

Extraction of Oil from *Jatropha* Seeds-Optimization and Kinetics

Sepidar Sayyar, Zurina Zainal Abidin, Robiah Yunus and Azhari Muhammad
Department of Chemical and Environmental Engineering,
Faculty of Engineering, UPM 43400 Serdang, Selangor, Malaysia

Abstract: Problem statement: *Jatropha curcas* is a wonder plant with a variety of applications and enormous economic potentials. Oil from the seeds can be used as alternative fuel and for making biodiesel which aims to overcome energy crisis problems. In this study, extraction of *Jatropha* oil from seeds was optimized using organic solvent based on the amount of the extracted oil. The kinetics of extraction was also investigated and its parameters were determined based on a second order model. **Approach:** The effects of five operating parameters on the oil extraction namely type of solvents, temperature, solvent to solid ratio, processing time and particle size of the meal were investigated to optimize the processing conditions for achieving maximum oil yield. The kinetics of extraction was assumed based on a second order mechanism. The initial extraction rate, the saturated extraction capacity, the rate constant of extraction and the activation energy were calculated using the model. **Results:** The optimum conditions were found at 8 h reaction time, temperature of around 68°C, coarse particle size (0.5-0.75 mm), solvent to solid ratio of 6:1 and hexane as solvent. The activation energy was found to be 8021.9 J mol⁻¹. **Conclusion:** Hexane was found to be the best solvent for the process as compared to petroleum ether, the kinetics of extraction conforms well to the second order model and the extraction of *Jatropha* seeds was an endothermic process.

Key words: Optimization, solid liquid extraction of *Jatropha* seed, *Jatropha curcas*, biodiesel fuel

INTRODUCTION

Jatropha is a genus of over 170 plants from the Euphorbiaceae family, native to the Central America but commonly found and utilized across most of the tropical and subtropical regions of the world. It has a yield per hectare of more than four times that of soybean and ten times that of corn^[1]. Among the different species of *Jatropha*, *Jatropha curcas* has a wide range of uses and promises various significant benefits to human and industry. Extracts from this species have been shown to have anti-tumor activity^[2], the leaves can be used as a remedy for malaria and high fever,^[3,4] the seeds can be used in treatment of constipation and the sap was found effective in accelerating wound healing procedure^[3]. Moreover, this plant can be used as an ornamental plant, raw material for dye, potential feed stock, pesticide, soil enrichment manure and more importantly as an alternative for biodiesel production^[5,6].

Diesel is the major fuel used in transportation especially for vehicles such as trucks and trains. There is a growing demand for transportation fuel in most

countries with the manifestation of the current world energy crisis. Thus it is important to explore the feasibility of substituting diesel with an alternative fuel that can be produced on a massive scale for commercial utilization. The non-edible vegetable oil of *Jatropha curcas* promises a commercially viable alternative to diesel as it has the desired physiochemical and performance characteristics comparable to diesel to facilitate continuous operation without much change in design.

Solid liquid extraction is a common and efficient technique in producing oil for biodiesel production^[7]. Solid liquid extraction, sometimes called leaching, involves the transfer of a soluble fraction (the solute or leachant) from a solid material to a liquid solvent. The solute diffuses from the solid into the surrounding solvent. Normally, solid liquid extraction is dependent on the nature of the solvent and oil, reaction time between solvent and seeds, temperature of the process, particle size of the meal and the ratio of solvent to the meal.

The objectives of the present study were to investigate the factors affecting oil extraction from

Corresponding author: Zurina Zainal Abidin, Department of Chemical and Environmental Engineering,
Faculty of Engineering, UPM 43400 Serdang, Selangor, Malaysia
Tel: +603-89464371 Fax: +603-86567120

Jatropha seeds using organic solvents and to study the kinetics and mechanism of solid liquid extraction of Jatropha seeds based on a second order model.

Theory: Various researches and studies have been conducted to describe the kinetics and mechanism of the extraction processes^[8-11]. A solid liquid extraction process is found to be most appropriately fitted by a second order model^[8-12]. According to the literature, it is typical of a second order process to take place in two subsequent stages. First, the major part of the solute gets extracted quickly because of the scrubbing and dissolution caused by driving force of the fresh solvent and then comes the next stage where the extraction process gets much slower accomplished by external diffusion of the remainder solute into the solution.

