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# Extraction Modeling, Nonlinear Kinetics, and Thermodynamics of Solvent Extraction of Neem Seeds Oil

John U. Sunday[1*], Igbokwe K. Philomena[1] and Nwabanne T. Joseph[1]
[1]Department of Chemical Engineering, Faculty of Engineering, Nnamdi Azikiwe University, Awka, Anambra State,Nigeria.
[*]CorrespondingAuthor's E-mail:su.john@unizik.edu.ng

**Abstract**
The oil extraction modeling, nonlinear kinetics, thermodynamics, and effects of process parameters on neem seed oil (NO) extraction were investigated via soxhlet extraction using ethanol. The nonlinear kinetic models of the power law, Elovich, parabolic-diffusion, and hyperbolic models were investigated. The process variables studied comprise, the extraction time, temperature, and average particle size. The thermodynamics parameters such as enthalpy, entropy, and Gibbs free energy were determined. The results revealed that oil yield increased with increase in temperature and time and decreased with increase in particle size. The maximum oil yield of 36.7% was recorded at 74 $^{o}$C, 0.1 mm, and 180 min. The best fitted kinetic models in order of performance were parabolic, power-law, elovich, and hyperbolic models. The average values of the sum of the squares of errors (SSE), root mean squared error (RMSE), coefficient of determination ($R^2$), and adjusted-coefficient of determination (adj-$R^2$) for parabolic-model as the best-fitted model is as follows: 4.538, 0.845, 0.971 and 0.965, respectively. The enthalpy, entropy, and Gibbs free energy values of the neem oil extraction process at 328K and 0.1mm were 28.74kJ/mol, 0.09kJ/mol, and -3.61kJ/mol, respectively, signifying irreversible, endothermic, and spontaneous-process.

**Keywords:**Nonlinear-kinetics, Thermodynamics, Empirical-models, Neem-seeds-oil, Statistical-model-analysis

## 1. Introduction

The growth and development of the oil extraction process and the vegetable oil sector at large are greatly significant due to their comparative benefit over petroleum base oils. Neem oil finds wide application in biofuel production, insecticides, pharmaceuticals, antiseptics, deodorants, flavor, perfumes, body soaps, body lotions, and beauty care facial packs, organic farming, and medicines, lubricants, drugs, cosmetics (soap, hair products, body hygiene creams, hand creams) and folklore traditional medicine, (in the cure of a broad range of afflictions), etc (Evbuomwan et al., 2015; Bereket and Tilahu, 2017). The neem nuts and seeds are the main vegetable oil resource exploited together for domestic, manufacturing, and industrial applications (Ahmad et al., 2011). Owing to the overall economic importance of the cultivation and industrial application of neem oil, the development and commercialization of the processes for both neem oil extraction and its industrial applications are extremely attractive and vital.

The kinetics and thermodynamics of the neem seeds-oil extraction process is a fundamental and vital pillar that informs and powers the commercialization and industrial application possibility (Kitanovic et al., 2008). The extensive investigation on the kinetics and thermodynamics of the neem oil extraction process is extremely significant due to its pivotal role in the neem oil extraction process and plant design, and development for industrial application. Numerous studies on oil extraction from neem oil-seeds such as Evbuomwan et al., 2015; Bereket and Tilahu, 2017; Usman et al., 2014; Radha and Manikandan, (2011); Banik et al., (2018); Magaji et al., (2018); Okoye et al., (2010); Adewoye and Ogunleye, (2012); Tanwar et al., (2013); Ochi et al., (2020); Bereket et al., (2018); Idris et al., (2018); Usman and Okonkwo, (2013); Solomon, (2018), and Awasthi and Shikha, (2019) have mainly concentrated on the oil yield determination and physicochemical characterization. Ulakpa et al., (2019); Yadessa and Jorge, (2017); Solomon, (2018); Ameh et al., (2013); Shruthi and Rahul, (2013); Radha and Manikandan, (2011); Banu et al., (2018);Banik et al., (2018); Magaji et al., (2018); Ochi et al., (2020); Tanwar et al., (2013); Usman et al., (2014); Idris et al., (2018); Awasthi and Shikha, (2019) studied the extraction and application of neem seeds oil in

the production of biofuel, alkyd resin, lubricating fluid, soap, and ecofriendly pesticides. None of these authors investigated the extraction kinetics and thermodynamics of neem oil extraction process. The neem seeds-oil extraction kinetics and thermodynamics studies have not received adequate attention. Liauw et al., (2008) and Tajane et al., (2017) modeled the kinetics of neem oil extraction from neem seeds and the kinetics of *Azadirachtin* extraction from whole neem fine powder formulation using a mass transfer equation. Their works were an exertion to force the oil extraction process to follow the designated mass transfer equation and feigned the oil extraction kinetics based on a mass transfer mechanism. Mass transfer coefficient was the only parameter determined to represent the extraction data with no specified statistical measure of fitness to the experimental data. However, the exact extraction kinetics and reaction mechanisms are multifaceted and incompletely comprehended, and hence, a very significant limitation to oil extraction process and plant design and development. Due to the complex heterogeneous nature of the oil extraction process and variety of real life experimental data, it's clumsy and inaccurate to use a simple linear relationship for description of the changing and trend of a process time series. A nonlinear function/modeling should be used for better description of real life process data (Yang et al., 2017) for potential design application.

