Industrial Crops & Products 123 (2018) 386–400

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Nonlinear Kinetics, Thermodynamics, and parametric studies of *Colocynthis vulgaris Shrad* seeds oil extraction

Chinedu M. Agu[a,*], Chukwuma H. Kadurumba[b], Albert C. Agulanna[c], Ozioma O. Aneke[a], Ijeoma E. Agu[d], Joy N. Eneh[e]

[a] *Department of Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria*
[b] *Department of Mechanical Engineering, Michael Okpara University of Agriculture, Umudike, Nigeria*
[c] *Materials and Energy Technology Department, Projects Development Institute (PRODA), Emene Industrial Area, Enugu, Nigeria*
[d] *Department of Civil Engineering, University of Nigeria, Nsukka, Nigeria*
[e] *Department of Electronic Engineering, University of Nigeria, Nsukka, Nigeria*

ARTICLE INFO

Keywords:
Kinetics
Nonlinear models
Thermodynamics
Colocynthis vulgaris shrad.

ABSTRACT

Nonlinear kinetics and thermodynamics of *Colocynthis vulgaris Shrad* Seeds oil (CVSSO) extraction were investigated using solvent extraction method. Parabolic diffusion, power law, hyperbolic, Elovich's, and pseudo second order models were the models studied. Seed average particle size, time and temperature were the considered process variables. Highest oil yield of 53.86% (by weight) was obtained at 55 °C, 0.5 mm and 150 min, while its physicochemical properties indicated its potential industrial utilization. In ascending order, the best fitted models are parabolic, Elovich's, pseudo second order and Hyperbolic (average R^2, RMS, SEE, ARE%, SSE, HYBRID%, MPSED% and SD: 0.9962, 0.02735, 0.3599, 1.7274, 4.1623, 2.879, 2.0386 and 0.0378). However, power law model failed to give adequate fitting to the experimental data. ΔH, ΔS and ΔG values of CVSSO extraction obtained at 0.5 mm and 328 K were 333.40 KJ/mol, 1.22 KJ/mol and - 64.82 KJ/mol, respectively, indicating endothermic, irreversible and spontaneous process.

1. Introduction

Predominantly, over 80% of the world's energy supply comes from conventional fossil fuels, such as crude oil (36%), natural gas (21%) and coal (23%) (Pujare and Paranjape, 2005). However, the fall in price of crude oil (petroleum) in the world market as well as the nonrenewable nature of the product has necessitated the need for alternative source of oil. This is because crude oil reserves from which mineral oil is obtained are limited and with the current rate of usage, will go into extinction soon (Fernandez et al., 2010).

Although mineral oil from petroleum base has primarily been used as lubricates, insulation and cooling fluids for more than a century (Fofana et al., 2002), its low flash and fire points are issues of great concern (Fernández et al., 2013). The primary concern of these short comings is the non-biodegradability nature; hence do not meet with the new health and environmental laws (Fernández et al., 2013). Thus, the need for biodegradability of the petroleum products as well as to meet the international regulatory standards become very paramount (Menkiti et al., 2017).

Nevertheless, the non-biodegradability and nonrenewable nature of oils from petroleum base is a major challenge that requires immediate attention. Vegetable oil is the main alternative to petroleum base oils, since they are environmentally friendly, bio-degradable as well as renewable (Ekpa and Isaac, 2013). In other words, the essence of the development of vegetable oil sector becomes very important due to its comparative advantage over mineral oils. Seeds and nuts are the major source of vegetable oil used for both domestic and industrial applications.