Second-order mechanism model: Considering a second-order rate law, the rate of dissolution for the oil contained in the solid to solution can be described by the following Eq. 1:

$$\frac{dC_t}{dt} = k(C_s - C_t)^2 \quad (1)$$

Where:

- k = The second-order extraction rate constant (L g⁻¹ min⁻¹)
- C_s = The extraction capacity (concentration of oil at saturation in g L⁻¹)
- C_t = The concentration of oil in the solution at any time (g L⁻¹), t (min)

By considering the boundary condition t = 0-t and C_t = 0-C_t, the integrated rate law for a second-order extraction was obtained:

$$C_t = \frac{C_s^2 kt}{1 + C_s kt} \quad (2)$$

Linear form of the Eq. 2 would be:

$$\frac{t}{C_t} = \frac{1}{kC_s^2} + \frac{t}{C_s} \quad (3)$$

The extraction rate can be written as the following Eq. 4:

$$\frac{C_t}{t} = \frac{1}{(1/kC_s^2) + (t/C_s)} \quad (4)$$

Then, when t approaches 0, the initial extraction rate, h, can be written as:

$$h = kC_s^2 \quad (5)$$

By rearrangement of Eq. 4, the concentration of oil at any time can be obtained as:

$$C_t = \frac{t}{\frac{1}{h} + \frac{t}{C_s}} \quad (6)$$

The initial extraction rate, h, the extraction capacity, C_s and the second order extraction constant, k, can be calculated experimentally by plotting t/C_t vs. t.

Calculation of activation energy: For a second order system, the rate constants increase with temperature and may be described by the Arrhenius law:

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (7)$$

Where:

- k = The extraction rate constant (L g⁻¹ min⁻¹)
- A = The temperature independent factor (L g⁻¹ min⁻¹)
- E = The activation energy (J mol⁻¹)
- R = The gas constant (8.314 J mol⁻¹ K⁻¹)
- T = The absolute suspension temperature (K)

Linearization of Eq. 7 as shown below will give the value of the Activation energy (E) and the temperature independent factor (A) from ln (k) against 1/T plot:

$$\ln(k) = \ln(A) + \left(\frac{-E}{R}\right) \frac{1}{T} \quad (8)$$

MATERIALS AND METHODS

Raw material preparation: *Jatropha curcas l.* seeds were cracked and the shells were carefully removed. The kernels were grinded with a sieve plate and shaker grinder (Fritsch Cutting Mill P19) by using 0.5 and 0.75 mm sieve plates. The seeds were categorized into three particle size classes: below 0.5 mm (powder size), 0.5-0.75 mm (coarse size) and above 0.75 mm.

Optimization of oil extraction from jatropha seeds: The effect of five main factors which are type of solvent, temperature, solvent to solid ratio, particle size of the meal and reaction time were investigated to optimize the extraction operating conditions for achieving maximum oil yield.

Twenty gm of grinded meal was extracted with two types of solvent namely n-hexane and petroleum ether. The extraction temperature was varied from room

temperature (29°C) to boiling point of the solvent while the reaction time was varied between 6-9 h. The solvent to solid ratio was investigated from 4:1-7:1 and seed size was fixed at three sizes namely below 0.5, 0.5-0.75 and above 0.75 mm. These parameters were varied one at a time to identify the optimum conditions for each type of solvent. At the end of the extraction, the micelle was filtered using a vacuum filtration (Millipore glass base and funnel) to remove suspended solids. Subsequently, the solvent was separated from the oil using rotary vacuum evaporator (Laborota 4000) and was collected in the receiving flask. The oil which was remained in the sample flask was weighed after the process was completed. The percentage of extracted oil was calculated by dividing the amount of obtained oil by the amount of the seeds multiply by 100. All experiments were repeated at least twice.

