Chapter

Kinetics and Thermodynamics of Oil Extracted from Amaranth

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Abstract

This chapter deals with the kinetics of solvent extraction of oil from Amaranth, as well as the thermodynamics of the extraction process. Brief introduction of Amaranth and Amaranth oil yields and compositions were given. The justifications of the choice of extraction method, as well as the solvent used in the kinetics and thermodynamic studies, were discussed. Known kinetic models used to model vegetable oils extraction process, were discussed, with the view of evaluating the feasibility of fitting the obtained experimental data into the models. The extraction kinetic models considered are the parabolic diffusion, power law, hyperbolic, Elovich's and pseudo second order models. The thermodynamics of oil extraction process were also considered. Hence, the thermodynamic parameters, enthalpy, entropy and Gibb's free energy change of the process were also discussed.

Keywords: kinetics, thermodynamics, Amaranth, oil extraction, solvent extraction method

1. Introduction

Amaranth plant is a strong and fast-growing pseudocereal that is nutritious and is presently used as food crop. The common species of Amaranth grains are *Amaranthus cruentus*, *Amaranthus caudatus*, and *Amaranthus hypochondriacus* [1]. It has lot of nutritional and health benefits due to its fiber content, tocols, high protein content, squalene, as well as diverse bioactive compounds. *Amaranthus* sp. grain also contains high concentration of minerals, vitamins, specially tocotrienols lysine amino acids and fatty acids [2]. Various species of Amaranth are planted in several parts of the world, such as South America, Africa, India, China and United States [3]. Composition of seeds from the several species of *Amaranthus* have been reported to contain protein, starch and oil, that are of high quality for food and animal feed purposes [4].

Amaranth grains have been reported by number researchers to contain about 6–9% oil [1, 4–6]. Although the oil yield of Amaranth is low, it is often not extracted from the seeds, though there are situations where it would be advantageous to extracted and use the oil [4]. This is because the oil is very rich in squalene, compared to other vegetable oils, like olive, rice bran, corn, peanut, rapeseed, cottonseed and sunflower [5–9]. The oil of Amaranth is reported to contain high quantity of squalene, of up to 7.3–11.2% [1, 3, 10]. Oil from *Amaranthus* sp., also contains other important substances like crude fat and some essential fatty acids [11].

It is important to know that the fatty acids present in Amaranth seeds oil, are similar to those present in other cereals, like cottonseed and sesame oils [1]. For instance, the oil of *Amaranthus cruentus*, have been reported to contain 6.3% crude fat, 38.2% linoleic acid, 33.3% oleic acid, 4% stearic acid, 1% linolenic acid, and 20% palmitic acid [11]. In Amaranth oil, the major carbon number present ranges from C50 to C54. This value is in the range reported for corn and cottonseed oils [12]. In addition, Amaranth oil has high amount of unsaponifiable matter of about 8%. This value is higher than the values of other oils, like sunflower (0.3–1.2), soybean (0.6–1.2) and olive (0.4–1.1) [1, 13]. Furthermore, Amaranth seeds oil contains other lipid components other than squalene. These components are phospholipids, glycolipids and sterols [14].

Of the lipid and oil components of Amaranth, squalene is of very high importance. This is because of its applications in various industrial products, hence, the need to briefly highlight it. Squalene is a type of unsaponifiable lipid which functions as a biosynthetic precursor, to all steroids (phytosterols and cholesterol) in both plants and animals [6, 15]. It is a triterpene ($C_{30}H_{50}$), often found in tissues of plants and animals [15]. Many research works have shown the biochemical importance squalene as antioxidant [15–18], as well as chemopreventive agent [19]. The economic and industrial importance of squalene cannot be overemphasized, due to its numerous applications. For instance, commercially, about 93 million dollars is the value of just 2500 tons of squalene that was produced in 2013 [15]. Industrially, it is used as an essential ingredient in skin cosmetics [1, 3, 10, 14, 15], due to it photoprotective ability, as well as a lubricant for computer disk [3, 10, 14], due to its thermostability [14]. Furthermore, in the area of health, squalene decreases different cancer(s) risk [10, 14], as well as reduces serum cholesterol levels [10].

From the forgoing, it could be seen that it is very important to extract oil from Amaranth seeds, especially due to the already highlighted vital industrial applications of its component, squalene. In other words, it is important to understand the extraction methods that could be used to extract oil from Amaranth, as well as justify the method to be used in the kinetics and thermodynamics studies of the extraction process. This chapter therefore, seeks to also look at the kinetics and thermodynamics of Amaranth seeds/grains oil extraction, using known extraction kinetics models. The models considered here are, parabolic diffusion, power law, hyperbolic, Elovich's and pseudo second order models. Also, the thermodynamic parameters evaluated are, enthalpy, entropy and Gibb's free energy change of the extraction process.