Colocynthis vulgaris Shrad also known as Melon seed is one of the seeds and nuts that has high yield of vegetable oil (Attah and Ibemesi, 1990). It is a member of the *Cucurbitaceae* family (Essien and Eduok, 2013). *Colocynthis vulgaris* Shrad is predominately cultivated in Africa especially in West Africa where it is used as soup thickener (Huang et al., 1994). In Nigeria especially the south-east, *Colocynthis vulgaris* Shrad is commonly known as "*egusi*" (Ogbonna and Obi, 2000). Its seeds contain high quantity of oil that is often underutilized. That notwithstanding, *Colocynthis vulgaris* Shrad is used in the production of sauces, salads, soups, juices and jellies (Essien and Eduok, 2013; Raj et al., 2015). In some African and Middle East countries, oil produced from *Colocynthis vulgaris* Shrad seeds (CVSS) are used for cooking and

* Corresponding author.
E-mail address: eduetal@yahoo.com (C.M. Agu).

https://doi.org/10.1016/j.indcrop.2018.06.074
Received 9 November 2017; Received in revised form 24 May 2018; Accepted 22 June 2018

Nomenclature

AOAC	Association of Official Analytical Chemists
ASTM	American Standard for Testing Materials
CVSS	*Colocynthis vulgaris Shrad* seeds
CVSSO	*Colocynthis vulgaris Shrad* seeds oil
GC	Gas Chromatography
RMS	Root Mean Square
SEE	standard error of estimation
ARE	Average relative error
SSE	Squares of the errors
HYBRID	Hybrid fractional error function
MPSED	Marquardt's percent standard deviation
SD	Standard Deviation
AARE	Absolute average relative error

frying (Ekpa and Isaac, 2013). The oil extracted from *Colocynthis vulgaris* Shrad seeds, has been reported to be useful in the production/preparation of metal soaps of zinc and cobalt (Igbum et al., 2015). Also, CVSS oil has been found to be a suitable substitute of soybean oil for the synthesis of oil-modified alkyd resins (Igwe and Ogbobe, 2000a) and medium-oil-length polyester resins (Igwe and Ogbobe, 2000b). Due to other important potential industrial utilization of *Colocynthis vulgaris Shrad* seeds oil, it is important to choose an appropriate method in extracting valuable oil from it.

Like other seeds/nuts, *Colocynthis vulgaris* Shrad seed oils can be extracted using either mechanical or solvent extraction methods (Liu et al., 2009; Amin et al., 2010; Sriti et al., 2011; Sulaiman et al., 2013; Attah and Ibemesi, 1990). However, solvent extraction method is preferred over mechanical method because of the high oil yield and low turbidity of the obtained oil (Amin et al., 2010; Sulaiman et al., 2013). Although residual solvent that is sometimes left on the product is the major drawback of solvent extraction method. This can be avoided by adequate and repeated solvent recovery after the extraction (Chiu et al., 2002; Liu et al., 2009; Sayyar et al., 2009).

As a very reliable method of oil extraction, solvent extraction has been used over the years for oil extraction from a wide range of seeds/nuts. Some of these seeds/nuts and their percentage oil yields includes but not limited to passion fruit (23.8%) (De Oliveira et al., 2013), *Plukenetia volubilis* seed (39%) (Niu et al., 2014), *Irvingia Gabonensis* seeds (65%) (Omeh et al., 2012), tiger nut (*Cyperus esculentus L.)* (26.28%) (Lasekan and Abdulkarim, 2012), cotton seed (74.14%) (Saxena et al., 2011), *Terminalia catappa* (60.45%) (Menkiti, et al., 2015), and sunflower (49.9%) (Perez et al., 2011).

Similarly, a number of researchers have extracted valuable oil from *Colocynthis vulgaris* Shrad seed using solvent extraction method. Some of these works and their percentage oil yields includes but not limited to the works of Attah and Ibemesi, (1990) (56.1 to 59.1%), Ekpa and Isaac, (2013) (43.49%), Isaac and Nsi, (2015) (40 to 60%), Ayodele and Shittu, (2013) (41.20 to 50.30%), and Ogunwa et al, (2015) (52.2%). Several studies on oil extraction from *Colocynthis vulgaris* Shrad seed have mainly focused on oil yield determination and physicochemical characterization for use as cooking and frying as well as its use in biodiesel production (Ekpa and Isaac, 2013; Essien and Eduok, 2013). As such, there is little or no attention on the kinetics and thermodynamics studies of *Colocynthis vulgaris* Shrad seed oil extraction. Although Nwabanne (2012) studied the kinetics and thermodynamics of oil extraction from fluted pumpkin seed using only linearized second order kinetic model but not on *Colocynthis vulgaris Shrad* seed. On the other hand, Isaac and Ekpa (2014), studied the kinetics of preparation of melon seed oils based biopolymers, but not on the extraction kinetics. In their separate studied, Fernández et al. (2012) and Menkiti et al. (2017) studied the kinetics of nonlinear extraction of canola and *Terminalia catappa L.* oils, respectively. To the best knowledge of the authors, there no existing published work on the nonlinear kinetics study of *Colocynthis vulgaris Shrad* seed oil extraction.

