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PARAMETRIC, NONLINEAR KINETIC AND THERMODYNAMIC MODELING OF PETROLEUM ETHER-BASED NEEM SEED OIL EXTRACTION PROCESS

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Abstract

The parametric, thermodynamic, and nonlinear kinetic modeling and the impacts of process factors on the Neem oil extraction process were studied using petroleum ether as solvent. Power law, pseudo-second-order, parabolic-diffusion, pseudo-first-order, Elovich, and hyperbolic models were the kinetic models examined. Process parameters such as average particle size, time, and temperature of the oil extraction were studied. The parameters of thermodynamics, including enthalpy, entropy, and Gibb free energy, were determined. It was discovered that while the yield of oil extraction varied inversely with an increase in particle size, it varied directly with increases in temperature and time. At 74 ^oC, 0.1 mm, and 180 minutes throughout the extraction process, the highest oil yield of 38.8% was achieved. In terms of performance, the hyperbolic, parabolic, elovich, and power-law models gave an excellent fitting to the experimental data. The models that best fitted the experimental kinetics data under investigation were the power-law and parabolic models, which concurrently had the lowest average SSE and RMSE values, and the highest R^2 and adj- R^2. Pseudo-first- and pseudo-second-order models, however, failed to provide a sufficient fit for the experimental data. The endothermic, irreversible, and spontaneous nature of the Neem oil extraction process was shown by the average Gibb free energy, enthalpy, and entropy values of the process at 328K and 0.1mm, which were -1.54kJ/mol, 30.13kJ/mol, and 0.10kJ/mol, respectively.

Keywords: kinetics, thermodynamics, empirical-models, neem-seeds-oil, petroleum-ether, statistical-model-analysis

INTRODUCTION

The nuts and seeds from plants are the main vegetable oil resource utilized for both home and industrial uses. The growth of the vegetable oil sector and the oil extraction process is incredibly lucrative and significant due to its relative advantage over petroleum-based oils (S. . John et al., 2021b, 2021a, 2023; Marasabessy & Moeis, 2011). The development and commercialization of the techniques for both Neem oil extraction and its industrial applications are highly desirable and important, given the overall economic significance of Neem oil cultivation and its industrial applications. Nigeria is endowed with suitable agroecology for Neem (Azadirachta indica) resources which serves as an excellent resource employed by the government to accomplish both goals of extensive investment in afforestation and reforestation initiatives for desertification management and revenue production to fund socio-economic and physical services. However, a critical study of the economics and the potential of its cultivation, production and resource development is yet crucial (Muhammad et al., 2020).

The fundamental principles of kinetics and thermodynamics in the oil extraction process catalyze the potential industrial application and commercialization of neem seed oil (S. . John et al., 2021b, 2021a; Kitanovic S., Milenovic D., Veeljkovic V.B., 2008). Because it is essential to the design and development of the oil extraction process and plant for industrial use, the in-depth study of the thermodynamics and kinetics of the oil extraction process from Neem seeds is highly significant. The assessment of oil yield and physicochemical characterization have been the main focus of several investigations on oil extraction from Neem seeds (S. John et al., 2021a, 2021b; U. S. John & John, 2015; Kumar et al., 2018; Marasabessy & Moeis, 2011; Ndasi et al., 2018; Rodríguez-acosta et al., 2010; Shalini, 2013; Suwito et al., 2012; Yaduvanshi & Patel, 2019; Yahaya et al., 2016). As a result, not much research has been done on the kinetics and thermodynamics of extracting oil from neem seeds.

However, the kinetics of extracting nut and seed oil have not been well studied by many researchers (Amin et al., 2010; Bispo et al., 2015; S. . John et al., 2021b, 2021a; Sayyar et al., 2009). Amin et al., (2010) reported that the reaction order was first-order kinetics after using the differential approach to ascertain the order of reaction. Sayyar et al., (2009) and Silmara et al., (2015) used a pseudo-second-order model to simulate the kinetics of oil extraction in their independent investigation. Their studies assumed that the kinetics of oil extraction were based on a second-order mechanism and attempted to compel the extraction process to adhere to the chosen pseudo-second-order model. On the other hand, John et al., (2021a, 2021b) in their study on oil extraction kinetics reported the inadequacy of the pseudo-first and second-order to give a sufficient fit to the experimental extraction kinetic data. Additionally, there is a major barrier to the design and development of oil extraction plants and processes since the precise extraction kinetics and reaction mechanisms are complicated and only partially understood.

Due to the significant role of kinetics in the oil extraction process, several physical and empirical models have been put forward to investigate the kinetics of the oil extraction process for a variety of oil seeds and nuts, including but not limited to olive cake, sunflower, sunflower collets, Terminalia catappa, rapeseed, Colocynthis vulgaris Schrad, and fluted pumpkin (Agu & Agulanna, 2020; Agu, Kadurumba, Orakwue, et al., 2018; Menkiti et al., 2015; Nwabanne, 2012; Perez et al., n.d., 2011). Generally, the empirical models—such as the hyperbolic model, Elovich's model, Peleg's model, parabolic diffusion model, power-law model, Weibull's model, pseudo-first-order, and pseudo-second-order models—are simpler, easier to comprehend, and less complex and therefore more suited for engineering drive (S. . John et al., 2021b, 2021a).