Kinetics of extraction of jatropha oil: Based on the optimum parameters achieved from the optimization process, the rate of extraction of *Jatropha curcas* oil was determined at three different temperatures namely 45, 60 and near the solvent boiling point (around 68°C). The extraction was carried out in eleven extraction cycles of 15 min-8 h. In each cycle, 20 g coarse size seeds were extracted using hexane with solvent to solid ratio of 6:1. At the end of each cycle, the micelle was filtered by a vacuum filtration and the amount of the extracted oil was determined by separation of oil and solvent using rotary vacuum evaporator. Each extraction cycle was repeated twice.

RESULTS

Effect of solvent: Two different solvents were used to evaluate their extraction efficiency. The oil extraction capabilities of n-hexane and petroleum ether are shown in Fig. 1. The extraction yield with n-hexane was found to be about 1.3% more than that of petroleum ether (47.3% and 46.0% respectively) under similar conditions.

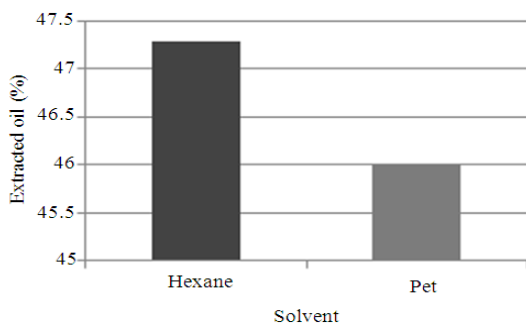


Fig. 1: Effect of solvent on amount of extracted oil with 6:1 ratio and coarse size seeds at boiling point temperature for 8 h.

Effect of extraction temperature: The effect of extraction temperature on the amount of extracted oil is shown in Fig. 2. When using hexane as the solvent, the amount of extracted oil increased around 1.5% by increasing the extraction temperature from room temperature to 45 and from 45-60°C. Extraction at boiling point (around 68°C) gives about 47.3% of oil, 2.3% higher than at 60°C. Similarly with petroleum ether, the oil yield increased with temperature until it reached the maximum value of 46.0% at near the boiling point temperature of 68°C.

Effect of reaction time: Figure 3 shows the total amount of oil extracted from *Jatropha* seeds at different reaction times. The amount of extracted oil by hexane and petroleum ether did not change significantly after 6 h. Most of the oil is extracted after 6 h although maximum extracted oil is achieved after 8 h with 47.3% and 46.0% for hexane and petroleum ether respectively.

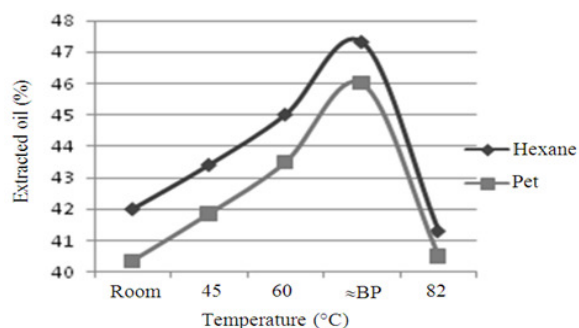


Fig. 2: The effect of extraction temperature on amount of extracted oil using hexane and petroleum ether as solvent, 6:1 ratio and coarse size seeds for 8 h

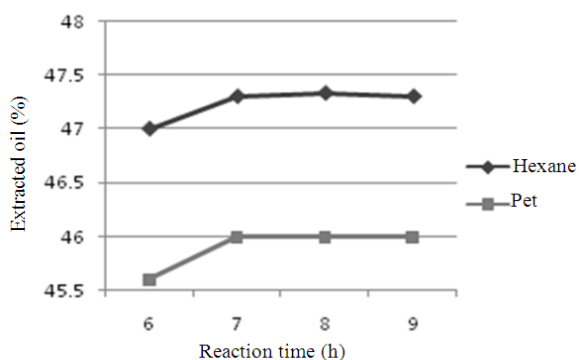


Fig. 3: The effect of reaction time on amount of extracted oil using hexane and petroleum ether as solvent, 6:1 ratio and coarse size seeds at boiling point temperature.

