Kinetics and Thermodynamics of Total Polyphenolic Compounds Microwave Assisted Extraction from the Roots of *Ximeniaamericana* (Olacaceae)

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Abstract: ***In this study the effect of temperature, kinetic and thermodynamic parameters of the total polyphenolics microwave assisted extraction (MAE) process of the roots of Ximeniaamericana were evaluated for different temperatures. The total polyphenolic content increased with increasing irradiation extraction time and temperature. The highest extraction temperature and longest irradiation extraction time of 80°C and 120 sec resulted in the highest total polyphenolic of 5013.07± 11.25 µg GAE/g. DW. The kinetics of the microwave assisted extraction process was tested by pseudo- first-order, pseudo-second order and Fick's Law. It was shown that extraction of total polyphenolic of Ximeniaamericana roots could be described by the pseudo-second order kinetic model. Besides that, the result of the initial microwave assisted extraction rate (h) calculated at each microwave temperature show that the initial rate at 80°C extraction temperature was almost six times higher than that of 30°C; the effective diffusion coefficients (D_{eff}) identified for different temperatures (303~353K: D_{eff} ranged from 2.215×10^{-13} to 7.232×10^{-13} m^2/s) increased with increasing temperature; The dependence of the mass transfer coefficient of the microwave assisted extraction process on temperature verified by using Arrhenius model in its linearized form show a value of activation energy Eaof 14.436 kJ/mol with a high determination coefficient ($R^2 = 0.859$, $P<0.05$).The thermodynamic study shows that the variations of enthalpy and entropy were positive; indicating that the process was endothermic and irreversible while Gibbs free energy was negative, indicating that extraction was spontaneous and thermodynamically favorablewith exception to extraction at 30 and 60 °C.***

Keywords: Total polyphenolic, Roots, *Ximeniaamericana*, microwave assisted extraction, kinetics, thermodynamics

1. Introduction

Ximeniaamericana L. is a shrub or a small tree of the family Olacaceae which is found in the tropical regions of America and Africa [1]. It is a plant extensively used among the Hausa communities in the Northern parts of Cameroon are reported to be one of the rich sources of bioactive compounds namely saponins, glicosydes, flavonoids, tannins, phenolics, alkaloids, quinones and terpenoidsetc. [2, 3, 4, 5]. Recently, *Ximenia Americana* roots have also been searched for their natural antioxidant anti-inflammatory and antimicrobial properties [6, 7]. It is widely accepted that biological activities of plant materials are strongly linked with their specific chemical composition, mainly the secondary metabolites such as plant phenolics and flavonoids [8].

Extraction methods for bioactive compounds extraction include maceration, Soxhlet extraction, ultrasonic extraction and microwave assisted extraction. Among these techniques, household microwave assisted extraction is one of the most economically favorable and technically simple method [9, 10]. The microwave assisted extraction technique has been found to be one of the most effective for the extraction of total polyphenolics compounds of the roots of *Ximeniaamericana* [7].

Several of these authors have observed that the yield of the extraction process using microwave assisted extraction technique is dependent on factors such as temperature, nature of the solvent and the plant, particle size, relationship between the solid mass and solvent volume, and time. Liauw et *al*. in 2008 [11] considered that for analysis and design of extraction units, especially on an industrial scale, kinetic and thermodynamic data of the process are critical.

Kinetic studies play a very important role in extraction processes and the knowledge of extraction rate, i.e., whether the extraction process is slow or fast can be easily obtained from the kinetic study of the process [12].Kinetic studies help in understanding various factors that affect the extraction rate. Thus, it is important to study the kinetics of the extraction process. Although various research papers are available which report the Microwave-assisted extraction, very few papers report the kinetic and thermodynamic aspects. To the best of our knowledge, the Microwave-assisted extraction kinetics and thermodynamics of total polyphenolic compounds has not been reported up to now. Thus, the objective of this study was to evaluate the effect of temperature on the yield and both kinetic and thermodynamic parameters for the total polyphenolic compounds of the roots of *Ximeniaamericana* microwave assisted extraction process.

2. Materials and Methods

2.1. Sample materials and chemicals

The roots of *Ximeniaamericana* were collected from Ngaoundere in the region of North Cameroun and authenticated by Professor Mapongmetsem, botanist and professor in the Department of Biological Sciences, Faculty of Science, University of Ngaoundere. The material was allowed to dry naturally, cut, ground using a mill (Model 14, Hamilton Beach, USA) and thensieved with mechanical shaker analysensieb, Model NFX 11-501, Germany, through a standard set of stainless steel sieves. The powder was kept in sealed polyethylene bags at room temperature.

2.2. Chemicals reagents

Gallic acid, Folin –Ciocalteusphenol reagent, sodium acetate, and methanol reagent were purchased from *Sigma-Aldrich* and were used as received. All other chemicals organics solvent used in the study were of analytical grade.