The kinetics of extracting neem seed oil using various models such as hyperbolic, parabolic diffusion, Elovich, and pseudo-first-order have not received much attention in published literature. Conducting comprehensive studies on the kinetics and thermodynamics of the oil extraction process from seeds and nuts is crucial for the development, industrialization, and commercialization of the extraction process, and the vegetable oil sector. This is a significant barrier that needs to be overcome to make the industrial application of neem oil feasible (S. . John et al., 2021b, 2021a). To better understand the kinetics of petroleum ether-based Neem oil extraction process, this work focuses on the application of non-linear empirical models (such as power law, parabolic, Elovich, hyperbolic, pseudo-second-order, and pseudo-first-order) to study the nonlinear kinetic, thermodynamic and impact of process factors on petroleum ether-based Neem seed oil extraction process. In addition, the values of the thermodynamic parameters (entropy, enthalpy, and Gibb free energy) were established.

Materials and Methods

Feedstock preparation

The first stage in extracting oil from Neem seeds is known as "seed cleaning," which involves removing the husk and seed coat. Cleaning seeds entails removing the shell or seed coat and separating the chaff. Sufficient screening was carried out on the seed samples to eliminate any spoiled or damaged seeds and clean the remaining viable ones. To make sure that no debris remained in the seeds once the oil was extracted, this was extremely important. The oil-bearing seeds or kernels were separated after the nuts were cracked, cleaned, dried, and kept at room temperature. To remove moisture, seeds were dried in the sun and by carefully heating them over a little fire (Heroor & Bharadwaj, 2013; S. John et al., 2021b, 2021a). Subsequently, more drying of the seeds was done at 65 °C in the oven to lower the moisture content to 1.3%. An electric grinder was used to grind the dried seeds. Using standard sieve plates, the ground seeds were separated into various average standard particle sizes (0.1 mm to 0.5 mm). The critical extraction procedure was started once this was finished. The analytical-grade extraction solvents were utilized without additional purification.

Extraction of neem seed oil

Petroleum ether was used as the extracting solvent in a soxhlet apparatus to perform soxhlet extraction. A commercial grinder was used to crush the dried Neem seeds. A predetermined 100ml of extracting solvent and ground neem seeds with a specific average particle size was added to a Soxhlet extractor that was attached to a condenser. The extraction cycle was run for 30 to 180 minutes at various temperatures (32 to 74 °C) and average particle sizes (0.1 to 0.5 mm). A straightforward evaporation technique was used to extract or evaporate the leftover solvent at 65 °C. The weight of the extracted oil was divided by the weight of neem seeds to find the percentage oil output of the Neem seeds using the equation (1):

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

One-factor-at-a-time analysis

In order to investigate the effects of extraction duration, temperature, and particle size on the percentage oil, batch-form one-factor-at-a-time (OFAT) experiments for Neem oil extraction using petroleum ether as solvent was devised and executed. Three different parameters were examined: extraction time (30–180min), particle size (0.1–0.5mm), and temperature (32–74^{o}C). The summary of the result of the impacts of the different extraction operating variables on the yield of oil is presented in Figures 1 - 2.

Kinetic models

Six kinetic models were studied in order to examine the kinetics of the petroleum ether-based Neem seed oil extraction process: power law, Elovich's, hyperbolic, parabolic diffusion, pseudo-first-order, and pseudo-second-order models. Table 1 displays the kinetic equations for the previously described models.

Table 1: Plotting characteristics, model names, and prediction equations for linear, and nonlinear frameworks

Kinetic models	Nonlinear equation	Linear equation	Linear predicted response	Linear plot	Slope	Intercept
Pseudo 1st order	$Y, (\%) = \frac{d(q_t)}{dt} = K(q_e - q_t)$	$Ln(q_e - q_t) = Inq_e - Kt$	$q_t = q_e - \exp(Inq_e - Kt)$	$Ln(q_e - q_t)$ VS t	-K	Inq_e
Pseudo 2nd order	$Y, (\%) = \frac{q_e{}^2Kt}{1 + q_eKt}$	$\frac{t}{q_t} = \frac{1}{Kq_e{}^2} + \frac{t}{q_e}$ $\frac{1}{h} = \frac{1}{Kq_e{}^2}$	$q_t = \frac{t}{(\frac{1}{Kq_e{}^2} + \frac{t}{q_e})}$	$\frac{t}{q_t}$ VS t	$\frac{1}{q_e}$	$\frac{1}{Kq_e{}^2}$
Hyperbolic	$Y, (\%) = \frac{C_1t}{1 + C_2}t$	$\frac{1}{Y}(\%) = \frac{1}{C_1} X \frac{1}{t} + \frac{C_2}{C_1}$	$Y, (\%) = \frac{1}{\left(\frac{1}{C_1} X \frac{1}{t} + \frac{C_2}{C_1}\right)}$	$\frac{1}{Y}(\%)$ VS $\frac{1}{t}$	$\frac{1}{C_1}$	$\frac{C_2}{C_1}$
Parabolic diffusion	$Y, (\%) = A_0 + A_1t^{1/2}$	$Y, (\%) = A_0 + A_1 lnt$	$Y, (\%) = A_0 + A_1 lnt$	Y, (%)VS lnt	A_1	A_0
Elovich's	$Y, (\%) = E_0 + E_1 lnt$	$Y, (\%) = E_0 + E_1 lnt$	$Y, (\%) = E_0 + E_1 lnt$	Y, (%)VS lnt	E_1	E_0
Power law	$Y (\%) = Bt^{1/2}$	$InY (\%) = InB + nLnt$	$Y, (\%) = \exp(InB + nLnt)$	InY (%) VS Lnt	n	InB

