives Equation (14)

$$\log K_o = (\Delta S/2.303R) - (\Delta H/2.303RT) \quad (14)$$

$$K_o = Y_L/Y_s \quad (15)$$

Where, K_o is equilibrium constant, Y_L is percentage yield of *T. peruviana* oil at equilibrium temperature, Y_s is percentage *T. peruviana* cake left after extraction (per mass of initial *T. peruviana* seed) at equilibrium temperature, R is gas constant, while ΔH, ΔS and ΔG are enthalpy, entropy and free energy of extraction respectively.

The value of K_o and ΔG for extraction of *T. peruviana* oil using petroleum ether as extracting solvent were determined using Equations (15) and (12) respectively and are given in Table 6, while correlation coefficient of extraction process R^2 was gotten to be 0.9912 from Figure 3. The values of enthalpy and entropy of extraction of *T. peruviana* oil from its oil bearing seeds are gotten from the slope (1525 K) and intercept (4.7967) of Van't Hoff plot (Figure 3) to be 29.20 and 91.84 $Jmol^{-1}$ respectively.

The correlation coefficient of extraction process R^2 being equal to 0.9912 showed that extraction process fitted well with the obtained thermodynamic data, positive values of enthalpy and entropy of extraction indicated that the extraction process was endothermic and spontaneous respectively while the negative values of free energy indicated that the extraction process were feasible and irreversible.

Conclusions

High percentage yield, abundance, biodegradability, renewability, and environmental friendly nature of the *T. peruviana* oil make it a not yet discovered potential alternative to petrochemical resource in industrial production of paint, varnish, biodiesel as diesel engine fuel, insecticides that brings about reduction in insects born disease in the community, soap, cosmetics, polyol and resin just to mention a few. Its inedible nature has a potential of facing out the use of edible oil as precursor in chemical industry, where by promoting food security, in an emerging economy like Nigeria. The soxhlet extraction process fitted well with pseudo second-order kinetic, the negative value of free energy, positive values of enthalpy and entropy of extraction indicated that the extraction

Table 5. Pseudo second-order volumetric mass transfer rate coefficient K and oil yield Y_e.

Temp. (K)	$Y_{e\ cal.}$	$Y_{e\ exp.}$	K (h^{-1})
313	45.7	45.9	0.040
318	50.0	50.1	0.041
323	55.0	54.8	0.037
328	58.6	58.1	0.039
333	62.3	62.2	0.042

Table 6. Equilibrium constant and thermodynamic parameters of *T. peruviana* oil extraction using petroleum ether.

Temp. (K)	1/T x 10^{-3} (K^{-1})	K	Log K_o	ΔG_0 (J/mol)	ΔH_0 (KJ/mol)	ΔS_0 (J/mol)
313	3.19	0.85	-0.071	454.08	29.20	91.84
318	3.14	1.00	0.000	-5.12	29.20	91.84
323	3.10	1.21	0.088	-464.32	29.20	91.84
328	3.05	1.39	0.143	-923.52	29.20	91.84
333	3.00	1.65	0.217	-1382.72	29.20	91.84

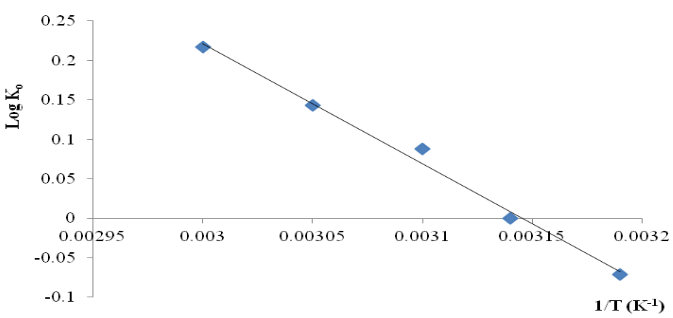

Figure 3. Van't hoff graph.

process was irreversible, endothermic and spontaneous. Cold extraction of the *T. peruviana* oil gave high quality and oil yield with a low production cost when compare with extraction at high temperature (soxhlet extraction). Therefore, cold extraction method is better than soxhlet extraction method, in term of oil yield and quality.