2.3. Microwave-assisted extraction process

Two point five grams of *Ximeniaamericana* powder roots of 200µm diameter were placed in a tube and mixed with 50mL of methanol-water (80:20, v/v). The extraction process was performed with domestic microwave (ER- 696 ETE, 2450MHz, and Toshiba, Japan) equipped with a digital timer and a power controller. After microwave extraction, the sample was filtrate with a wattman paper and the microwave extract was evaporated by rotary evaporation to remove solvent. Three replicates were performed in each extraction. Samples (the microwave extracts) were stored in 4°C prior to analysis. Their radiation extraction time was assessed as shown in the results and the desired temperature was maintained through the timer.

2.4. Determination of total polyphenolic content in the roots of *Ximeniaamericana*

Determination of total polyphenolic content (TPP) in the roots of *Ximeniaamericana* was determined using the Folin–Ciocalteau method. Microwave extracts were mixed with 0.2 ml of Folin–Ciocalteau reagent (pre-diluted at a ratio of 1:16 with distilled water) and allowed to stand at room temperature for 5 min, and then 0.2 ml of sodium bicarbonate (1M) was added to the mixture. After standing for 20 min at room temperature, absorbance was measured at 760 nm. Results were expressed as µg Gallic acid equivalents/ dry weight sample (µg GAE per g of dry weight (DW)) [13].

2.5. Kinetic model

The extraction kinetics of total polyphenolic content (TPP) from the roots of *Ximeniaamericana* using MAE technique at different microwave temperatures of 30, 60, 700, and 80°C were studied. Three kinetic models, namely Fick's Law, First and Second-order Rate Law were used to model the total polyphenolic microwave assisted extraction.

2.5.1. Extraction first-order model

The pseudo first-order equation of Lagergren, (1898) and Ho, (2004), can be rewritten in its differential form as follows [14, 15] (Equation 1):

$$\frac{dY_t}{dt} = k_1 (Y_S - Y_t) \quad (1)$$

Where k_1 is the first-order extraction rate constant (sec^{-1}), and t (sec) the time. Equation (2) was integrated with application of the boundary conditions Yt = 0 at t = 0 and Yt = Y_t at t = t, Equation 2.

$$ln\left(\frac{Y_s}{Y_s - Y_t}\right) = k_1 t \quad (2)$$

Equation (2) may be rearranged to obtain the linear form, (Equation 3):

$$log(Y_s - Y_t) = log(Y_s) - \frac{k_1}{2.303} t \quad (3)$$

The plots of log (Y_S - Y_t) versus t were analyzed to allow a calculation of the constant k1 from the slope and the equilibrium extraction capacity Y_S (yields obtained at saturation) from the intercept log (Ys).

2.5.2. Extraction second-order model

The second-order kinetic equation for the extraction [15]rate can be written as follows:

$$\frac{dY_t}{dt} = k_2 (Y_s - Y_t)^2 \quad (4)$$

In Equation (4), Y_t is the content of polyphenols (µgGAE/g.DW) at any time *t*, $Y_s$is the equilibrium content of polyphenols (µgGAE/g.DW) and $k_2$is the second order rate constant (g.DW/µgGAE.sec). By considering the initial and boundary conditions, $t = 0$ to t and $Y_t = 0$ to Y_t, the integrated rate law for second-order extraction was obtained:

$$Y_t = \frac{Y_s^2 k_2 t}{1 + Y_s k_2 t} \quad (5)$$

By transforming Eq. (5), a linear form shown in Eq. (6) can be obtained and the extraction rate can be written as Eq. (7):

$$\frac{1}{Y_t} = \frac{1}{k_2 Y_s^2} + \frac{t}{Y_s} \quad (6)$$

$$\frac{Y_t}{t} = \frac{1}{\frac{1}{k_2 Y_s^2} + \frac{t}{Y_s}} \quad (7)$$

The initial extraction rate *h*, as Y_t/t when *t* approaches 0, can be defined as:

$$h = k_2 Y_s^2 \quad (8)$$

and, the total polyphenolic content at any time can be expressed after rearrangement as:

$$Y_t = \frac{t}{\frac{1}{h} + \frac{t}{Y_s}} \quad (9)$$

The initial extraction rate *h*, the extraction capacity Y_S, and the second-order extraction rate constant *k*, can be determined experimentally from the slope and intercept by plotting t/Y_t versus *t*.