The pseudo-first and second-order model oil concentration parameter in the mixture extract (gL^{-1}) is represented by the initial extraction rate, h = Kq_e; A_0 , A_1 symbolize parabolic diffusion model parameters; washing coefficient (initial extraction rate) and rate of diffusion constant (min-1), respectively. E_0 and E_1

represent Elovich model parameters related to initial rate and rate constant (L); n = power law exponential diffusion; K = rate constant. The power law model parameter B is related to the characteristic of the extraction rate constant (min^{-1}). qe, qt, equilibrium extraction capacity or yield (mmol/g), and extraction capacity at a time t, respectively. C_1 and C_2 are the initial extraction rate and rate constant for the maximum oil extraction yield (min^{-1}), Y" oil extraction yield, and t = time (min).

Statistical Method

The evaluation of the root mean squared error (RMSE), coefficient of determination (R^2), adjusted coefficient of determination (adj-R^2), absolute average relative error (AARE), hybrid fractional error function (HYBRID%), the sum of squares of the errors (SSE), Marquardt's percent standard deviation (MPSED%), standard deviation (SD), total sum of squares (SST), and standard error of estimation (SEE) was used to determine the statistical degree of fitness of the kinetic models on the experimental data (Agu, Kadurumba, Orakwue, et al., 2018; Alirezaei, M., Zare, D., Nassiri, S.M., 2013; S.. John et al., 2021b, 2021a, 2023; Kitanovic S., Milenovic D., Veeljkovic V.B., 2008; Menkiti et al., 2015; Mortazavian et al., 2019). By using the provided equations (2) through (11) the R^2, adj-R^2, RMSE, AARE, HYBRID%, SSE, MPSED%, SD, SST, and SEE were calculated.

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

$$\mathrm{AARE} = \frac{\sum_{i=1}^{N}\left[\frac{q_{exp}-q_{model}}{q_{exp}}\right]}{n} \tag{3}$$

$$\mathrm{SD} = \sqrt{\frac{\sum_{i=1}^{N}\left[q_{exp\,(i)}-q_{model(i)}\right]^2}{n-1}} \tag{4}$$

$$\mathrm{HYBRID\%} = \frac{\sum_{i=0}^{n}\left(\frac{y_i-\hat{y_i}}{y_i}\right)}{N-P_r} * 100 \tag{5}$$

$$R^2 = 1 - \frac{\sum(y_i-\hat{y})^2}{\sum(y_i-\bar{y})^2} \tag{6}$$

$$\mathbf{SSE} = \frac{\sum_{i=0}^{n}(y_i-\hat{y})^2}{n} \tag{7}$$

$$\mathbf{Adj - R^2} = \frac{(1-R^2)(N-1)}{N-P_r-1} \tag{8}$$

$$\mathrm{MPSED\%} = \sqrt{\frac{\sum_{i=0}^{n}\left(\frac{y_i-\hat{y_i}}{y_i}\right)^2}{N-P_r}} * 100 \tag{9}$$

$$\mathrm{SEE} = \sqrt{\frac{\sum(y_i-\hat{y})^2}{dt}} \tag{10}$$

$$\mathrm{SST} = \frac{\sum_{i=0}^{n}(y_i - \bar{y}_1)^2}{n} \qquad (11)$$

In this case, n is the number of sample runs or data points, Pr is the number of predictors, q_{exp} = experimental response while q_{model} = model predicted response; N is the total sample size, y_i represents the experimental response values, $\hat{y}$ is the predicted response values, and $\overline{y_1}$ indicates the mean predicted response values. Greater goodness of fit (S. . John et al., 2021b; Kitanovic S., Milenovic D., Veeljkovic V.B., 2008; Mortazavian et al., 2019) and a fit that is more practical and convenient for prediction are indicated by higher R^2 and adjusted-R^2, as well as lower values of RMSE, SSE, AARE, HYBRID%, SEE, MPSED%, SST, and SD (S. John et al., 2021b, 2021a).