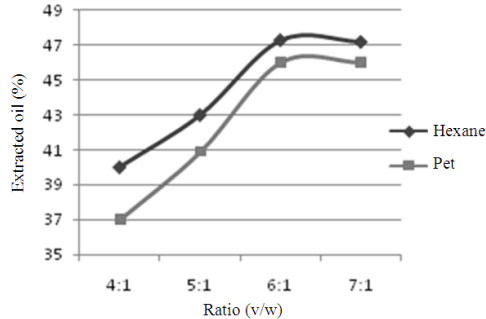


Fig. 4: The effect of solvent to solid ratio on amount of extracted oil using hexane and petroleum ether as solvent with coarse size seeds at boiling point temperature for 8 h

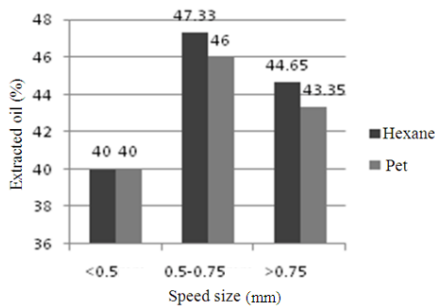


Fig. 5: The effect of seed size on amount of extracted oil with 6:1 ratio, at boiling point temperature for 8 h

Effect of solvent to solid ratio: Figure 4 shows the amount of extracted oil by hexane and petroleum ether at four different solvent to solid ratios (v/w). By increasing the ratio from 4:1-6:1, the total amount of extracted oil using hexane increased from 40.0-47.3%, whereas extracted oil using petroleum ether increased from 37.0-46.0%.

Effect of particle size: The effect of particle size of meal on extraction yield is shown in Fig. 5. The extraction was carried out using three different meal sizes namely 0.5 mm and below, between 0.5-0.75 and 0.75 mm and above. The highest percentage of oil yield was obtained from the intermediate size particle (0.5-0.75 mm) which is 47.3% and 46% using hexane and petroleum ether respectively.

Kinetics of extraction of jatropha oil: The kinetics of oil extraction from Jatropha seeds was studied at

different temperatures as shown in Fig. 6. The experiments were carried out under optimum reaction conditions namely using hexane as solvent, coarse particle size meal and solvent to solid ratio of 6:1.

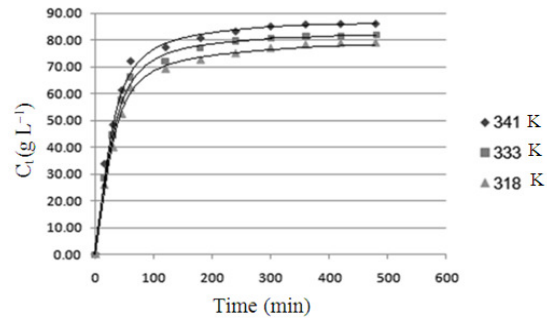


Fig. 6: Amount of extracted oil versus time at different temperatures in solid liquid extraction of Jatropha seeds using hexane as solvent, solvent to solid ratio of 6:1 and coarse size seeds for 8 h

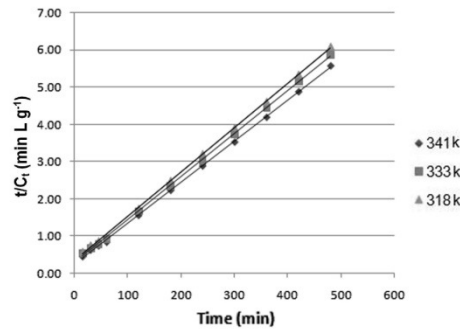


Fig. 7: Second order extraction kinetics of Jatropha seeds oil at different temperatures using hexane as solvent, solvent to solid ratio of 6:1 and coarse size seeds for 8 h

Table 1: Linearization of second order kinetic model of solid liquid extraction of Jatropha seed for at different temperatures using hexane as solvent, solvent to solid ratio of 6:1 and coarse size seeds

T (K)	C _s (g L ⁻¹)	k (L g ⁻¹ min ⁻¹)	h (g L ⁻¹ min ⁻¹)	R ²
318	84.03	4.2×10 ⁻⁴	2.94	0.9996
333	86.21	4.8×10 ⁻⁴	3.60	0.9995
341	90.91	5.1×10 ⁻⁴	4.21	0.9997

As shown in Fig. 6, the rate of extraction was very fast at the beginning of the operation, followed by a slower rate for the remaining of the extraction period until it reaches the plateau after 400 min of extraction. More than 30.0% of extractable oil is obtained in the first hour of the extraction. The experimental results

were analyzed using a second order model by plotting t/C_t versus time as shown in Fig. 7.