2.5.3. Estimation of effective diffusion coefficient

Fick's second law was used to model diffusion during the MAE of total polyphenolic from the root of *Ximeniaamericana*. Considerations regarding diffusion were applied by following these assumptions: assuming particles to be spherical. Mass transfer resistance in the liquid phase was considered to be negligible due to continuous stirring during MAE. No degradation of polyphenols or flavonoids was expected during MAE under the present experimental conditions. The change in total polyphenolic in the solid phase with respect to time and radial position during MAE can be described using Fick's second law as follows [16]:

$$\frac{\partial Y}{\partial t} = D_{eff}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Y}{\partial r}\right)\right] \qquad (10)$$

The initial condition for solving the diffusion equation is shown below:

$$Y(r,0) = Y_i \qquad R \geq 0 \qquad (11)$$

$$\frac{\partial Y(0,t)}{\partial r} = 0, \qquad t \geq 0 \qquad (12)$$

$$Y(r,t) = 0, \qquad t \geq 0 \qquad (13)$$

(Assuming no solubility limitation)

Where, Y is the total polyphenols in the solid particles (µgGAE/g.DW) transfer yield, D_{eff} is the effective diffusivity coefficient ($m^2.s^{-1}$), *r* is the radius of solid particles (mm), and *t* is the irradiation time (sec). Based on Fick's second law, the mathematical expression that linked between the Y and D_{eff} of the solute can be described as follows [16]:

$$\frac{Y_t}{Y_s} = 1 - \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{D_{eff}\pi^2 t}{r^2}\right) \qquad (14)$$

Where, *n* is the positive root of the Bessel function of the first kind of order zero. However, following the short extraction period, only the first term of the series solution is considered to be significant.

$$\frac{Y_t}{Y_s} = 1 - \frac{6}{\pi^2}\exp\left(-\frac{D_{eff}\pi^2 t}{r^2}\right) \qquad (15)$$

It's generally assumed that, for extraction from plant matrixes where external resistance is negligible, the first term of the series solution can be used with little error. Consequently, when the logarithm of Y is plotted against time, a straight line should be obtained and the diffusivity can be assessed from its slope

$$\ln\frac{Y_s}{Y_s - Y_t} = \ln\frac{\pi}{6} + \frac{D_{eff}\pi^2 t}{r^2} \qquad (16)$$

The effective diffusion coefficient (D_{eff}) can be estimated from the experimental data using the linearized form Equation (16).
The dependence D_{eff} on the temperature follows a first-order rate process, generally described by the Arrhenius equation.

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (17)$$

Where Ea, is the activation energy ($J.mol^{-1}$), T is the temperature (K), k_0 is the pre-exponential factor (sec^{-1}), and R is the gas constant (8.314 $J.K^{-1}.mol^{-1}$). Therefore, activation energy can be graphically determined, as the straight line obtained by plotting the lnk as a function of 1/T would have a slope that is equal to *–Ea*.

2.6. Thermodynamics parameters

Thermodynamics parameters (differential enthalpy ΔH°, differential entropy ΔS° and Gibbs free energy ΔG°) for MAE of total polyphenols from the roots *of Ximeniaamericana* method can be determined using second law of thermodynamic equations.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (18)$$

$$\Delta G^\circ = -RT\ln K_e \qquad (19)$$

Equating Equations (18) and (19) gives Equation (20)

$$\text{Log}K_e = -\frac{\Delta H^\circ}{2.303\,R}\frac{1}{T} + \frac{\Delta S^\circ}{2.303\,R} \qquad (20)$$

$$K_e = \frac{Y_e}{Y_{max} - Y_e} \qquad (21)$$

According to our previous study, Ymax, the total polyphenolic in the solid phase at equilibrium (µgGAE/g.DW) were equal to 7872.24 µgGAE / g.DW [17]. In the equation (21), (Y_{max}-Y_e) is the total polyphenolic in the roots of *Ximeniaamericana* not extracted at equilibrium, obtained by mass balance. While ΔH°, ΔS° and ΔG° are enthalpy, entropy and free energy of microwave assisted extraction respectively. Having calculated the values of K_e for each evaluated condition (different temperature), graphs were generated with the data $\text{Log}K_e$ versus 1/*T*, and data was adjusted to linear regression models. The values obtained for the angular coefficients of the lines represent the quantities ($\Delta H^\circ/R$) and the linear coefficients of the quantities ($\Delta S^\circ/R$).

2.7. Statistical Analysis

The results were expressed as the mean ± standard deviation (mean ± SD) of triplicate data set, from an independent experiment. Statistical analysis was performed using the analysis of variance (ANOVA), followed by Duncan's multiple range test (DMRT).The differences were considered significant if $p < 0.05$ (95 % confidence interval).The coefficient of determination R^2 of the regression equation was used for selecting the best kinetic equation. A mean relative percentage deviation (MRPD) was used to describe the fitting ability of the selected equation in the form (22),

$$MRDP = \frac{100}{n}\sum\frac{|Yexp - Ycal|}{Ycal} \qquad (22)$$

Where *n* is the number of observations and $|Yexp - Ycal|$is the absolute value of the difference between experimentally Yesp and predicted Ycal.