Conflict of Interest

The authors have not declared any conflict of interest.

REFERENCES

Sahoo NK, Pradhan SR, Pradhan C, Naik SN (2009). Physical properties of fruit and kernel of Thevetia peruviana J. A Potential Biofuel Plant. Int. Agrophys. 23:199-204.

Usman LA, Oluwaniyi OO, Ibiyemi SA, Muhammed NO, Ameen OM (2009). The potential of oleander (Thevetia peruviana) in African agricultural and industrial development: A case study of Nigeria. J. Afr. Biosci. 24:1477- 1487.

Ibiyemi SA, Fadipe VO, Akinremi OO, Bako SS (2002). Variation in oil composition of Thevetia peruviana juss 'yellow oleander' fruit seeds. J Afr. Sci. Environ. Manage. 6:61-66.

Balusamy T, Manrappan R (2007). Performance evaluation of direct injection diesel engine with blends of Thevetia peruviana seed oil and diesel. J. Sci. Ind. Res. 66:1035-1040.

Mohibbe AM, Waris A, Nahar NM (2005). Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. Biomass Bioener. 29:293-302.

Kareru PG, Keriko JM, Kenji GM, Gachanja AN (2010). Anti-termite and antimicrobial properties of paint made from Thevetia peruviana (Pers.) schum oil extract. Afr. J. Pharm. and Pharmacol. 4(2):087-089.

Liauw MY, Natan FA, Widiyanti P, Ikasari D, Indraswati N, Soetaredjo FE (2008). Extraction of neen oil (Azadirachta indica A. Juss) sing n-hexane and ethanol: study of oil quality, kinetic and thermodynamic. J. Eng. Appl. Sci. 3:49-54.

Adeeko KA, Ajibola OO (1990). Processing factors affecting yield and quality of mechanically expressed groundnut oil. J. Agric. Eng. Res. 45:31-43.

Mongkholkhajornsilp D, Douglas S, Douglas PL, Elkamel A, Teppaitoon W, Pongamphai S (2005). Supercritical CO2 extraction of nimbin from neem seeds: “a modelling study. J. Food Eng. 71:331-340.

Herodez APS, Hadolin M, Akerget M, Knez Z (2003). Solvent extraction study of antioxidants from balm (Melissa officinalis L) leaves. Food Chem. 80:275-282.

Khraisha YH (2002). Retorting of oil shale followed by solvent extraction of spent shale: experiment and kinetic analysis. Fuel. Ener. Abstr. 43:101-105.

Baba AA, Adekola FA, Fapojuwon DPT, Otokhina FO (2011). Dissolution kinetics and solvent extraction of lead from anglesite ore. J. Chem. Soc. Nig. 36:157-164.

Firestone D (2009). Official methods and recommended practices of the AOCS, (6th Ed.). Amer. Oil Chem. Soci.

Odeomelam SA (2005). Proximate, composition and selected physicochemical properties of African oil bean (Pentacle thrumarcrophile). PJN. 4:382 - 383.

Abayeh OJ, Ismail A, Abayeh OM (2011). Quality characteristics of pumpkin seed oil. J. Chem. Soci. Nig, 36:220-223.

Adelaja JO (2006). Evaluation of mineral constituents and physicochemical properties of some oil seeds. Electro. J. Env., Agric. Food Chem. 8:102-110.

Akanni MS, Adekunle SA, Oluyemi EA (2005). Physicochemical properties of some non-conventional oil seeds. J. Food Tech. 3:177-

181.
Jauro A, Oshieke KC, Adamu HM (2011). Extraction and characterisation of Pentaclethra macrophylla seed oil. J. Chem. Soci. Nig. 36:180-184.
Sodeke VA (2005). Extraction of oil from water melon seeds and analysis. Quart Resear. Serv. pp. 25-30.
Gunstone F (2004). The Chemistry of oils and fats: Sources, composition, properties and uses. Oxford UK. WileyBlackwel.
Eromosele IC, Eromosele CO, Innazo P, Njerim P (1998). Studies on some seeds and seed oils. Biores. Technol. 64:245-247.