2. Methods of oil extraction from Amaranth seeds/grains

A number of very important factors affect extraction processes, irrespective of the substance being extracted (in this case Amaranth seeds), or the extraction method used. These factors include, but not limited to matrix properties of the material (plants, seeds, nuts, and leaves), solvent, extraction time, temperature, pressure [20, 21]. Oil extraction from seeds/nuts such as, Amaranth can be done using different methods. These extraction methods can be categorized into conventional (common) and non-conventional (new/novel techniques) methods [22–24].

Conventional (common) methods comprise of hydro-distillation (HD), steam distillation, cold pressing (CP), mechanical pressing, solvent extraction and simultaneous distillation-extraction methods, among others [23, 25]. On the other hand, non-conventional (novel) extraction methods include supercritical fluid extraction [26–29], pressurized liquid extraction (PLE) or pressurized fluid extraction (PFE) or accelerated fluid extraction (ASE) or enhanced/accelerated solvent extraction (ESE) or high pressure solvent extraction (HPSE) [30, 31], microwave-assisted extraction (MAE) [32–34], ultrasound-assisted extraction (UAE) [35–37], pulsed-electric field extraction (PEF) [38, 39], enzyme-assisted extraction (EAE) [40, 41], among others [23, 24].

Though the conventional techniques have been used over the years for various extraction purposes, with Amaranth oil extraction inclusive, they have their peculiar shortcomings, such as, low extraction efficiency in case of cold pressing and hydro distillation. Also, in the mechanical pressing and steam distillation conventional methods, degradation of unsaturated, or ester compounds through thermal or hydrolytic effects, are the main disadvantages associated them. In the case of solvent extraction method, the likely residual toxic solvent in the extracts or oil is its major shortcoming [23].

As a result of these short comings associated with traditional conventional (hydro-distillation, steam distillation, cold pressing, mechanical pressing, solvent extraction and distillation) methods, several non-conventional techniques earlier stated, are currently in use for oil extraction and other extracts from seeds/nuts, plants, flowers, leaves etc. [23, 24]. These novel methods have the advantage of functioning efficiently at elevated operating conditions (temperatures and/or pressures), thus decreasing the extraction time, significantly [24].

Nonetheless, conventional extraction methods, such as solvent extraction using Soxhlet extractor, is still considered as one of the reference methods, to compare success with the newly developed non-conventional (novel) methods [22, 24]. Soxhlet extraction as a well-established technique is more efficient than other conventional extraction methods, except in limited applications like, the extraction of thermo labile compounds [24]. It is important to state that Soxhlet extractor was first proposed by German chemist, Franz Ritter Von Soxhlet in 1879. Initially, it was designed primarily for lipid extraction, but presently it is no longer limited to this purpose alone. Soxhlet extractor is now widely used for the extraction of valuable substances such as bioactive compounds, oils, etc. [22], with Amaranth oil not being left out.

3. Justifications for the choice of Soxhlet extractor and solvent(s)

In the operation of Soxhlet extractor, it uses solvent in its operation for the extraction of valuable substances from the solute. In this case, for extraction of oil from Amaranth seeds/grains. For the operation of the extractor, different types of solvents, which can be used for extraction purposes, exist. These solvents will yield different quantities of the Amaranth oil. However, the most widely-used solvent for the extraction of oils from plants, seeds and nuts, irrespective of whether is Amaranth or any other seed/nut, is hexane. Hexane has a fairly narrow boiling point range of approximately 63–69°C, and it is an excellent solvent for oil extraction, especially in terms of solubility and ease of recovery [24].

Over the years, solvent extraction (by Soxhlet apparatus) using different solvents, have been used to extract oil from Amaranth seeds. For instance, He and Corke [6] successfully used Soxhlet apparatus to extract oil from *Amaranthus* grain, using petroleum ether (boiling point range 40–60°C) as the extracting solvent. They obtained an average Amaranth oil yield of 5.0%. Similarly, Ortega et al. [14] used Soxhlet apparatus in the extraction of Amaranth oil, using hexane as the solvent. In the work of Krulj et al. [2], Soxhlet apparatus was also used for *Amaranthus* sp. grain oil extraction, using petroleum ether (boiling point range 40–60°C), with obtained oil yield of 70–75.7 g/kg weight. Even as early as 1987, Lyon and Becker [4] had used Soxhlet apparatus for oil extraction from Amaranth seed, using hexane as solvent, and obtained oil yield of 7.01%. Several authors have also used this Soxhlet apparatus for oil extraction from Amaranth seeds.