3. Results and Discussion

3.1. Effect of temperature and time on extraction kinetics

To study the effect of temperature on the extraction kinetics process, the microwave assisted extraction process was carried out by changing the extraction temperature while keeping other parameters constant. The tested extraction temperatures were in the range of 30 – 80°C with other parameters set as follows: particle size of 600 microns, methanol concentration 80%: v/v, extraction time 120 sec and ratio of material to solvent 20 mL/g. This effect of temperature on the extraction kinetics under microwaved is illustrated in Table.1. The extraction yields increased with increasing temperature from 30 to 80°C. After 120 sec of extraction, the extraction yields of total polyphenolics at 30°C were 2037.30 µg GAE/g. DW while the corresponding yields increased to 3166.09, 4317.09 and 5013.07 µg GAE/g. DW at 60, 70 and 80°C respectively. The degradation of total polyphenolic compounds in the temperature range investigated was not observed. In the literature, the enhancement on the extraction efficiency of microwave assisted extraction (MAE) can be attributed to: (1) an improvement in the solubility and mass transfer effects and (2) an increased disruption of surface equilibrium [18, 19]. There are reduced viscosity and improved diffusivity of solvent which allow better penetration through the matrix particles. Therefore, in this study, the high temperatures could disrupt the surface equilibrium. The increased temperature can overcome the total polyphenolic–matrix interaction caused by van der Waals forces, hydrogen bonding, dipole attraction of the total polyphenolic molecules and active sites in the matrix. Thus, the supplied thermal energy can disrupt cohesive (total polyphenolic–total polyphenolic) and adhesive (total polyphenolic –matrix) interactions, providing the necessary activation energy required for desorption process. The transfer of the analytes from matrix to solvent is achieved by the diffusion and convection processes [20].The results also show an increase in the total polyphenolics (TPP) content with increasing irradiation extraction time [21]. The highest extraction temperature and longest irradiation extraction time of 80°C and 120 sec resulted in the highest total polyphenolic of 5013.07± 11.25 µg GAE/g. According to our previous work [22], this yield was better than that of Soxhlet extraction 4339.31 ± 10.35 µg GAE/g. [22], used microwave irradiation to investigate the effect of extraction temperature on the extraction yield and purity of the phenolic compounds of herb Artichoke (*Cynarascolymus*L.). The result shows that 70˚C was the maximum allowable extraction temperature and was considered as the optimum for achieving a high recovery yield of active constituents. Literature reports similar behaviors which corroborates the results assessed in this work. For example, the positive influence of high temperature, also observed by Silva et *al*., in 2016and Guerra et *al*., in 2016 [23, 24], may be due the increase of solubility and diffusivity as well as, a decrease in the viscosity of the phenolic compounds. Both effects improve the mass transfer and accelerate the extraction rates. The kinetic approach modelling would allow us to have a better understanding of the extraction rates and possible extraction mechanisms of the total polyphenolic compounds in the microwave assisted extraction method. Three kinetic models, namely Fick's law, First and Second-order Rate Laws were then employed to fit the experimental kinetic data of TPP extraction from the roots of *Ximeniaamericana*.

Table 1: The yield of total polyphenolic of the roots of *Ximeniaamericana* at various extraction temperature and time (Particle size = 200-µm, Methanol-water (80:20 v/v)= 50 mL, microwave power = 600 W)

Time (sec)	TPP (µg GAE/g.DW) *			
	30°C	60°C	70°C	80°C
20	680.69 ± 12.75	1308.27 ± 12.20	2265.21 ± 11.72	2710.12 ± 10.70
40	1106.19 ± 11.53	1559.04 ± 10.28	2701.33 ± 9.38	3509.51 ± 8.25
60	1295.02 ± 11.05	2475.05 ± 9.44	3658.82 ± 10.44	4426.57 ± 11.77
80	1749.71 ± 9.99	2930.87 ± 11.74	4162.88 ± 8.25	4945.11 ± 10.81
100	1986.85 ± 9.35	3101.89 ± 11.52	4264.31 ± 10.27	5007.42 ± 9.16
120	2037.30 ± 10.18	3166.09 ± 9.24	4317.09 ± 12.19	5013.07 ± 11.25

*Average of three replicated of polyphenols compounds extraction.

Note: GAE: Gallic Acid Equivalent; DW: Dry Weight

3.2. Kinetics studies

To investigate the kinetics of microwave assisted extraction of TPP of the roots of *Ximeniaamericana*, the Lagergren-first-order model, Ho's pseudo-second-order model and Fick's law were used. The values of the parameters, the correlation coefficients, and the mean relative percentage deviation (MRPD) for the various kinetic models obtained are listed in Table 2- (A) and Table 2- (B). The fit of the experimental data to the kinetics models are illustrated in Fig.1-A and Fig.1-B.Consistently high values of R^2 for the regression and much lower MRPD for most isotherms under all experimental conditions were used as the basis for selecting the best equation. The result shows that Ho's pseudo-second-order model and Fick's law equations gave consistently higher values of R^2 than the other equation. However when the MRPD values were calculated for the all equations, the Ho's pseudo-second-order equation gave much lower MRPD for most temperatures. In addition, the predicted Y_e of Ho's pseudo-second-order equation was more accurately than the other model investigated. The Ho's pseudo-second-order equation could therefore adequately treat the extraction experimental data of the microwave assisted extraction of total polyphenolics from the roots of *Ximeniaamercana*. A number of researchers have reported that the pseudo-second-order equation could describe polyphenols extraction from plant materials [26, 27, and 28].