In other words, extensive studies on the kinetics and thermodynamics of seeds/nuts oil extraction process become very vital. Since is an important determinant of the possible use of such raw material industrially (Kitanovic et al., 2008). Therefore, the objectives of this study were to carry out extensive kinetics study of *Colocynthis vulgaris Shrad* seed oil extraction at different temperatures and seeds particle sizes, as well as to fit the obtained experimental data into five nonlinear extraction kinetic models (parabolic, power law, hyperbolic, Elovich's and pseudo second order models), so as to determine the model that best fit the experimentally obtained data. Additionally, the coefficient of determination (R^2) and seven statistical error functions [standard error of estimation (SEE), average relative error (ARE%), sum of the squares of the errors (SSE), hybrid fractional error function (HYBRID %), Marquardt's percent standard deviation (MPSED%) and standard deviation (SD)], were used to study the fitting of the extraction kinetics models to the experimentally obtained kinetics data (Riahi et al., 2013). Furthermore, the physicochemical and fatty acid composition characterizations of the extracted oil were investigated. Lastly, the thermodynamic parameters (entropy, enthalpy, and Gibb free energy) were determined.

2. Materials and method

2.1. Sample preparation

The *Colocynthis vulgaris Shrad* seeds (CVSS) were procured from Nkwo-Agu market in Umuaga, Udi L.G.A, Enugu State, Nigeria. Two 25 kg bags of *Colocynthis vulgaris Shrad* seeds were purchases from the market in February 2017. This was to ensure availability, and uniformity of the seeds throughout the research period. Proper screening was carried out on the CVSS samples to remove spoilt ones. Thereafter, the remaining seeds were manually cleaned. The essence of this was to ensure there was no debris in the seeds prior to the oil extraction. *Colocynthis vulgaris Shrad* seeds were then sun dried under the sun to remove moisture. Further drying of the seeds was carried out in the oven at 65 °C to reduce moisture content to 1.2%. The dried seeds were then milled using electric grinder and separated with five different standard sieve plates of sizes, 0.5 mm, 1.0 mm, 1.5 mm, 2.0 mm and 2.5 mm. This was done to ensure that 5 different average particle sizes of 0.5 mm, 1.0 mm, 1.5 mm, 2.0 mm and 2.5 mm, respectively, were obtained. Analytical grade of n-hexane and other reagents were purchased from Conraw chemical vendor located along Presidential Road, Enugu, Enugu State. The entire reagents were used without further purification.

2.2. Extraction of *Colocynthis vulgaris Shrad* seed oil

15 g of milled *Colocynthis vulgaris Shrad* seeds (CVSS) of a particular average particle size and 150 ml of n-hexane were placed in a Soxhlet extractor connected to a condenser. Oil extraction was carried out using Soxhlet extractor according to procedure reported in the literature (Menkiti et al., 2015; Sulaiman et al., 2013). The ratio of the *Colocynthis vulgaris Shrad* seeds to the solvent was 1:10 g/ml. The extracted oil trickled through the pores of the Soxhlet thimble and filled siphon tube. It then flowed into the 250 ml round bottom flask. Series of Soxhlet extractors were placed in a thermostatic bath at 35, 40, 45, 50, 55 °C. The extraction cycle was performed at each of the individual temperature (35–55 °C) using n-hexane and for five different average particles sizes (0.5 – 2.5 mm). At every temperature, extraction was carried out for 30, 60, 90, 120 and 150 min. At the end of every extraction