The benefits of Soxhlet apparatus have also attracted its use for other vegetable oils extraction, from a wild number of other seeds/nuts, using different solvents. For instance, in the extraction of oil from African star apple (*Chrysophyllum albidum*) using Soxhlet extractor, Adebayo et al. [42] used hexane solvent and 10.71% yield was recorded. In case of oil extraction from *Hibiscus cannabinus* L. seed, Chan and Ismail [43] obtained a yield of 24.81%, using hexane; while Mariod et al. [44] got a yield of 62.38% using the same solvent. Furthermore, in the extraction of oil from *Plukenetia volubilis* seed using petroleum ether, Niu et al. [45] reported an oil yield of 39% using Soxhlet apparatus. Omeh et al. [46] reported a yield of 65% for the extraction of oil from *Irvingia Gabonensis* seeds, using hexane. Lasekan and Abdulkarim [47] successfully extracted oil from tiger nut (*Cyperus esculentus* L.), using n-hexane and yield of 26.28% was obtained. In case of *Terminalia catappa* oil extraction using Soxhlet extractor, yields of 49, 60.45 and 61.98% were reported by Dos Santos et al. [48], Menkiti et al. [49] and Adepoju et al. [50], respectively, using hexane. Many other authors too numerous to mention, have also successfully used Soxhlet extractor for oil extraction from seeds/nuts, because of its benefits/advantages.

This extensive use of Soxhlet apparatus (in solvent extraction) method was possible due to a number of its advantages. The advantages of using conventional Soxhlet extraction method include: (1) the displacement of transfer equilibrium by repeatedly bringing fresh solvent in contact with the solid matrix, (2) maintaining a relatively high extraction temperature with heat from the distillation flask, (3) cheapness and simplicity in operating the Soxhlet apparatus, and (4) filtration is not required after leaching [24, 51]. That notwithstanding, solvent extraction method using Soxhlet apparatus, is not without a number of shortcomings. Some of the disadvantages of conventional Soxhlet extraction include: (1) large quantity of solvent is required, (2) lengthy extraction time, (3) inability to provide agitation in the device in other to speed up the process [24].

On the other hand, N-hexane has been extensively used over the years as the preferred solvent for oil extraction from Amaranth seeds [4, 5, 14], as well as other seeds/nuts [49, 65], compared to other solvents [2, 6]. This was attributed to its nonpolar nature (low polarity index of 0.0), compared to the polarity indexes of other nonpolar solvents, like petroleum ether [49]. **Table 1** shows the oil yield,

Solvent	Yield[a] (%)	Boiling Point °C	Polarity	Polarity Index
Hexane	60.45	68.7	Nonpolar	0.0
Petroleum ether	56.00	60 – 80	Nonpolar	0.1
Benzene	48.50	80.1	Nonpolar	2.7
Chloroform	40.00	61.2	Polar	4.1
Ethanol	30.00	78.37	Polar	5.2

[a] Experimental oil yield values at 55°C and 150mins

Table 1.
Oil yield, boiling point and polarity/polarity index of solvents used in Terminalia catappa kernel oil extraction (source, Menkiti et al. [49]).

boiling point, polarity/polarity index of solvents, used in the preliminary evaluation of solvents effects on the oil yield of *Terminalia catappa* kernel (source, Menkiti et al. [49]). Also, its high boiling point 63–69°C, when compared to other solvents like petroleum ether, benzene, chloroform, methanol etc., is another added advantage [24, 49]. Lately, new solvents have been tested in extraction processes. Some of the tested solvents include but not limited to acetone, ethanol and isopropanol [52–56]. Nevertheless, only ethanol, isopropanol and occasionally acetone are permitted for use as solvents in the food industry, due to their minimal waste generation [57]. Thus, the advantages of hexane still supersede those of these solvent. Therefore, Soxhlet apparatus and hexane were used for ease of discussion of the kinetics and thermodynamics of Amaranth seed oil extraction.

4. Kinetics and kinetic models that could be used to model oil extraction from Amaranth seeds/grains

During solvent extraction using Soxhlet extractor, it is important to determine the rate at which equilibrium is attained between a miscella and oil and solvent, within the particles, irrespective of the seeds/nuts [58, 59]. There is therefore need to study the kinetics of Amaranth seed oil extraction, prior to evaluation of the existing kinetic models, that could be used to fit the obtained extraction kinetics data. Within the knowledge disposal of the author, there is no published article on the results of the kinetics of oil extraction from Amaranth seeds, hence, the need to evaluate the possible kinetic models that could be used to fit its oil extraction data, when obtained.