Thermodynamics of neem oil extraction

The extraction thermodynamics parameters such as enthalpy, Gibb free energy, and entropy were calculated using equations (12) through (15) to examine the viability and nature of the oil extraction process.

$$\Delta G = -RT\ln K \qquad (12)$$

$$\mathrm{In}\ K = \frac{-\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (13)$$

In this case, K is the equilibrium constant, ΔS is the change in entropy (KJ/mol), T is the temperature (K), R is the universal gas constant (8.314 KJ/Kmol), and ΔG is Gibbs energy or free energy (KJ/mol) (Bispo et al., 2015; S. . John et al., 2021b, 2021a, 2023).

$$K = \frac{Y_{Te}}{Y_{Ue}} \qquad (14)$$

where Y_{ue} is the percentage of oil that remains unextracted and Y_{Te} is the oil yield (%) at temperature T. ΔH and ΔS were found by plotting lnK versus 1/T, which yields -ΔH/R as the slope and ΔS/R as the intercept. Equation 8 was utilized to calculate ΔG* based on these values.

$$\Delta G = \Delta H - T\Delta S \qquad (15)$$

RESULTS AND DISCUSSION

Impact of temperature and time on oil extraction

By conducting studies at five distinct extraction temperature levels—32, 50, 55, 68, and 74°C—and time intervals of 30, 60, 105, 150, and 180 minutes at a particle size of 0.1 mm, the effects of temperature and time variation on oil extraction yield were examined. Figure 1 presents the results of the investigation into how temperature change affects the pace at which oil is extracted from Neem seed meal using petroleum ether as the solvent medium.

It is clear from Figure 1 that as temperature and extraction duration increased, so did the fraction of recoverable oil. Up to 68°C, it was found that the oil extraction yield increased with temperature; beyond that, additional temperature increase led to a negligible rise in the amount of oil recovered. The reason for the observed increase in oil yield with temperature rise is that higher temperatures lead to improved oil extraction yield, decreased oil viscosity, enhanced diffusion, and an enhanced mass transfer coefficient of extraction (S. John et al., 2021b, 2021a; Menkiti et al., 2015; Sulaiman et al., 2013). Additionally, a slight rise in temperature causes a marginal decrease in fluid density, which leads to solute solubility reduction (S. . John et al., 2021b, 2021a, 2023).

The oil extraction process started out quickly and tapered down after around 100 to 180 minutes. This is consistent with the results of Menkiti et al. (2015), who used n-hexane to extract oil from Terminalia catappa L seeds. According to this study, the free oil that was discarded to fresh solvent on the surface of the ground jatropha seed may have caused the first, quick oil extraction process that was seen at the beginning. Rapid oil extraction was made possible by the free oil's susceptibility to solvent at the surface of neem seed particles (Amin et al., 2010; Menkiti et al., 2015; Sayyar et al., 2009; Sulaiman et al., 2013). Generally speaking, slow diffusion-controlled regimes and early quick washing action-controlled regimes might account for the ultimate slow rate yields seen with extraction and the initial rapid rate yields (Amin et al., 2010; Kitanovic S., Milenovic D., Veeljkovic V.B., 2008; Menkiti et al., 2015; Sayyar et al., 2009). However, as temperature and duration increased, so did the oil extraction yield from neem seed using petroleum solvent. The highest percentage of oil extraction, 38.8%, was seen at 74°C and 150 minutes.

Influence of particle size on neem oil extraction

The extraction process is often influenced by the properties of a beginning material, such as its particle size (S. . John et al., 2021b, 2021a; Menkiti et al., 2015; Sulaiman et al., 2013). Particle size is a significant feature of interest in studies on oil extraction since it is related to the surface area of the reaction. Therefore, tests at various 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 were conducted to examine the effect of particle size variation on oil extraction yield.

Figure 2 exhibits the results of the study on the impact of particle size variation on the rate of oil extraction from Neem seed meal using petroleum ether as the solvent medium. The figure shows that when the neem seed meal particle size increased with time, the percentage of oil extracted decreased. The plot of the results makes it clear that larger particle sizes were associated with lower oil yields, whereas smaller particle sizes were associated with higher oil yields. The greater surface area that the smaller particle sizes have over the larger particle sizes is the reason for the higher and lower oil yields at smaller and larger particle sizes, respectively. Maximum oil extraction of 38.82% was obtained with a 0.1 mm particle size at 180 minutes.

Since the diffusion path for smaller particle sizes is shorter, an improvement in oil production with increasing particle size is typically attributed to a larger interfacial area of the solid particles and a decrease in intra-particle diffusion resistance. Because larger particles have a higher intra-particle diffusion rate, the reduction in oil output is more noticeable at larger particle sizes. Because of the tiny contact surface area and low oil diffusion from the pores of the larger particles to the bulk of the solvent, not all of the oil was extracted in the larger particle sizes, as was demonstrated experimentally. However, more milling results in smaller particle sizes with a surface area that is larger, which enhances the rate of oil extraction by releasing more oil from cells for solvent extraction. Due to a reduced diffusion path, a higher rate of mass transfer, and a higher rate of oil dissolution in the solvent, the study observed a phenomenon that was clearly evident in the extraction of oil from Neem seed meals at smaller particle sizes, which was more quickly than at larger particles (S. . John et al., 2021b, 2021a; Menkiti et al., 2015).