Due to the importance of kinetics concerning the design and development of oil extraction processes and plants, a considerable number of physical and empirical kinetic models have been implied to investigate the kinetics of the oil extraction process for various oil seeds and nuts (Nwabanne, 2012; Agu and Agulanna, 2020; John et al., 2021). Normally, empirical kinetic models like Elovich's model, hyperbolic model, parabolic diffusion model, Peleg's model, Weibull's model, and power-law model, are leisurely, easier, simpler, and clearer than physical models, and therefore, more appropriate for engineering pushes (Agu and Agulanna, 2020; Yi and Mashitah, 2016). Currently, there is little or no published work existing on the neem seed oil extraction kinetics employing parabolic diffusion, hyperbolic, power-law, and elovich models. As a pivotal clincher and significant pillar for the attainable industrial application of neem oil, extensive and comprehensive oil extraction process kinetics and thermodynamics studies is a functionality that is fundamental to the development and commercialization of the oil extraction process and the vegetable oil sector at large. Hence, this study is geared toward the application of non-linear empirical kinetics models: parabolic, Elovich, power-law, and hyperbolic models to examine the kinetics of neem oil extraction using ethanol as a solvent medium. Also, the thermodynamic parameters: entropy, enthalpy, and Gibbs free energy were also determined.

## 2.0 Material and methods

### 2.1 Preparation of Feedstock

The removal of the seed-coat and husk, called seed cleaning, was the first step in the extraction of oil from neem seeds. This involved the elimination and separation of the seed coat or shell and chaff. The samples were sufficiently screened to eliminate and separate the spoilt or damaged seeds from the good ones. This was very essential to ensure the total elimination of debris from the seeds before oil extraction. Subsequently, the nuts were bashed and cracked. The oil-bearing seeds or kernels were sieved and separated, cleaned and dried by sun-drying or by heating carefully on the fire for a short while (Shruthi and Rahul, 2013), and stored at room temperature. The seeds were further dried at 65$^{o}$C for a reduction of the moisture content to 1.3%. The dried seeds were subsequently milled with an electric grinder and sieved with standard sieve plates into different average standard particle sizes (0.1 mm to 0.5 mm). Consequently, the crucial oil extraction process was commenced. The extraction solvent used was of analytical grade and required no further purification.

### 2.2.Neem Seed Oil Extraction

Soxhlet extraction was carried out using ethanol as the extracting solvent in a soxhlet apparatus. The dried neem seeds were crushed with a commercial grinder. 10g of milled neem seeds of specific average particle size and 150ml of extracting solvent were placed in a Soxhlet extractor fitted to a condenser. The extraction cycle was carried out at different temperatures (32–74 °C), average particle sizes (0.1–0.5 mm), and time (30 – 180 min). The percentage of extracted oil yield was determined and recorded at the end of each cycle of extraction. The residual solvent was separated and recovered from the extracted oil using a plain evaporation method or rotary evaporator, at 65 °C. The percentage oil yield of neem seeds was estimated as a ratio of the weight of extracted oil to the total weight of the seed sample using the eq. (1).

$$\text{Oil yield}(\%) = \frac{\text{weight of oil extracted (g)}}{\text{weight of seed sample (g)}} \text{x } 100 \qquad (1)$$

**2.3 One-Factor-At-a-Time Analysis**

The one-factor-at-a-time (OFAT) experiments for NO extraction using ethanol as solvent was designed and carried out in the batch form to examine the influence of extraction time, temperature, and particle size on the percentage oil yield. The range of variables studied were extraction temperature ($32^oC$ – $74^oC$), particle size (0.1mm – 0.5mm) and extraction time (30 – 180min). Fig. 1-2 summarizes the result of the effects of the different extraction process variables on the oil yield.

**2.4.Kinetic Models**

To investigate the kinetics of neem seeds oil extraction via ethanol route, the non-linear form of four kinetic models: power law, Elovich's, hyperbolic and parabolic diffusion were studied. The kinetic equations of the designated models were presented in Table 1.

**Table 1: Models and nonlinear equations**

| Kinetic models | Nonlinear equation | Equation parameters |
|---|---|---|
| Hyperbolic | $Y,(\%) = \frac{C_1 t}{1 + C_2}$ | Y = oil extraction yield<br>t = time (min)<br>$C_1$, $C_2$ acts for the initial extraction rate and rate constant for the maximum oil extraction yield ($min^{-1}$) |
| Parabolic diffusion | $Y,(\%) = A_0 + A_1 t^{1/2}$ | Ao, A1 denote parabolic diffusion model parameters;<br>Ao = washing coefficient (initial extraction rate)<br>A1= rate of diffusion constant ($min^{-1}$) |
| Elovich's | $Y,(\%) = E_0 + E_1 lnt$ | $E_o$ and $E_1$ represent Elovich model parameters relating initial rate and rate constant (L);<br>B = the power-law model parameter relating the extraction rate constant characteristic ($min^{-1}$). |
| Power law | $Y,(\%) = Bt^{1/2}$ | ½ = n, the power law exponential diffusion |