Therefore, due to the importance of kinetics with respect to oil extraction, a number of kinetic models have been proposed to analyze the kinetics of oil extraction processes for different seeds/nuts. Some of these seeds, nuts and kernels include but not limited to, partially dehulled sunflower [60], rapeseed [61, 62], confectionery, oilseed and wild sunflower [63], sunflower collets [64], *Terminalia catappa* [49], *Colocynthis vulgaris* Schrad [65] and olive cake [66].

These kinetic models can be classified into physical and empirical ones. Physical models are the models that are based on the physical phenomena of mass transfer, through the seeds/nuts particles and from external solid surfaces, into the bulk of the liquid phases [49, 67, 68]. On the other hand, empirical models are the models that describe mathematically variations of extractive substance amount in either seeds/nuts material or liquid extract with time [49, 68].

However, the empirical models would be treated in this section. These empirical models are ordinarily simpler than physical ones, and are also suitable for engineering purposes [49, 67]. Some examples of these models includes: power law model, hyperbolic model, parabolic diffusion model, Elovich's model, Weibull's model, pseudo second order model, and pseudo first order model [49, 67, 68]. These empirical kinetic models have been successfully used to model oil extraction from a number of seed/nuts. For instance, Menkiti et al. [49, 68], used power law, parabolic diffusion, hyperbolic, Elovich's and pseudo second order models, for *Terminalia catappa* kernel oil extraction kinetics study.

Similarly, Agu et al. [65] used these five models to study the kinetics of oil extraction from *Colocynthis vulgaris* Schrad seed. They reported that with the exception of power law model, all the other models gave relatively good fit to the experimental extraction kinetic data. This can be clearly seen in **Figure 1**. **Figure 1** shows the nonlinear kinetic plots of the experimental data, as well as the studied models, at varying particles sizes and at 55°C, for the extraction of oil from *Colocynthis vulgaris* Schrad seed (source, Agu et al. [65]). In the work of Menkiti et al. [49], they found that hyperbolic, Elovich's and pseudo second order models