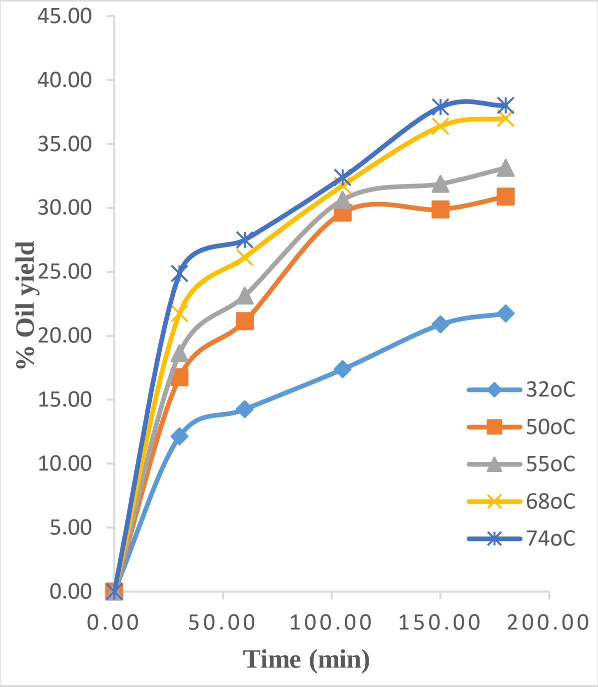

Fig.1 Effect of temperature variation on Neem oil yield using petroleum ether

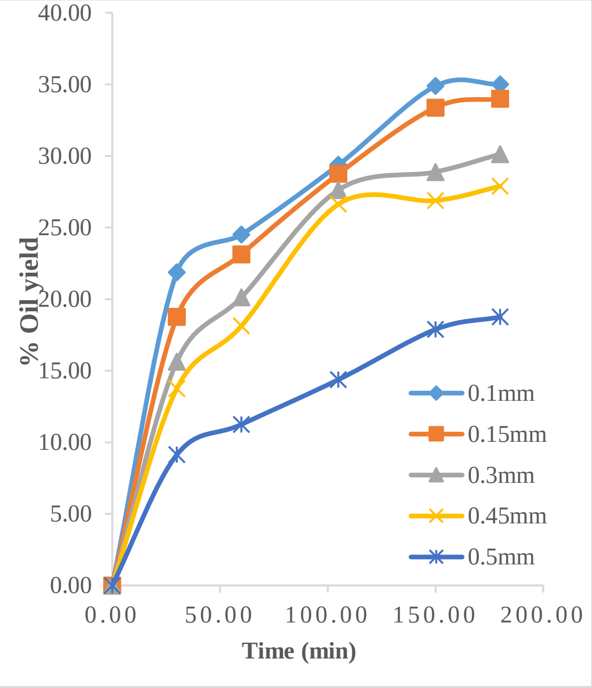

Fig.2 Effect of particle size variation on Neem oil yield using petroleum ether

Kinetic parameters for petroleum ether-based neem oil extraction

Table 2 presents the findings of the nonlinear kinetic parameter values for the four kinetic models—power law, parabolic diffusion models, hyperbolic models, and Elovich's models, respectively—that were examined at various temperatures and particle size variations during Neem oil extraction using petroleum ether as the extraction solvent.

For the hyperbolic model, it was shown that the parameters C_1 and C_2 varied inversely with increasing particle size but proportionally with rising temperature. The improved oil yield observed with increasing temperature and decreasing particle sizes, as well as the negligible recorded differences between the models' predicted oil yields and the experimental values, are linked to the increases in C_1 and C_2 that are observed with these changes. High initial rate and overall oil recovery at high temperatures and smaller particle sizes are indicated by the trend of C_1 and C_2 seen across the temperature and particle size regimes. This is in line with the report on the kinetic and parametric studies of the extraction of oil by John et al. (2021a, 2021b). A similar pattern was noted for parabolic diffusion, power law, and Elovich kinetic model parameters.

It was discovered that the parabolic diffusion, power-law, and Elovich kinetic models A_1, A_o, B, E_1 and E_O parameters all consistently increased as temperature and particle size decreased. The studies by Kitanovic et al. (2008) and Agu et al. (2018) on the solvent extraction of resinoid from the aerial part of Hypericum perforatum L using various solute-to-solvent ratios and the solvent extraction method used to extract Colocynthis vulgaris Shrad Seeds oil (CVSSO) showed a similar pattern of results. It was found that the power-law parameters, n, and B, changed inversely in response to changes in particle size and directly proportionate to temperature, respectively. It was discovered that the corresponding parameter values of C_2, A_1, and E_O were respectively lower than the hyperbolic, parabolic, and Elovich parameter values of C_1, A_O, and E_1. The parameter values published by Kitanovic et al. (2008), Agu et al. (2018), Menkiti et al. (2015), 2016, 2019, and Yi et al. (2016) are in agreement with this. While the C_2values acquired in this study were (+0.1 or 0.2) higher than the C_2 values reported by the same authors, the C_1 values recorded in this work were marginally (-0.1 or -0.2) lower than the C_1 values published by Agu et al., (2018), and Menkiti et al., (2015, 2016, 2019). Conversely, the C_1 and C_2values obtained from this investigation were found to be approximately comparable to those published by Kadurumba et al. (2018) on the solvent extraction of oil from Colocynthis vulgaris Shrad (melon) seeds across all temperature and particle size variations. Higher or lower initial quick oil extraction rates and final slow diffusion rate actions, respectively, for oil extraction from the various seeds under study are implied by the higher or lower values of C_1 and C_2, as reported by the various authors. Thus, early quick washing action and slow diffusion controlled regimes, respectively, could account for the variance in the final slow rate yield and the initial rapid rate yield reported by the different authors.