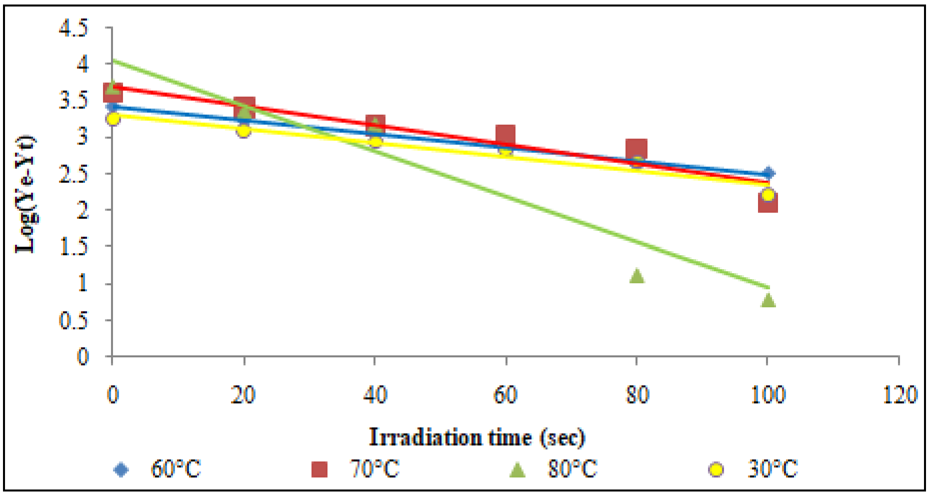
Table 2: Statistical parameters of the kinetic modelling (A) and Kinetics parameters (B) for microwave assisted extraction of total polyphenolic of the roots of *Ximeniaamericana*

(A)

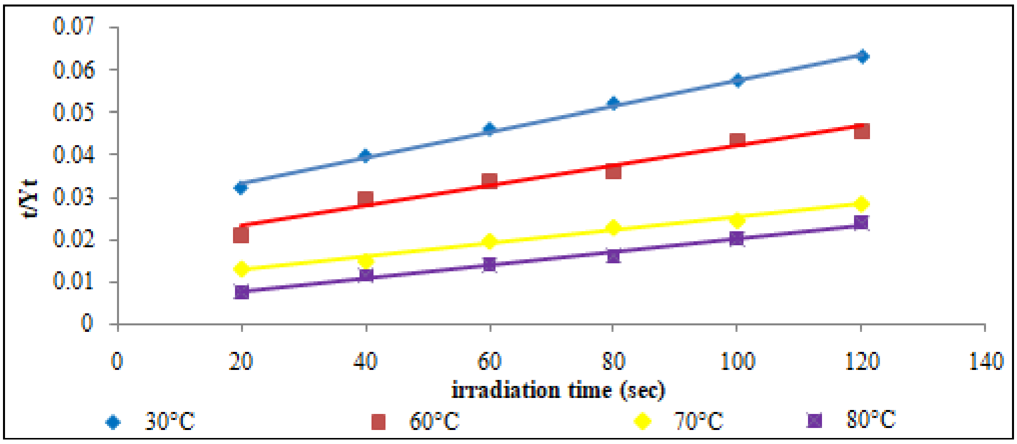
Extraction temperature (°C)	First-order Rate Laws		Second-order Rate Laws		Fick's Law	
	MRPD (%)	R^2	MRPD (%)	R^2	MRPD (%)	R^2
303	35.846	0.930	12.197	0.954	25.556	0.930
333	32.556	0.983	12.530	0.967	20.776	0.983
343	27.983	0.900	17.589	0.984	15.988	0.901
353	25.965	0.880	15.790	0.991	13.652	0.921

(B)

T (°K)	First-order model		Pseudo-second-order model			Fick's Law
	K_1 (sec^{-1})	Ycal (µg GAE/g.DW)	K_2 (µgQAE/ gDWsec)x10^6	Ycal (µg AE/g.DW)	h (gDW/µgGAE sec)	D_{eff} x10^{13}
303	0.0042	2125.690	3.596	2302.34	34.843	2.251
333	0.0040	2710.815	5.197	3455.56	54.644	2.160
343	0.0098	6110.930	5.751	4515.13	105.263	3.124
353	0.0134	11028.082	9.091	5100.00	227.272	7.232



(a)



(b)

Figure 1: Fit of the pseudo-first-order (A) and pseudo-second-order (B) kinetics models for the microwave assisted extraction of TPP from the roots of *Ximeniaamericana*

As one can notice, the initial extraction rate values (*h*) were calculated at each microwave assisted extraction temperature using Equation (9). Figure 2 shows a positive correlation between *h* and temperature with a determination coefficient of 0.86. This correlation higher than 0.8 proves that the MAE technique can extract a high amount of TPP at a short time at a higher temperature [29]. It is also noticed from Figure2 that the initial rate (*h*) at the very beginning of the extraction process increased with the microwave assisted extraction temperature. The initial rate at 80°C microwave assisted extraction temperature was almost six times higher than that of 30°C, which explains the higher microwave assisted extraction efficiency at a higher temperature.