**2.5. Statistical Method**

The degree of statistical fitness of the kinetic models on the experimental data was determined by the examination of the sum of squares of the errors (SSE), the root mean squared error (RMSE), coefficient of determination ($R^2$), and adjusted-coefficient of determination (adj-$R^2$) (Kitanovic et al., 2008; Alirezaei et al., 2013; Riahi et al., 2013; Soroosh et al., 2019; John et al., 2021). The SSE, RMSE, $R^2$, and adj-$R^2$ were computed by applying the given eq. (2) - (5).

$$RSME = \sqrt{\frac{\sum\left[\frac{q_{exp\ (i)} - q_{model\ (i)}}{q_{exp\ (i)}}\right]^2}{n}} \quad (2)$$

$$R^2 = 1 - \frac{\sum(y_i - \hat{y})^2}{\sum(y_i - \overline{y})^2} \quad (3)$$

$$SSE = \frac{\sum_{i=0}^{n}(y_i - \hat{y})^2}{n} \quad (4)$$

$$Adj - R^2 = \frac{(1 - R^2)(N - 1)}{N - P_r - 1} \quad (5)$$

Where $y_i$ is the experimental response values, $\hat{y}$ = predicted response values, $\bar{y}_i$" denotes the mean predicted response values, n number of sample runs or data points, $P_r$ = number of predictors, N = Total sample size. Higher $R^2$ andadjusted- $R^2$,and lower RMSE and SSE values, indicate better goodness of fit (Kitanovic et al., 2008; Soroosh et al., 2019) and a fit that is more useful and convenient for prediction (John et al., 2021).

**2.6 Thermodynamics of Neem Oil Extraction**

To examine the feasibility and nature of the neem oil extraction process, the extraction thermodynamics parameters such as Gibs free energy, enthalpy, and entropy were determined from the given eq. (6) – (9).

$$\Delta G = -RT ln\, K \quad (6)$$

$$In\, K = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

Where K is the equilibrium constant, ΔS is the change in entropy (KJ/mol), ΔG is Gibbs energy or free energy (KJ/mol), ΔH is the change of enthalpy (KJ/mol), T is the temperature (K), R is Universal gas constant (8.314KJ/Kmol) (Silmara et al., 2015; John et al., 2021).

$$K = \frac{Y_{Te}}{Y_{Ue}} \quad (8)$$

Where $Y_{Te}$ is (%) yield of oil at temperature, T, and $Y_{ue}$ is the (%) oil unextracted. The plot of lnk against 1/T gives will give -ΔH/R as slope and ΔS/R as intercept, henceforth ΔS and ΔH were computed. These parameteric values were employed to determine ΔG* from eq. (9)

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

**3.0 Results and Discussions**

**3.1 Influence of Temperature and Time**

The oil extraction temperature and time variation impact on oil extraction yield was examined by carrying out experiments at different extraction temperatures of 32, 50, 55, 68, and 74$^o$C and time intervals of 30, 60, 105, 150, and 180 minutes at a particle size of 0.1mm. The result of the temperature variation influence on the oil extraction rate from neem seeds meal using ethanol as the solvent medium is presented in Figures 1. It is evident from Figure 1, that the fraction of recovered oil varied proportionally with an increase in temperature and time. The oil extraction yield was seen to increase with the increase in temperature up to 68$^o$C, after which further temperature increase resulted in no significant rise in the amount of recovered oil. The observed increase in yield of oil with an increase in temperature is a result of the fact that increase in temperature would result in enhanced extraction mass transfer coefficient, decreased viscosity of oil, increased diffusion, and improved oil extraction yield (Wang et al., 2008; Meziane and Kadi, 2008; Bimakar et al., 2011; Eikani et al., 2012; Sulaiman et al., 2013; Menkiti et al., 2015; John et al., 2021).Also, modicum temperature rise results in a bordering fluid density reduction which in twist leads to reduced solute solubility (Roop et al., 1989; Bimakar et al., 2011; Menkiti et al., 2015, John et al., 2021).

An initial rapid oil extraction process was recorded and later decelerated down at about 100 – 180minutes. This is in the similitude of Menkiti et al., (2015) findings in their report on extraction of oil from the seeds of Terminalia catappa *L* using n-hexane. In this study, the observed initial rapid oil extraction process is suggested to be due to the disposal of free oil to fresh solvent at the surface of milled neem seed. The vulnerability of the free oil at the surface of neem seed particles caused the oil to be readily soluble in the solvent, and thereby leading to fast oil extraction (Reverchon and Marrone, 2001; Sulaiman et al., 2013; Amin et al., 2010; Sayyar et al., 2009; John et al., 2021). Generally, the initial rapid rate and final decelerated rate of yields observed with extraction could be clarified by initial fast washing action and slow diffusion controlled regimes, respectively (Kitanovic et al., 2008; Amin et al., 2010; Sayyar et al., 2009). The maximum percentage oil extraction of 36.70% was recorded at the temperature of 74$^o$C and time of 150 min.