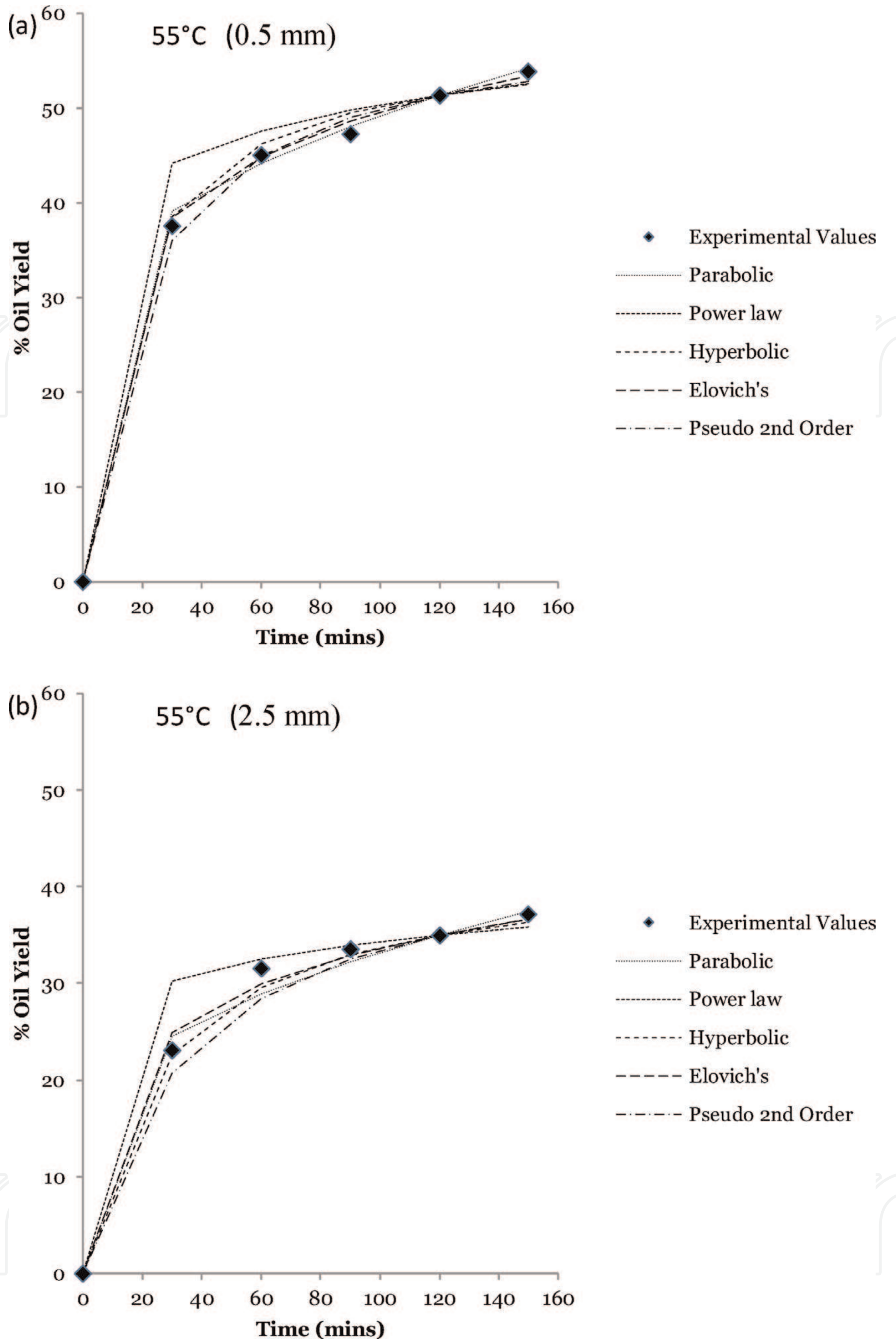

Figure 1.
Nonlinear kinetic plots at varying particle sizes (0.5 and 2.5 mm) at 55°C for Colocynthis vugaris Shrad seeds oil extraction (source, Agu et al. [65]).

studied, gave good fit to the experimental kinetic data, with pseudo second order models as the best. However, in the work of Menkiti et al. [68], they found that in the nonlinear fitting of the extraction kinetics data into these five models, that it was only hyperbolic and pseudo second order models, that gave well fit to the extraction data. In their separate studies on safflower seed oil extraction, Han et al. [69] and Ayas and Yilmaz [70], used the Sovova's extended Lack's Model (SLM) alone, to model the extraction process and reported that the model gave good fit to the experimental data.

Several researchers too numerous to mention have successfully used different extraction models to fit oil extraction kinetic data of a number of oil seeds/nuts. Over time, most researchers have modeled the extraction process they studied, using the pseudo second order model. This is because pseudo second order model has always fitted best to most solid-liquid extraction processes, as evident from some of the works earlier mentioned [49, 65, 68]. There is therefore need for researchers to direct their research interest, into the evaluation of the kinetics of Amaranth seed oil extraction, using these models.

Some of these known empirical kinetic models used to model solid-liquid extraction are briefly descried. The five two-parametric empirical kinetic models often used to model oil extraction from seeds/nuts are: parabolic diffusion, power law, hyperbolic, Elovich's and pseudo second-order models. Kinetic parameters of these models could be generated using both linear [49] and non-linear [65, 68] equations of the models. Prior to the empirical modeling of the extraction process, for Amaranth seed oil extractions, following assumptions are made on the basis of the empirical models:

- seed particles are isotropic and of equal size;
- distribution of extractive substances (oil) within the seed particles is uniform and varied only with time;
- neto diffusion occurs only towards the external surface of the seed particles;
- diffusion coefficient of extractive substances (oil) is constant.

However, for some models, there could be additional, specific assumptions that are introduced [49, 65, 68]. **Table 2** shows the linear and nonlinear forms of the extraction kinetic models equations that could be used to fit Amaranth seed oil kinetic data. These models equations are briefly described sequentially.

4.1 Parabolic diffusion model

The generalized form of the parabolic diffusion model equation is shown in Eq. (1).

$$\bar{q} = A_0 + A_1 t^{1/2} + A_2 t \tag{1}$$

Kinetic Models	Nonlinear Equs.	Linear Equs.
Parabolic diffusion	$\bar{q} = A_0 + A_1 t^{1/2}$	$\bar{q} = A_0 + A_1 t^{1/2}$
Power law	$\bar{q} = Bt^{1/2}$	$In\bar{q} = InB + nLnt$
Hyperbolic	$\bar{q} = \frac{C_1 t}{1 + C_2 t}$	$\frac{1}{\bar{q}} = \frac{1}{C_1} \times \frac{1}{t} + \frac{C_2}{C_1}$
Elovich's	$\bar{q} = E_0 + E_1 Int$	$\bar{q} = E_0 + E_1 Int$
Pseudo 2nd order	$\bar{q} = \frac{C_S^2 Kt}{1 + C_S Kt}$	$\frac{t}{C_t} = \frac{t}{KC_S^2} + \frac{t}{C_S}$

Table 2.
Models names, nonlinear and linear forms of equations that can be used to model Amaranth seed oil extraction data.