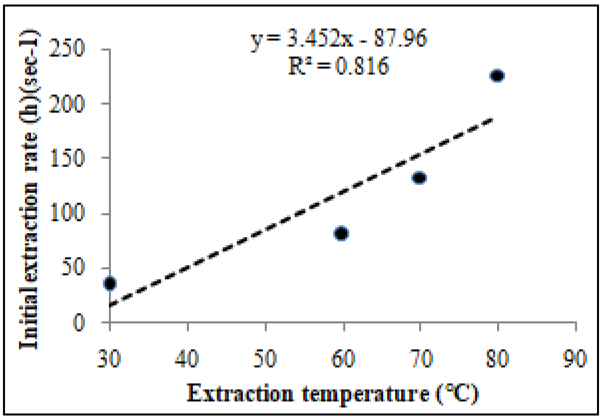


Figure 2: Effect of the extraction temperature on the initial extraction rate of extraction from the roots of *Ximeniaamericana* using the MAE according to the second-order Rate Law model

3.2.1. Effective Diffusion coefficient

The total polyphenolic transfer from the solid-to-liquid phase is affected by transport properties such as effective diffusion coefficient [30].The Fick laws are the common laws used to explain solvent diffusion into the dried plant particles and its diffusion type [12]. To determine the solvent diffusion coefficient (Table 2) during microwave assisted extraction at the different temperatures of the total polyphenolics from the roots of *Ximeniaamericana*, T versus (ln (Ye / (Ye-Yt)) figures were plotted (Figure 2). The diffusion coefficients were calculated from the slopes of the straight line equations. The results show that the effective diffusion coefficients increased with the increasing temperature. The obtained value of D_{eff} ($2.215 \times 10^{-13} \sim 7.232 \times 10^{-13}$ m^2/s) was much lower than that for the microwave extraction of flavonoids from *P. emblica* ($1.15x10^{-11}$ - $2.08x10^{-11}$) [12] andMicrowave assisted extraction of polyphenols from Sugarcane Bagasse (1.604-$2.125X10^{-12}$ m^2/s) [31but similar to the result for navy beans [32]. The obtained values of D_{eff} from this study lie within the general range 10^{-8} to 10^{-15} m^2 s^{-1} for extraction of plant materials. According to Chemat et *al.* in 2013 [33], the microwave assisted extraction (MAE) provides greater access to the solute resulting in a high diffusion coefficient and this is a consequence of an increase in the rate of solute mass transfer through the particle of plant surface as a result of solvent molecules activation in the presence of microwave irradiation.

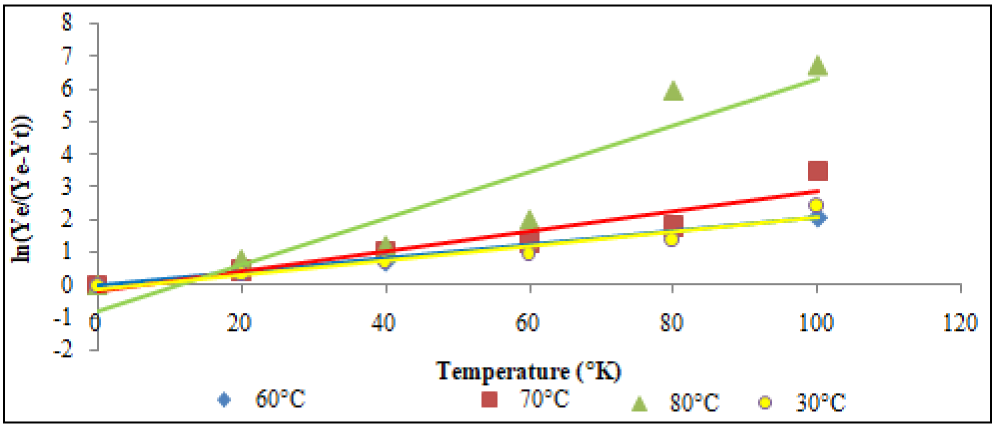


Figure: 3. Effective diffusion at different temperature

3.2.2. Activation energy

The activation energy, which is an energy barrier for total polyphenolic transfer, was determined by linearizing the Arrhenius model. For that, the energy required for total polyphenolic extraction according to the Second-order model was then calculated through plotting lnk_2 versus 1/T according to equation (17) and plotted in Figure 3. The fit for this relationship was adequate, with a determination coefficient higher than 80% and P values lower than 5% (Table 2).Typical Activation energy of the microwave assisted extraction process (*Ea*) values observed in some researches is presented in Table 3 along with the result obtained in this work. The estimated values of *Ea* for total polyphenolic studied were Ea=14.436 $KJ.mol^{-1}$.