### 3.2 Influence of Particle Size

The starting material characteristics like the particle size, generally, influence the oil extraction process (Sulaiman et al., 2013; Desai et al., 2014, Menkiti et al., 2015; John et al., 2021). The particle size is comparative to the surface area of reaction and thus a very significant factor of interest in neem oil extraction study.Hence,the neem-oilseed particle size variation impact on oil extraction yield was investigated by conducting experiments at different neem seed particle sizes of 0.1, 0.15, 0.3, 0.45, and 0.5mm and time intervals of 30, 60, 105, 150, and 180 minutes at the extraction temperature of 68$^{o}$C. The effect of particle size variation findings on the rate of oil extracted from neem seeds meal using ethanol as the solvent medium is presented in Figures 2. The Figure reveals that the percentage of neem-oil extracted with time decreased as the particle size of the neem seed meals was increased. It's evident from the plotted results, that higher oil yields were attained at smaller particle sizes, while lower oil yields were achieved at bigger particle sizes. The higher and lower oil yield observed at smaller and bigger particle sizes, respectively, is attributed to the higher surface area possessed by the smaller particle sizes than the bigger particle sizes. Generally, an increase in oil yield with increasing particle size is bound to a bigger interfacial area of the solid particles which results in lesser intraparticle diffusion resistance for the smaller particle sizes as a result of a shorter diffusion path. The decrease in oil yield is pronounced in bigger particle sizes due to the high intra-particle diffusion domicile in bigger particles. This was experimentally observed because not all the oil was extracted in the larger particle sizes owing to small contact surface area and minimal oil diffusion from the pores of the larger particles to the bulk of solvent. On the other hand, greater milling increases the surface area of the resultant smaller particle sizes, thus, increasing the rate of oil extraction by freeing more oil from cells and getting them easily disposed to solvent for extraction. This phenomenon was observed clearly in this study as the rate of extraction of oil from neem seed meals at smaller particle sizes were more rapid than the larger particles, due to reduced diffusion path, higher rate of mass transfer, and a higher rate of oil dissolution in solvent (Louli et al., 2004; Kriamiti et al., 2002; Ozkal et al., 2005; Xue et al., 2009; Menkiti et al., 2015; John et al., 2021). The maximum oil extraction of 36.70% was achieved using the particle size of 0.1mm at 180 minutes.

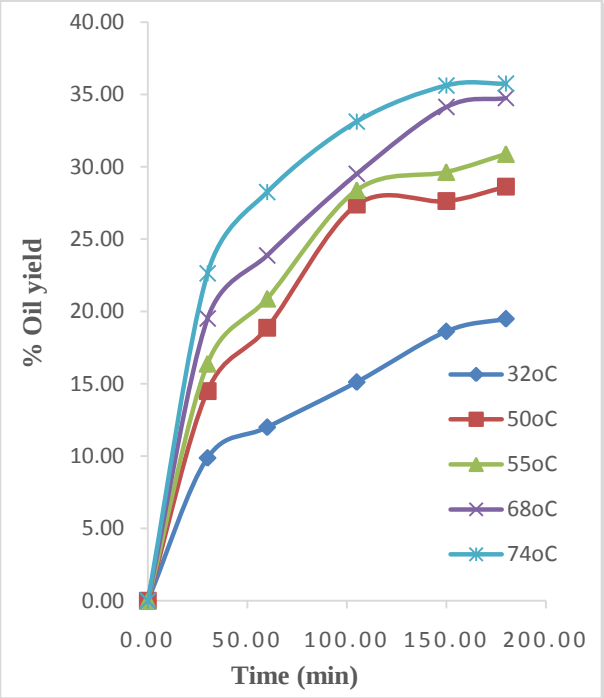


**Figure 1: Effect of temperature variation on % oil yield**

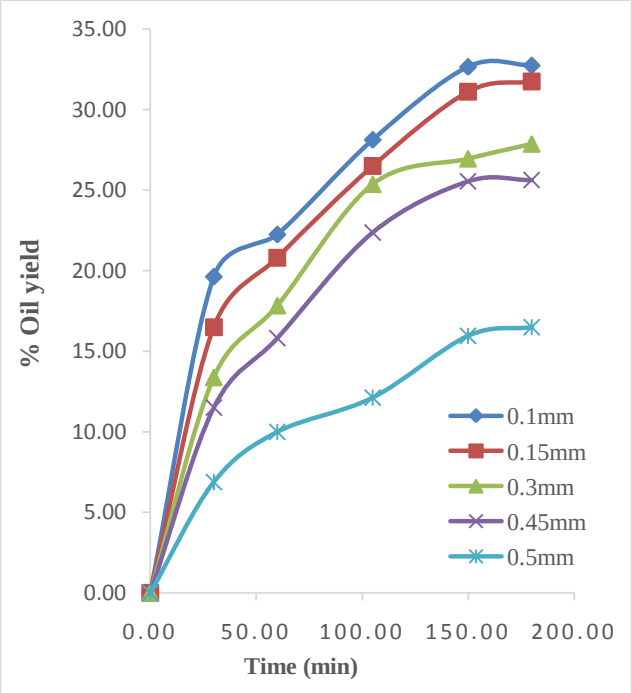


**Figure 2: Effect of particle size variation on % oil yield**

### 3.3 Kinetic Parameters

The result of the nonlinear kinetic parameters values for the four nonlinear kinetic models of power-law, parabolic diffusion models, hyperbolic, and Elovich's models, respectively, studied at different temperature and particle size variation for NO extraction using ethanol as extraction solvent are presented in Table 4. It was observed that the parameters C1 and C2 for the hyperbolic model varied proportionally with increasing temperature but varied