However, the power-law parameter, n, fluctuated in direct proportion to the particle size variation and did not show any clear pattern across the many temperature variations examined. As a result, the models' oil extraction yield is better or greater. This is generally explained by the observed, consistent increase in kinetic parameter values with temperature, which is attributed to the prevalence and power of diffusion rate in excess of the washing mechanism process (Agu, Kadurumba, Agulanna, et al., 2018; S. . John et al., 2021b, 2021a; Menkiti et al., 2015). Similarly, the oil yield attained at smaller and larger particle sizes corresponds to the steady increase of the kinetic parameters with decreasing particle sizes. This is explained by the fact that smaller particle sizes have a larger surface area than larger particle sizes. This phenomenon was amply demonstrated in this investigation, wherein smaller particle sizes of neem seed meals showed a higher rate of oil extraction than bigger ones. This was attributed to a decreased diffusion path, an increased mass transfer rate, and a higher rate of oil dissolution in solvent (S. . John et al., 2021b, 2021a).

Table 2. Oil extraction kinetic parameters at different temperatures and particle sizes

Temperature (ºC)							**Particle size (mm)**						
Parameter	**32 (ºC)**	**50 (ºC)**	**55 (ºC)**	**68 (ºC)**	**74(ºC)**	**Temp. Ave.**	**0.1mm**	**0.15mm**	**0.3mm**	**0.45mm**	**0.5mm**	**Part. Size Ave.**	**Total Ave.**
HYPERBOLIC													
C_1	0.623	0.908	1.040	1.265	1.743	1.116	1.375	0.982	0.791	0.682	0.382	0.842	0.979
C_2	0.025	0.024	0.026	0.032	0.043	0.030	0.036	0.025	0.021	0.019	0.016	0.023	0.027
PARABOLIC DIFFUSION													
A1	1.210	1.861	1.878	1.949	1.687	1.717	1.687	1.949	1.878	1.861	1.210	1.717	1.717
Ao	5.069	7.291	8.766	10.930	15.00	9.411	12.000	7.930	5.766	4.291	2.069	6.411	7.911
ELOVICH													
E1	5.233	8.341	8.335	8.523	7.311	7.549	7.311	8.523	8.335	8.341	5.233	7.549	7.549
Eo	-6.563	-11.910	-10.240	-8.220	-1.274	-7.641	-4.274	-11.220	-13.24	-14.910	-9.563	-10.641	-9.141
POWER LAW													
B	3.566	5.354	6.161	7.444	10.16	6.537	8.069	5.658	4.504	3.801	2.005	4.807	5.672
n	0.343	0.344	0.327	0.307	0.250	0.314	0.279	0.344	0.370	0.391	0.425	0.362	0.338

Comparative statistical fitness degree for the kinetics models

The statistical degree of fitness for various non-linear kinetic models that were analyzed for the kinetics of Neem oil extraction using petroleum ether as solvent is presented in this section. SSE, R^2, Adj-R^2, and RMSE were the ideal criteria needed to determine which of the kinetic models—hyperbolic, parabolic diffusion, power law, and Elovich's—fitted the experimental data the best. A better model's goodness of fit to the experimental data is typically indicated by higher values of R^2 and Adj-R^2, and lower values of RMSE and SSE (Agu, Kadurumba, Agulanna, et al., 2018; Alirezaei, M., Zare, D., Nassiri, S.M., 2013; S. John et al., 2021b, 2021a; Kitanovic S., Milenovic D., Veeljkovic V.B., 2008; Menkiti et al., 2015; Meziane et al., 2009; Mortazavian et al., 2019). Table 3 displays the statistical fitness degree results for the examined kinetic models.

According to the table, for power law, elovich, parabolic, and hyperbolic models, the R^2 and adjusted- R^2 fluctuated straight proportionately with temperature, however, the SSE and RSME decreased as the temperature increased. The observed trend of the R^2 and adjusted- R^2 values shows that oil recovery rises with increasing temperature and decreasing particle sizes and that the models can explain a larger percentage of the overall variation in the data about the average. In other words, greater oil output at higher temperature regimes and smaller particle sizes is indicated by lower or declining values of SSE and RSME and higher values of R^2 and adjusted- R^2 at those temperature domains and smaller particle sizes. The trend of SSE and RSME that has been seen for the nonlinear kinetic models indicates that the models are more convenient and useful for making predictions.

Nonetheless, it was evident that the hyperbolic, parabolic, elovich, and power-law models were estimated to have average SSE (≤ 10.72) and RMSE (≤ 0.898) values. The models' predicted R^2 and Adj- R^2 values fell between $\geq 90.2\% \leq 96.6\%$. The kinetic models' R^2 and Adj- R^2 values were parabolic (0.966, 0.959), power-law (0.964, 0.956), elovich (0.949, 0.939), and hyperbolic (0.918, 0.902), in decreasing order. The nonlinear kinetic models, hyperbolic, parabolic, elovich, and power law, provided an excellent fit to the experimental data, as indicated by the values of average SSE, RMSE, R^2, and Adj- R^2. The degree of fitness of the researched kinetic models to the experimental data is given in increasing order based on the average SSE, RMSE, R^2, and Adj- R^2 values: hyperbolic → elovich → power-law → parabolic. The models that best suited the experimental kinetics data under investigation were the power-law and parabolic models, which concurrently had the lowest average SSE and RMSE values, and the highest and approximate R^2 and adj- R^2.