Compared with other polyphenolics compounds (Table 3), the estimated *Ea*value for total polyphenolic of the roots of *Ximeniaamericana* in the range of temperature studied was similar to the activation energy of total phenol from black tea **[34],** lower than that of caffeine molecules of *Paulliniacupana* **[35]**; higher than those observed of flavonoids from *P. emblica* **[12], a**nd caffeine molecules of *Paulliniacupana* **[36]**.This indicates that the structure of the extraction residue layer of the *Ximeniaamericana* roots powder particle was very open and allows easy transport of methanol to total polyphenolics moleculesand also easy transport of the methanol extract of total polyphenolic from roots of *Ximeniaamericana* particles.

Compared with other extraction techniques, the estimated activation energy of total polyphenolic of the roots of *Ximeniaamericana* extraction under microwave assisted extraction (*Ea* = 14.44 KJ/mol) obtained was lower than the values for: the extraction of caffeine from guarana seed under the action of ultrasonic field ((Ea=19.40 kJ/mol) **[37]**; the extraction of caffeine from guarana seed under of conventional heating (Ea = 21.8 kJ/mol) **[37]**; The extraction of phenolic compounds from milled grape seed (23–24) kJ/mol under batch solid–liquid extraction **[38]**; More-over the *Ea* of the extraction of individual flavanols from green tea (range from 30 to 50 $kJmol^{-1}$) under maceration **[39]**. Rodríguez-Pérez et *al.*, in 2016 **[40]** reported that the activation energy required during extraction process can be reduced by thermal energies, thus promoting the disruption of the strong solute-matrix and solute–solute interactions. Hereby, it was deduced that the collapse of cavitation bubbles could provide the thermal energies for the decline of activation energy during the extraction.

Table 3: Activation energy of the microwave assisted extraction process of some plants in different temperature ranges

Plants material	compounds	Temperature (ºC)	*Ea (kJ mol$^{-1)}$	Author
P. emblica	flavonoids	40-100	7.58	KRISHNAN et *al.*, 2017 [12]
(Paulliniacupana	caffeinemolecules	40-60	13.02	Biljana et al., 2017 [37]
black tea	total phenol	55–90	14.63	Spigno et *al.*, 2009 [34]
*guarana*powder	caffeinemolecules	50-80	18.8	Eisenberg DS et *al* 2005 [35]
X. americana	Total polyphenolic	30-80	14.44	This work

* Activation Energy

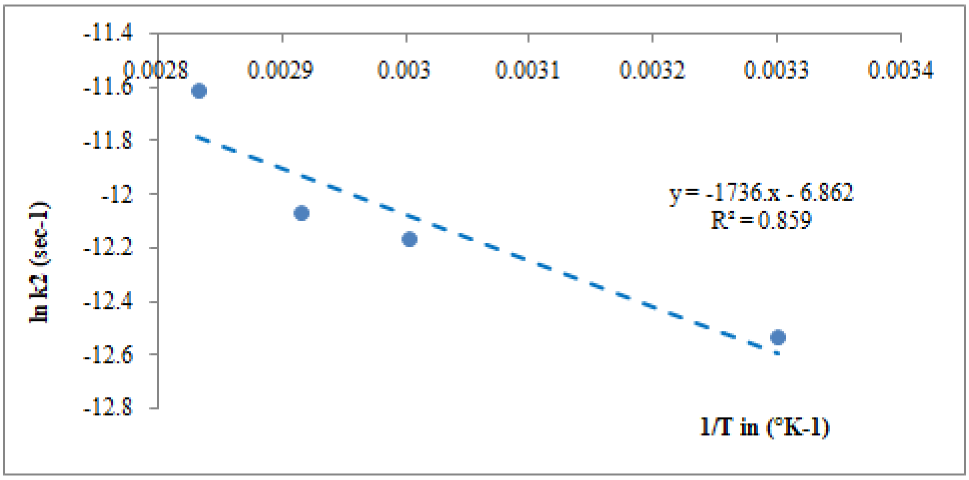


Figure 4: Determination of the activation energy for extraction of TPP of the roots of *Ximeniaamericana* using the MAE in the range of 240 – 280 °C