inversely with increasing particle size. The increase in C1 and C2 observed with increase in temperature and decrease in particle size is associated with an improved yield of neem oil recorded with increasing temperature and decreasing particle sizes, and the insignificant recorded differences between the models' predicted oil yields and the experimental values. The observed trend of C1 and C2 observed across the temperature and particle size regimes signify a high initial rate and overall oil recovery at high temperatures and smaller particle sizes. This is consistent with the report of John et al., (2021) on kinetic and parametric studies of jatropha oil extraction. A similar trend was observed to be consistent for parabolic diffusion, power-law, and Elovich kinetic model parameters. The A1, Ao, B, E1, and Eoparameters for parabolic diffusion, power-law, and Elovich kinetic models were found to maintain consistent increase with increasing temperature and decreasing particle sizes. A similar pattern of results was observed in the study of Kitanovic et al., (2008) and Agu et al., (2018) for the solvent extraction of resinoid from the aerial part of *Hypericum perforatum* L using different solute to solvent ratios and Colocynthis vulgaris Shrad Seeds oil (CVSSO) extraction using solvent extraction method, respectively. The power-law parameters: n and B were observed to vary directly proportional with temperature and inversely proportional with particle size variations, respectively.

The hyperbolic, parabolic, and Elovich parameter values of C1, Ao, and E1 were found to be higher than the corresponding parameter values of C2, A1, and Eo, respectively. This is in agreement with the parameter values reported by Kitanovic et al., (2008), and Yi et al., (2016). However, the C1 values recorded in this work were slightly (-0.1 or -0.2) lower than the C1 values reported by Agu et al., (2018), and Menkiti et al., (2015, 2016), while the C2 values obtained in this study were (+0.1 or 0.2) higher than the C2 values reported by the same authors. On the other hand, the C1 and C2 values from this study across all temperature and particle size variations were found to be comparably approximate with the ones reported by Kadurumba et al., (2018) on solvent extraction of oil from Colocynthis vulgaris Shrad (melon) seeds. The higher or lower values of C1 and C2 as reported by the various authors implies, higher or lower initial rapid oil extraction rate and final slow diffusion rate action, respectively, for oil extraction from different seeds studied. Hence, the variation in the initial rapid rate and final slow rate yields reported by the various authors could be explained by initial fast washing action and slow diffusion controlled regimes, respectively.

On the other hand, the power-law parameter, n, was found to vary inversely proportional with temperature variation and directly proportional with particle size variation. Generally, the observed consistent increase of the kinetic parameter values with temperature is attributed to the prevalence and power of diffusion rate above the washing mechanism process, therefore, leads to better/greater oil extraction yield in the models (Menkiti et al., 2015; Linares et al., 2010; Agu et al., 2018; John et al., 2021). Likewise, the consistent increase of the kinetic parameters with decreasing particle sizes is correspondent to the higher and lower oil yield achieved at smaller and bigger particle sizes, respectively. This is ascribed to the higher surface area possessed by the smaller particle sizes than the bigger particle sizes. This prodigy was observed clearly in this study as the rate of extraction of oil from neem seed meals at smaller particle sizes were more rapid than the larger particles, due to reduced diffusion path, higher rate of mass transfer, and a higher rate of oil dissolution in the solvent.

**Table 2: Extraction kinetic parameters at different temperature and particle sizes**

| | Temperature (°C) | | | | | | Particle size (mm) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **32 (°C)** | **50 (°C)** | **55 (°C)** | **68 (°C)** | **74 (°C)** | **Temp. Ave.** | **0.1mm** | **0.15mm** | **0.3mm** | **0.45mm** | **0.5mm** | **Part. Size Ave.** | **Total Ave.** |
| **HYPERBOLIC** | | | | | | | | | | | | | |
| C1 | 0.435 | 0.735 | 0.850 | 1.049 | 1.462 | 0.906 | 1.128 | 0.795 | 0.629 | 0.524 | 0.245 | 0.664 | 0.785 |
| C2 | 0.018 | 0.020 | 0.022 | 0.026 | 0.038 | 0.025 | 0.031 | 0.021 | 0.017 | 0.015 | 0.010 | 0.019 | 0.022 |
| **PARABOLIC DIFFUSION** | | | | | | | | | | | | | |
| A1 | 1.210 | 1.861 | 1.878 | 1.949 | 1.687 | 1.717 | 1.687 | 1.949 | 1.878 | 1.846 | 2.021 | 1.876 | 1.797 |
| Ao | 2.814 | 5.042 | 6.512 | 8.677 | 12.750 | 7.159 | 9.751 | 5.680 | 3.516 | 1.670 | -0.181 | 4.087 | 5.623 |
| **ELOVICH** | | | | | | | | | | | | | |
| E1 | 5.234 | 8.339 | 8.335 | 8.523 | 7.311 | 7.548 | 7.311 | 8.523 | 8.335 | 8.199 | 5.233 | 7.520 | 7.534 |
| Eo | -8.819 | -14.160 | -12.500 | -10.470 | -3.530 | -9.896 | -6.524 | -13.470 | -15.49 | -16.850 | -11.81 | -12.829 | -11.362 |
| **POWER LAW** | | | | | | | | | | | | | 0.000 |
| B | 2.360 | 4.169 | 4.898 | 6.087 | 8.574 | 5.218 | 6.599 | 4.438 | 3.398 | 2.785 | 1.095 | 3.663 | 4.440 |
| n | 0.401 | 0.378 | 0.358 | 0.334 | 0.271 | 0.349 | 0.305 | 0.378 | 0.410 | 0.436 | 0.518 | 0.409 | 0.379 |