In the case of application of Eq. (1), for seed particles extraction, where chemical reaction is not involved, Eq. (1) can then be simplified to obtain Eq. (2) [71].

$$\overline{q} = A_0 + A_1 t^{1/2} \tag{2}$$

Eq. (2) is known as the parabolic diffusion equation. This model corresponds to the simple two-step extraction mechanism that consists of washing, followed by diffusion. The expression for A_0 is given in Eq. (3), while the constant A_1 is the diffusion rate constant. A_0 represents the extraction oil yield recovered instantaneously as the seed/nut material (Amaranth) is submersed into the solvent (i.e. at t = 0), and is called the washing coefficient [67].

$$A_0 = \frac{\overline{q}_w}{\overline{q}_0} \tag{3}$$

Where $\overline{q}_w$ is the amount of extractive substance (oil) washed away instantaneously as the sample material (Amaranth seed) is submersed into the solvent, $\overline{q}_0$ is the amount of extractive substance in the sample material (Amaranth seed). Both $\overline{q}_w$ and $\overline{q}_0$ are expressed as g/100 g of the sample material. From Eq. (2), a plot of % yield, $\overline{q}$ verses $t^{1/2}$, gives A_0 as the intercept, and A_1 as the slope.

4.2 Power law model

This model equation was used to reveal the mechanisms that governed the diffusion of any active agent through non-swelling devices [67]. In terms of modeling oil extraction from seeds, Menkiti et al. [68] and Agu et al. [65], successfully fitted the obtained experimental kinetic data, from *Terminalia catappa* kernel and *Colocynthis vulgaris* Schrad seed extractions, respectively, into power law model equation. As such, this model can also be used successfully to model oil extraction from Amaranth seeds/grains. Eq. (4) is the generalized form of power law model equation.

$$\overline{q} = Bt^n \tag{4}$$

Where, B is a constant incorporating the characteristics of the carrier-active system, and n is the diffusional exponent, indicative of transport mechanism. For extraction of materials (such as Amaranth seed), it is $n < 1$. The extraction yield predicted by this equation does not approach to unity (1) with time [67].

Hence, Eq. (4) can be re-written and n, replaced with 1/2, since at any time, n must be <1. Therefore, Eq. (4) can now be written as Eq. (5).

$$\overline{q} = Bt^{1/2} \tag{5}$$

Eq. (5) is then linearized to obtain Eq. (6).

$$In\overline{q} = InB + nLnt \tag{6}$$

By plotting $In\overline{q}$ against Int, the intercept is obtained as InB, while n is the slope.

4.3 Hyperbolic model

Hyperbolic model is a kinetic model that is often applied in food engineering science as pelegs model. This model has also been applied for oil extraction modeling from seeds/nuts. For instance, Menkiti et al. [49, 68], and Agu et al. [65], applied the nonlinear form of this model in oil extraction from *Terminalia catappa* kernel and *Colocynthis vulgaris* Schrad seed extractions, respectively. Eq. (7) is the general form of hyperbolic model [67, 72].

$$\overline{q} = \frac{C_1 t}{1 + C_2 t} \tag{7}$$

The extraction is first-order at the beginning, and decreases to zero-order in the later phase of the process. When $C_2 t << 1$, Eq. (7), then reduces to Eq. (8).

$$\overline{q} = C_1 t \tag{8}$$

On linearizing Eqs. (7) and (9) is obtained.

$$\frac{1}{\overline{\overline{q}}} = \frac{1}{C_1} \times \frac{1}{t} + \frac{C_2}{C_1} \tag{9}$$

The plot of $1/\overline{q}$ that is $1/yield$ against $1/t$ in Eq. (9), gives intercept as C_2/C_1 and the slope as $1/C_1$.

C_1 and C_2 are hyperbolic model parameters extraction rate at the beginning (min^{-1}), and constant related to maximum extraction yield (min^{-1}), $\overline{q}$, respectively.