As a result, the ranks for the kinetic models' goodness of fit to the experimental data were, in ascending order, hyperbolic, elovich, power-law, and parabolic.

Table 3. Statistical fitness degree for the kinetic of Neem oil extraction

	Temperature (ºC)						**Particle size (mm)**						
Parameter	**32(ºC)**	**50(ºC)**	**55 (ºC)**	**68 (ºC)**	**74(ºC)**	**Temp. Ave.**	**0.1mm**	**0.15mm**	**0.3mm**	**0.45mm**	**0.5mm**	**Part. Size Ave.**	**Total Ave.**
HYPERBOLIC													
SSE	6.494	10.170	10.554	13.631	15.982	11.366	14.709	11.918	9.444	9.589	4.734	10.078	10.722
R^2	0.899	0.938	0.935	0.919	0.872	0.913	0.882	0.929	0.942	0.942	0.926	0.924	0.918
Adj-R^2	0.879	0.926	0.922	0.902	0.846	0.895	0.859	0.915	0.930	0.930	0.912	0.909	0.902
RMSE	1.140	1.426	1.453	1.651	1.788	1.492	1.715	1.544	1.374	1.385	0.973	1.398	1.445
PARABOLIC													
SSE	0.645	13.596	8.623	2.327	1.185	5.275	1.185	2.327	8.623	13.596	0.645	5.275	5.275
R^2	0.990	0.917	0.947	0.986	0.991	0.966	0.991	0.986	0.947	0.917	0.990	0.966	0.966
Adj-R^2	0.988	0.901	0.936	0.983	0.989	0.959	0.989	0.983	0.936	0.901	0.988	0.959	0.959
RMSE	0.359	1.649	1.313	0.682	0.487	0.898	0.487	0.682	1.313	1.649	0.359	0.898	0.898
ELOVICH													
SSE	3.549	9.964	7.972	6.507	6.470	6.892	6.470	6.507	7.972	9.964	3.549	6.892	6.892
R^2	0.945	0.939	0.951	0.961	0.948	0.949	0.948	0.961	0.951	0.939	0.945	0.949	0.949
Adj-R^2	0.934	0.927	0.941	0.953	0.938	0.939	0.938	0.953	0.941	0.927	0.934	0.939	0.939
RMSE	0.843	1.412	1.263	1.141	1.138	1.159	1.138	1.141	1.263	1.412	0.843	1.159	1.159
POWER LAW													
SSE	1.316	11.781	7.679	3.191	3.247	5.443	2.954	2.953	7.846	12.290	0.942	5.397	5.420
R^2	0.980	0.928	0.953	0.981	0.974	0.963	0.976	0.982	0.952	0.925	0.985	0.964	0.964
Adj-R^2	0.975	0.914	0.943	0.977	0.969	0.956	0.972	0.979	0.942	0.910	0.982	0.957	0.956
RMSE	0.513	1.535	1.239	0.799	0.806	0.978	0.769	0.768	1.253	1.568	0.434	0.958	0.968

Thermodynamics parameters for the kinetic of oil extraction

Table 4 displays the thermodynamic parameters and equilibrium constant for the petroleum ether-based Neem seed oil extraction process. Figure 3 shows the plots of In K against 1/T for the various particle sizes (0.1, 0.3, and 0.45 mm) that were used to calculate the values of the thermodynamics parameters. For the various particle sizes, the predicted enthalpy values for the oil extraction process varied from 31.53 to 28.78 kJ/mol. When oil is extracted from Jatropha curcas L. using ethanol as a solvent by Silmara et al. (2015), the enthalpy results obtained in this work are higher than those reported by Silmara et al. (2015), which range from 14.27 to 18.60 KJ/mol. Furthermore, a lower enthalpy value of (4 - 13.5 kJ/mol) for olive cake oil was found by Meziane and Kadi (2008). The observed difference might be explained by the various morphologies of the seeds, which could have an impact on the oil extraction process. An endothermic process is involved in the oil extraction, as indicated by the positive enthalpy value. Consequently, for an extraction process to be effective, external energy input is required (Amin et al., 2010; Bispo et al., 2015; Sulaiman et al., 2013). On the other hand, the obtained enthalpy results are in similar agreement with the values reported by Amin et al. (2010) and Rodrigues et al. (2010) for the extraction process of soybean oil using renewable solvent and the extraction of Jatropha curcas oil in aqueous acidic hexane solutions.

Moreover, differential entropy values were found to be positive in every instance. This suggests that the process is irreversible and that the degree of molecular disarray increased during the extraction procedure. Mixing two distinct materials or substances is the cause of the rise in extraction process disturbance (Akintujoye & Labtech, n.d.; Bispo et al., 2015; S. . John et al., 2021b). In their experiments for the extraction of oil processes from various oilseed raw materials, researchers such as 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.