### 3.4 Comparative Statistical Fitness Degree for the Kinetics Models

This section presents the statistical degree of fitness for different non-linear kinetic models investigated for the kinetics of NO extraction using ethanol as solvent. The optimal criteria required for the determination of the best

fitness of the kinetic models (hyperbolic, parabolic diffusion, power-law, and Elovich's) to the experimental data were SSE, $R^2$, Adj-$R^2$, RMSE. Usually, higher values of $R^2$ and Adj-$R^2$, and lower values of RMSE and SSE, would indicate better model goodness of fit to the experimental data (Menkiti et al., 2015; Kitanovic et al., 2008, Agu et al., 2018, Alirezaei et al., 2013, Soroosh et al., 2019, John et al., 2021). The results of the statistical fitness degree for thefour kinetic models studied were presented in Table 3. From the table, the SSE and RSME were found to decrease with increasing temperature while the $R^2$ and adjusted-$R^2$ varied directly proportional with temperature for power-law, elovich, parabolic and hyperbolic models. The observed trend of the $R^2$ and adjusted-$R^2$ results illustrates the capability of the models to account for a greater proportion of total variation in the data about the average and that oil recovery increases with increasing temperature and decreasing particle sizes. That is, the lower or decreasing values of SSE and RSME and higher values of $R^2$ and adjusted-$R^2$ at higher temperature regime and smaller particle sizes indicates higher oil yield at higher temperatures regime and smaller particle sizes. The observed trend of SSE and RSME for the nonlinear kinetic models is an indication of the models' more usefulness and convenience for prediction (John et al., 2021).

However, it could be seen that the total average values of SSE (9.55, 4.54, 6.58, and 5.40) and RMSE (1.36, 0.845, 1.135, and 0.951) were estimated for hyperbolic, parabolic, elovich, and power-law models, respectively. The $R^2$ and Adj-$R^2$ values of the kinetic models in descending order were parabolic (0.971, 0.965), power-law (0.964, 0.957), elovich (0.951, 0.941), and hyperbolic (0.929, 0.914). The values of average SSE, RMSE, $R^2$, and Adj-$R^2$ show that the nonlinear kinetic models: hyperbolic, parabolic, elovich, and power law, gave a good fit to the experimental data. Based on the average SSE, RMSE, $R^2$, and Adj-$R^2$ values of the kinetic models investigated, their degree of fitness to the experimental data in ascending order is presented as given: hyperbolic → elovich → power-law → parabolic. The power-law and parabolic models having the highest and approximate $R^2$and adj-$R^2$, and lowest average SSE and RMSE values were chosen concurrently as the extraction kinetic models that best fit the experimental kinetics data investigated.

**Table 3: Statistical fitness degree for the different extraction kinetic models**

| | Temperature (°C) | | | | | | Particle size (mm) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Parameter** | **32°C** | **50°C** | **55°C** | **68°C** | **74°C** | **Temp Ave** | **0.1mm** | **0.15mm** | **0.3mm** | **0.45mm** | **0.5mm** | Part.Size (Ave.) | **Total Ave.** |
| **HYPERBOLIC** | | | | | | | | | | | | | |
| SSE | 15.055 | 12.391 | 9.724 | 9.710 | 5.233 | 10.423 | 13.556 | 10.422 | 8.590 | 7.822 | 3.025 | 8.683 | 9.553 |
| $R^2$ | 0.880 | 0.919 | 0.926 | 0.940 | 0.941 | 0.921 | 0.891 | 0.938 | 0.947 | 0.952 | 0.953 | 0.936 | 0.929 |
| Adj-$R^2$ | 0.855 | 0.902 | 0.911 | 0.928 | 0.929 | 0.905 | 0.870 | 0.925 | 0.936 | 0.943 | 0.944 | 0.924 | 0.914 |
| RMSE | 1.735 | 1.574 | 1.395 | 1.394 | 1.023 | 1.424 | 1.647 | 1.444 | 1.311 | 1.251 | 0.778 | 1.286 | 1.355 |
| **PARABOLIC** | | | | | | | | | | | | | |
| SSE | 13.588 | 8.618 | 2.328 | 1.183 | 0.647 | 5.273 | 1.185 | 2.327 | 8.623 | 6.237 | 0.645 | 3.803 | 4.538 |
| $R^2$ | 0.917 | 0.947 | 0.986 | 0.990 | 0.991 | 0.966 | 0.991 | 0.986 | 0.947 | 0.962 | 0.990 | 0.975 | 0.971 |
| Adj-$R^2$ | 0.901 | 0.936 | 0.983 | 0.988 | 0.989 | 0.959 | 0.989 | 0.983 | 0.936 | 0.954 | 0.988 | 0.970 | 0.965 |
| RMSE | 1.649 | 1.313 | 0.682 | 0.486 | 0.360 | 0.898 | 0.487 | 0.682 | 1.313 | 1.117 | 0.359 | 0.792 | 0.845 |
| **ELOVICH** | | | | | | | | | | | | | |
| SSE | 9.967 | 7.960 | 6.518 | 6.471 | 3.555 | 6.894 | 6.470 | 6.507 | 7.972 | 6.789 | 3.549 | 6.257 | 6.576 |
| $R^2$ | 0.939 | 0.945 | 0.948 | 0.951 | 0.961 | 0.949 | 0.948 | 0.961 | 0.951 | 0.959 | 0.945 | 0.953 | 0.951 |
| Adj-$R^2$ | 0.927 | 0.934 | 0.938 | 0.941 | 0.953 | 0.939 | 0.938 | 0.953 | 0.941 | 0.950 | 0.934 | 0.943 | 0.941 |
| RMSE | 1.412 | 1.262 | 1.142 | 1.138 | 0.843 | 1.159 | 1.138 | 1.141 | 1.263 | 1.165 | 0.843 | 1.110 | 1.135 |
| **POWER LAW** | | | | | | | | | | | | | |
| SSE | 12.139 | 7.788 | 3.031 | 3.018 | 1.047 | 5.405 | 2.700 | 2.764 | 8.046 | 12.829 | 0.600 | 5.388 | 5.396 |
| $R^2$ | 0.926 | 0.952 | 0.976 | 0.982 | 0.984 | 0.964 | 0.978 | 0.984 | 0.950 | 0.922 | 0.991 | 0.965 | 0.964 |
| Adj-$R^2$ | 0.911 | 0.942 | 0.971 | 0.978 | 0.980 | 0.957 | 0.974 | 0.980 | 0.940 | 0.906 | 0.989 | 0.958 | 0.957 |
| RMSE | 1.558 | 1.248 | 0.779 | 0.777 | 0.458 | 0.964 | 0.735 | 0.743 | 1.269 | 1.602 | 0.346 | 0.939 | 0.951 |