3.3. Extraction thermodynamics

The thermodynamics consideration of the microwave assisted extraction process was necessary to conclude whether the process was spontaneous or not. Thermodynamics parameters such asenthalpy change (ΔH°), entropy change (ΔS°) and Gibb's free energy (ΔG°) for microwave assisted extraction of total polyphenols from the roots of *Ximeniaamericana* were determined using second law of thermodynamic equations. The value of Ke and ΔG° for extraction of polyphenols from the roots of *Ximeniaamericana* were determined using Equations (21) and (19) respectively and are given in Table 6, while correlation coefficient of extraction process R^2 was gotten to be 0.9385 from Figure 3, the values of enthalpy and entropy of extraction of polyphenols from the roots of *Ximeniaamericana* are gotten from the slope (-1459 K) and intercept (4.3195) of Van't Hoff plot (Figure 6) to be 27.351 KJ.mol^{-1} and 80.975 J.mol^{-1} respectively. The correlation coefficient of the extraction process R^2 being equal to 0.9385 showed that extraction process fitted well with the obtained thermodynamics data.The positive differential entropy value obtained indicates irreversibility of the process and an increase in the degree of molecular disorder during the process. According to Olakunle and Umar in 2019 [40], the extraction process involves mixing two different substances cause an increase in their disorder. Negative values of ΔG° was obtained for the extraction performed at temperatures of 70 and 80 °C indicating the viability and spontaneous nature of the process under these conditions. For other conditions (temperature of 30 and 60°C), positive values indicate that the energy consumed in the microwave assisted extraction process for the disorganization of total polyphenolics molecules in the solvent medium (ΔH°) was greater than the energy consumed for the reorganization of molecules in the medium (TΔS°) and the process is not spontaneous; that is, under these conditions the process is not thermodynamically favorable. Finally positive values of enthalpy and entropy of total polyphenolic extraction indicated that the microwave assisted extraction process was endothermic and spontaneous respectively while the negative values of free energy indicated that the microwave assisted extraction process were feasible and irreversible as observed by Liauw et al. in 2008 [11] and other authors including Krishnan et *al.*, in 2017 [12], Spigno et *al.*, in 2009 [34], and Silmara et *al.*, in 2015 [42].

Table 4: Equilibrium constant and Thermodynamic parameters for MAE of polyphenols from *the roots of Ximeniaamericana*

T (°K)	1/T x 10^{-3} (°K)	Ke	LogKe	ΔH° (kJ/mol)	ΔS° (J/mol.)	ΔG° (J/mol)
303	3, 300	0, 349	-0, 457	27.351	80.975	2815, 526
333	3, 003	0, 672	-0, 173	27.351	80.975	386, 271
343	2, 915	1, 214	0, 084	27.351	80.975	-423, 480
353	2, 833	1, 753	0, 244	27.351	80.975	-1233, 232

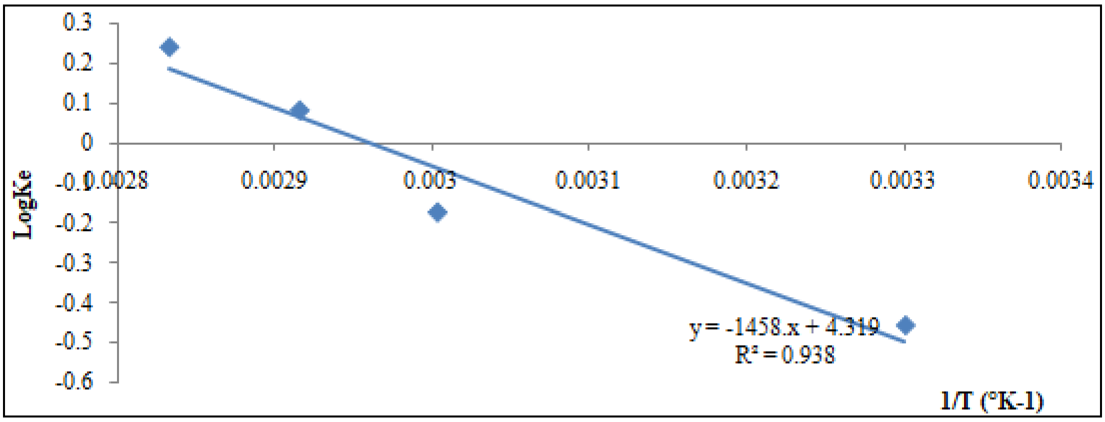


Figure 5: Van'thoff graph

4. Conclusion

In this study, the kinetics and thermodynamics of the microwave-assisted extraction of TPP of *Ximeniaamericana* roots was explored experimentally, and the results were checked by using three models. The established theoretical equations were used to correlate the experimental data for the kinetics of the extraction. Optimum time and temperature were 120 sec and 353.15 K, respectively. Total polyphenolic microwave assisted extraction obeys second order kinetics. The activation energy *Ea* was found to be 14, 436 KJ/mol and the enthalpy value was 27.351 KJ/mol and other thermodynamic parameters at optimum temperature of 353.15 K were $\Delta G^\circ=-1.233$KJ/mol and $\Delta S^\circ=0.0809$KJ/mol. This result shows that the variations of enthalpy and entropy were positive; indicating that the process was endothermic and irreversible while Gibbs free energy was negative, indicating that extraction was spontaneous and thermodynamically favorable.

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