4.4 Elovich's equation

The general form of Elovich's equation written as a logarithmic relation is shown in Eq. (10) [71, 73]. Like in the other three models already discussed, Elovich's model has also been applied to oil extraction modeling. In the works of Agu et al. [65], and Menkiti et al. [49, 68], Elovich's model was applied using the nonlinear form of the model, for oil extraction modeling of *Terminalia catappa* kernel and *Colocynthis vulgaris* Schrad seed, respectively. Hence, Elovich's model can also be applied to the modeling of Amaranth seeds oil extraction.

$$\overline{q} = E_0 + E_1 Int \tag{10}$$

The equation is derived under the assumption that the rate of extraction (in this case Amaranth oil extraction), decreases exponentially with increasing extraction yield, as could be seen in Eq. (11).

$$\frac{d\overline{q}}{dt} = \beta \times \exp\left(-\alpha\overline{q}\right) \tag{11}$$

Where $\beta = E_1 \times \exp\left(E_0/E_1\right)$ and $\alpha = 1/E_1$. When $\overline{q} \to 0$, then $d\overline{q}/dt \to \beta$, thus β is the initial extraction rate. A plot of yield $\overline{q}$ verse $In\ t$ in Eq. (10), gives E_0 as the intercept and E_1 as the slope. Where, E_0, and E_1 are Elovich equation parameters (L).

4.5 Pseudo second order model

In the case of the second-order rate law, the dissolution rate of the oil contained in the solid (in this case Amaranth seeds), into the solvent can be described by Eq. (12). Pseudo second order model equation has also been used to fit oil extraction data, obtained from oil seeds/nuts. This model was also used in its nonlinear form in the works of Agu et al. [65], and Menkiti et al. [49, 68], to fit the experimentally obtained kinetic data of *Colocynthis vulgaris* Schrad seed and *Terminalia catappa* kernel extractions, respectively. This model can also be used to the model of Amaranth seeds oil extraction.

$$\frac{dC_t}{dt} = K\,(C_s - C_t)^2 \tag{12}$$

where K is the second-order extraction rate constant (L g^{-1} min^{-1}); C_s is the extraction capacity (concentration of oil at saturation in g L^{-1}); C_t is the concentration of oil in the solution at any time (g L^{-1}), t (min).

The initial extraction rate defined as h, when t and C_t approach 0, can be expressed as shown in Eq. (13).

$$h = KC_s^2 \tag{13}$$

Considering the boundary conditions at $t = 0$ to t and $C_t = 0$ to C_t, the integrated rate law for pseudo second-order extraction was obtained as Eq. (14).

$$\overline{q} = \frac{C_s^2 Kt}{1 + C_s Kt} \tag{14}$$

The linearized form of Eq. (14), gives rise to Eq. (15).

$$\frac{t}{C_t} = \frac{t}{KC_s^2} + \frac{t}{C_s} \tag{15}$$

The initial extraction rate, h, the extraction capacity, C_s and the pseudo second order extraction rate constant, k, can be calculated experimentally by plotting t/C_t versus t in Eq. (15) [74].

5. Thermodynamic studies of oil extraction from Amaranth seeds

It is very important to consider the thermodynamic of any oil extraction process. In the case of the thermodynamics of Amaranth seed oil extraction, there could be little or no information available. There is therefore need for researcher to carry out this research. Thermodynamic parameters like enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) can be estimated using known thermodynamic equation [49].

The thermodynamic parameters (ΔH, ΔS and ΔG) for the extraction of oil from a particular seed, such as Amaranth seed, using n-hexane as solvent, can be estimated using Eqs. (16) and (17). However, Eq. (18) is used occasionally to calculate the equilibrium constant K.

$$\Delta G = -RTIn\ K \tag{16}$$

$$In\ K = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{17}$$

$$K = \frac{Y_T}{Y_u} = \frac{m_L}{m_s} \tag{18}$$

Where K is equilibrium constant, Y_T is the yield of oil at temperature T, Y_u is the percentage of the unextracted oil. Similarly, m_L is amount of a particular seed oil (in this case Amaranth oil) in liquid at equilibrium temperature T, while m_s is amount of a particular seed oil (Amaranth oil) in solid at equilibrium temperature T. R is gas constant (8.314 J/mol K), while ΔH, ΔS and ΔG are the enthalpy, entropy and Gibbs free energy of extraction (KJ/mol K), respectively [75].

Eq. (17) is a Van't Hoff relation, and plotting of *In K* against $1/T$, is used to determine the values of ΔH, ΔS and ΔG. The plot gives ΔH/R as the slope and ΔS/R as the intercept. The values of K, ΔH, ΔS and ΔG for the extraction of a particular seed oil (e.g. Amaranth oil) using n-hexane can be calculated using Eqs. (16)–(18).