### 3.5 Thermodynamics Parameters

The thermodynamics parameters and the equilibrium constant for neem seeds oil extraction with ethanol solvent are shown in Table 4. The plots of In K against 1/T for the different particle sizes (0.1, 0.3, and 0.45 mm) used for the estimation of the thermodynamics parameters values were presented in Figure 3. The determined enthalpy values for

the oil extraction process ranged between 29.74 – 28.70 kJ/mol for the different particle sizes. The enthalpy results obtained in this work are higher than (14.27 – 18.60 KJ/mol) reported by Silmara et al., (2015), for oil extraction from Jatropha curcasL. using ethanol as a solvent. Also, Meziane and Kadi (2008) reported a lower enthalpy value of (4 - 13.5 kJ/mol) for olive cake oil. The observed variation may be explained by the morphology of the different seeds which could affect the extraction of oil. The positive enthalpy value is an indication that the oil extraction is an endothermic process. Therefore, external energy input is needed for an efficient extraction process (Sulaiman et al., 2013; Amin et al., 2010; Silmara et al., 2015). However, the obtained enthalpy results are incomparable agreement with the values reported by Amin et al., (2010) and Rodrigues et al., (2010) for JatrophaCurcas oil extraction in aqueous acidic hexane solutions and soybean oil extraction process using a renewable solvent.

Furthermore, in all cases, the values of differential entropy were observed to be positive. This is an indication of the irreversibility of the process and a rise in the molecular disorder degree during the extraction process. The increase in disorder of the extraction process is attributed to the mixing of two different matters/substances (Johnson and Lusas 1983; Silmara et al., 2015). Other researchers like Meziane and Kadi, (2008); Sayyar et al., (2009); Liauw et al., (2008); Amin et al., (2010); Sulaiman et al., (2013); Perez et al., (2011); Topallar and Gec¸gel, (2000); Kosti´c et al., (2014) and Silmara et al., (2015) reported similar observations in their experiments for extraction of oil processes from different oilseed raw materials, irrespective of the extraction solvent employed. On the other hand, the entropy values for neem oil extraction using ethanol ranged between 0.09 and 0.08 kJ/mol. This is in close agreement with the entropy values reported by Meziane and Kadi (2008), Topallar and Gec¸gel, (2000), and Silmara et al., (2015). The values of mixture entropy were all positive in all cases and varied inversely with the increase in the particle size, due to oil molecules extraction. This indicates the irreversibility of the oil extraction process. This is consistent with the observations of different authors such as Sulaiman et al., (2013); Meziane and Kadi (2008); Menkiti et al., (2015), Amin et al., (2010), Topallar and Gecgel (2000), Agu et al., 2018; Silmara et al., (2015) and John et al., (2021).

Gibbs free energy change ($\Delta G\circ$) values recorded for the oil extraction were found to be negative, indicating feasibility and spontaneity of the extraction process under the experimental conditions studied. The comparatively high negative values of Gibbs free energy change suggest that the oil extraction process was highly spontaneous (Sulaiman et al., 2013; Agu et al., 2018, Menkiti et al., 2015, Silmara et al., 2015; John et al., 2021). Conclusively, it is evident from the thermodynamic study results, that the energy necessary to destroy the solid-solid and liquid-liquid bonds and interactions were smaller than the energy released in solid-liquid interaction (John et al., 2021; Sulaiman et al., 2013; Silmara et al., 2015). Hence, the larger the particle sizes the further away the process is from spontaneity (Silmara et al., 2015; John et al., 2021).