Conversely, the entropy values for the petroleum ether method of neem oil extraction varied from 0.10 to 0.09 kJ/mol. The entropy values given by Meziane and Kadi (2008), Topallar and Gec¸gel (2000), and Silmara et al. (2015) are closely aligned with this. Because of the extraction of oil molecules, the mixture entropy values were always positive and varied inversely with an increase in particle size. This suggests that the process of extracting oil is irreversible. This aligns with the findings of several reports, including Meziane and Kadi (2008), Menkiti et al. (2015), Amin et al. (2010), Topallar and Gecgel (2000), Agu et al. (2018), and Silmara et al. (2015). Sulaiman et al. (2013) have made similar conclusions.

The oil extraction process was shown to have a negative Gibb-free energy change (ΔG°), suggesting that the procedure was feasible and spontaneous given the experimental conditions examined. According to several studies (Sulaiman et al., 2013; Agu et al., 2018, Menkiti et al., 2015, Silmara et al., 2015), the oil extraction process was largely spontaneous because of the relatively high negative values of the Gibb free energy change. In conclusion, it is clear from the findings of the thermodynamic analysis that less energy was required to break the bonds and contacts between solids and liquids than was released during solid-liquid interaction (Sulaiman et al., 2013; Silmara et al., 2015). Hence, the more the process is farther from spontaneity the greater the particle sizes (Silmara et al., 2015).

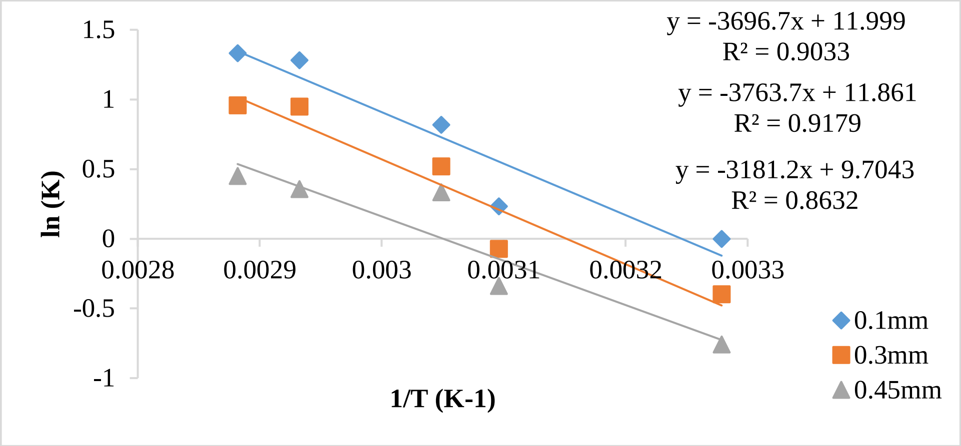

Fig. 3 Plot of In K (equilibrium constant) vs. 1/T (temperature, K^{-1}) for different particle sizes

Table 4. Thermodynamics parameter for petroleum ether-based Neem oil extraction

	0.1mm				**0.3mm**				**0.45mm**							
Temp (K)	**(Δ)G**	**K**	**(Δ)H**	**(Δ)S**	**(Δ)G**	**K**	**(Δ)H**	**(Δ)S**	**(Δ)G**	**K**	**(Δ)H**	**(Δ)S**	**Ave. (Δ)G**	**Ave. K**	**Ave. (Δ)H**	**Ave. (Δ)S**
305	-0.14	1.24	31.53	0.10	0.91	0.71	30.07	0.10	1.28	0.59	28.78	0.09	0.68	0.85	30.13	0.10
323	-2.01	1.57			-0.81	1.06			-0.34	0.89			-1.05	1.17		
328	-2.53	2.57			-1.29	2.13			-0.79	1.93			-1.54	2.21		
341	-3.88	3.93			-2.53	2.43			-1.97	1.98			-2.79	2.78		
347	-4.51	5.43			-3.10	2.79			-2.51	2.19			-3.37	3.47		

Conclusion

From this work, it can be concluded with certainty that the kinetics of petroleum ether-based Neem oil extraction from seeds progressed through the first quick washing action and the last slow diffusion phase, as observed in the kinetic analysis. As temperature and time increased, the oil output rose, but as particle size increased, it fell. The highest oil output of 38.8% was observed at 180 minutes, 0.1 mm, and 74 °C. Hyperbolic, parabolic, elovich, and power law models provided the best fits to the experimental data, according to the comparative statistical degree of fitness for the six extraction kinetics models. This was indicated by their low average values of RMSE, SSE, AARE, SEE, MPSED%, SST, SD, and high average values of R^2 and adjusted-R^2. Nonetheless, the experimental kinetic data was not adequately fitted by either the pseudo-first-order or pseudo-second-order model. Furthermore, the most well-fitting kinetic models could provide important and useful basis equations for plant and process design drives. In summary, the values of Gibb free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS) obtained for the thermodynamic parameters under various extraction process circumstances indicate that the oil extraction process is endothermic, irreversible, and spontaneous.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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