It is important to know that the values of ΔG, ΔS and ΔH for the extraction of oil from seeds/nuts, using solvent extraction method, differ for different seeds/nuts. As such, the thermodynamic of oil extraction from Amaranth seeds needs to be evaluated by researchers, as limited or no research article in that regards is available. Due to the differences in the thermodynamic parameters of different seeds/nuts, several researchers have reported the thermodynamics of oil extraction for good number seeds/nuts.

For instance, the values of ΔG, ΔS and ΔH, respectively, were 10.94–13.35 kJ/mol, 33.10–39.57 J/mol K and 0.12–1.25 kJ/mol, for solid coconut waste oil extraction [76]. Amin et al. [77], reported that for *Jatropha curcas*, the ΔG, ΔS and ΔH values were, −4.928 kJ/mol, 15.275 J/mol K and 0.1586 kJ/mol, respectively. For fluted pumpkin extraction, the ΔG, ΔS and ΔH values were −3.902 to −8.909 kJ/mol K, 0.234 kJ/mol K and 78.84 kJ/mol, respectively [78]. In the work of Agu et al. [65], the values of ΔG, ΔS and ΔH, respectively, were −64.82 kJ/mol, 1.22 J/mol K and 333.40 kJ/mol, for *Colocynthis vulgaris* Schrad seed oil extraction. Furthermore, for sunflower oil extraction process, Topallar and Geçgel [79], reported that the ΔG, ΔS and ΔH values were −1.07 kJ/mol, 36.75 J/mol K and 11.2 kJ/mol, respectively.

As earlier highlighted, the thermodynamic parameters for the extraction of oil from Amaranth seeds/grains could be evaluated by the plotting of In K against $1/T$. Since there is no literature information on thermodynamics of Amaranth seeds oil extraction, figure from similar published work was used as an illustration. For instance, **Figure 2**, shows the plots of In K (equilibrium constant) verses $1/T$, at different particle sizes, for *Colocynthis vulgaris* Schrad seed [65]. Finally, from the values of ΔG, ΔS and ΔH, obtained by the aforementioned authors, they indicated the spontaneity, irreversibility and endothermic nature of the extraction processes.

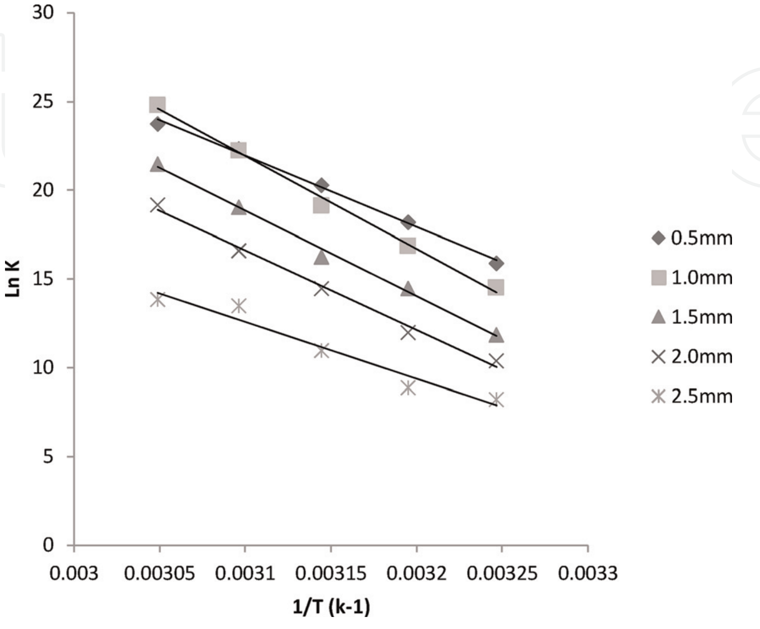

Figure 2.
Plot of In K (equilibrium constant) versus 1/T (temperature, K^{-1}) for the five different particle sizes (source, Agu et al. [65]).

6. Conclusion

It could be concluded from this chapter that due to the industrial, economic and health/nutritional benefits of Amaranth seeds oil, the insight into research on the kinetics and thermodynamics of Amaranth seed oil extraction has be made. It has also been justified that Soxhlet apparatus, using solvent like hexane, is an excellent conventional method for Amaranth seed/grains oil extraction. This chapter has highlighted the importance of oil extraction kinetics, as well as fitting experimentally obtained kinetic data, into known empirical kinetic models. Also, the need for thermodynamics studies of oil extraction processes, especially with respect to Amaranth seed oil extraction process, has been emphasized. Finally, there is need for researchers to now direct their studies towards the kinetics and thermodynamics of Amaranth seed oil extraction process, since there is little, or no literature information in this regards.

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