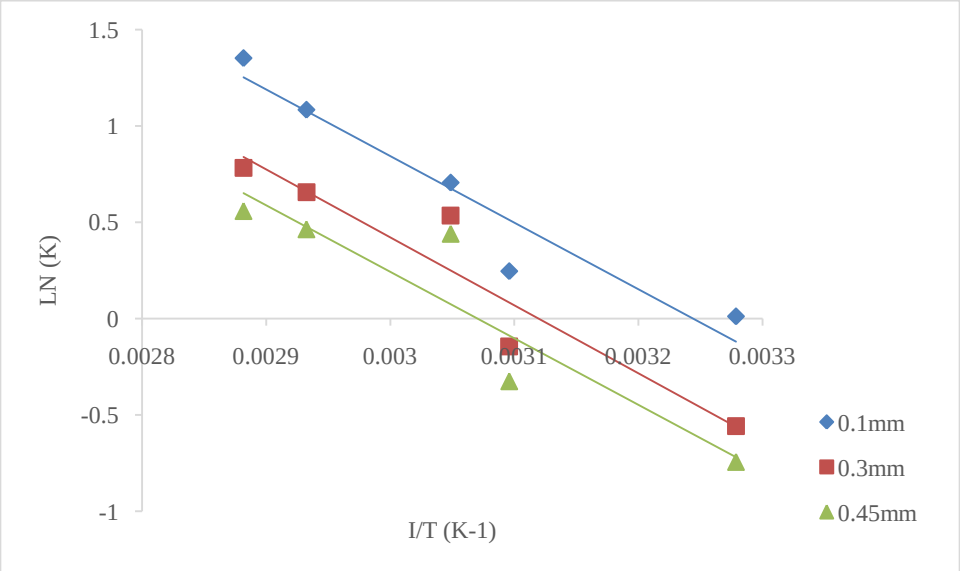


**Figure 3: Plot of In K (equilibrium constant) vs. 1/T (temperature, $K^{-1}$) for different particle sizes**

**Table 4: Thermodynamic parameters**

| | 0.1mm | | | | 0.3mm | | | | 0.45mm | | | | | Average | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp (K) | ΔG (KJ/mol) | K (KJ/mol) | (Δ)H (KJ/mol) | ΔS (KJ/mol.K) | ΔG (KJ/mol) | K (KJ/mol) | ΔH (KJ/mol) | ΔS (KJ/mol.K) | ΔG (KJ/mol) | K (KJ/mol) | ΔH (KJ/mol) | ΔS (KJ/mol.K) | Ave. ΔG (KJ/mol) | Ave. K (KJ/mol) | Ave. ΔH (KJ/mol) | Ave. ΔS (KJ/mol.K) |
| 305 | 0.30 | 1.01 | 28.74 | 0.09 | 1.43 | 0.57 | 29.35 | 0.09 | 1.82 | 0.48 | 28.70 | 0.09 | 1.18 | 0.69 | 28.93 | 0.09 |
| 323 | -1.37 | 1.28 | | | -0.22 | 0.87 | | | 0.24 | 0.72 | | | -0.45 | 0.96 | | |
| 328 | -1.84 | 2.03 | | | -0.68 | 1.71 | | | -0.20 | 1.55 | | | -0.91 | 1.76 | | |
| 341 | -3.05 | 2.96 | | | -1.87 | 1.93 | | | -1.35 | 1.59 | | | -2.09 | 2.16 | | |
| 347 | -3.61 | 3.86 | | | -2.42 | 2.19 | | | -1.88 | 1.75 | | | -2.64 | 2.60 | | |

## 4.0. Conclusion

It could be decisively affirmed from this work that the neem seeds oil extraction kinetics has been determined to proceed through the initial rapid washing action and final decelerated diffusion phase as established in the kinetic analysis. The yield of oil varied proportionally with increasing temperature and time but varied inversely with an increase in particle size. The maximum oil yield of 36.70% was recorded at 74 °C, 0.1mm, and 150 min. The relative statistical degree of fitness for the four nonlinear kinetic models showed that elovich, parabolic, power law, and hyperbolic models fitted the experimental data well, as affirmed by their low average values of RMSE and SSE, and high average values of $R^2$ and adjusted-$R^2$. Hence, the tested nonlinear kinetic models could dish up as vital and significant base equations for plant and process design pushes. Conclusively, the determined thermodynamics parameters values for enthalpy change (ΔH), Gibbs free energy (ΔG), and entropy change (ΔS) at the different oil extraction process acclimatization indicate the spontaneity, irreversibility, and endothermic nature of the neem oil extraction process.

## 5.0 Recommendation

Ethanol is recommended for solvent extraction of neem seed oil and other seed/nuts oil due to the comparatively high yield recorded. Nonlinear kinetic models are recommended for extraction kinetic modeling due to the overall comparative fitness to the experimental data. However, the parabolic diffusion model is highly recommended for oil kinetic modeling because it gave the best fit to the extraction kinetic data. The tested nonlinear kinetic models and thermodynamic parameters are highly recommended for plant and process design pushes as vital and significant base equations.

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