The saturation extraction capacity, C_s , the extraction rate constant, k , the initial extraction rate, h and the coefficient of determination, R^2 , were determined according to the linear curves. The data are shown in Table 1. The saturated extraction capacity, C_s ,

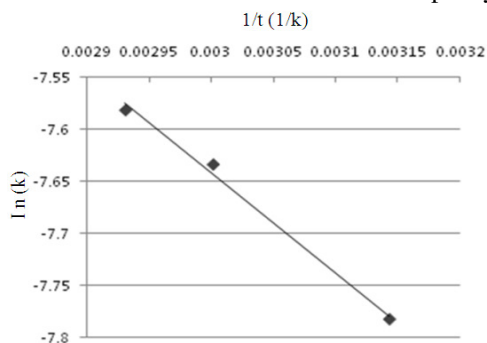


Fig. 8: Linear relationship between second order extraction constant, $\ln(k)$ and temperature for solid liquid extraction of *Jatropha* seed

increased from 84.0-90.9 g L⁻¹ when the temperature increased from 318-341 K. Similar trend was also observed for the extraction rate constant, k and the initial extraction rate, h , where changing the temperature from 318 to 341 K, increased their values from 4.2×10^{-4} to 5.1×10^{-4} L g⁻¹ min⁻¹ and 2.94 to 4.21 g L⁻¹ min⁻¹ respectively.

Calculation of activation energy: The second order extraction rate constant, k increases with temperature as shown in Table 1 and the changes can be described by the Arrhenius Equation.

Figure 8 shows a linear representation of Arrhenius Eq. The relationship between k and T can be defined by the linearized Arrhenius Eq. (Eq. 8), where A and activation energy were found to be 0.0087 L g⁻¹ min⁻¹ and 8021.9 J mol⁻¹ respectively obtained from the intercept and the slope of the plotted graph.

DISCUSSION

Based on the findings, hexane is a better solvent for *Jatropha* oil extraction. For both solvents, the yield was found to increase with increasing temperature up to the boiling point temperature (around 68°C) and decrease afterwards as most of the solvent had vaporized. By increasing the temperature approaching to the boiling point of the solvent, both the diffusion coefficient and the solubility of the oil in the solvent are enhanced, thus improve the extraction rate [13]. The

optimum extraction temperature for both solvents would be near their boiling point to ensure the maximum recovery of oil.

Increasing solvent to solid ratio up to a specific limit will increase the yield since the concentration gradient between the solid and the liquid phase becomes greater which favors good mass transfer. Based on the results, the solvent to solid ratio of 6:1 would be sufficient for both solvents to extract the maximum amount of oil and only marginal increment of oil amount can be obtained by increasing the ratio to 7:1. Therefore ratio 6:1 is the optimal solvent to solid ratio.

Less oil is extracted from the larger particles (>0.75 mm) compared to the smaller size particles. The reason is that larger particles with smaller contact surface areas are more resistant to solvent entrance and oil diffusion. Therefore, less amount of oil will be transferred from inside the larger particles to the surrounding solution in comparison with the smaller ones. Nevertheless, when the particle is too small i.e., below 0.5 mm, only 40.0% of oil can be extracted even though the contact surface area for small particle is supposed to be significantly higher than the larger particles. This may be due to the agglomeration of the fine particles which reduces the effective surface area available for the free flow of solvent to solid [13,14]. This problem is more apparent when oily *Jatropha* seeds are in use since the oily particles stick together easily to form paste material which prevents free interactions between solid and solvent. It can be concluded that the medium particle size meal between 0.5 and 0.75 mm (can be referred to as coarse size seeds) are more suitable for solid liquid extraction of *Jatropha* seeds.

In kinetics study, by increasing the extraction temperature, the optimum extraction duration can be reduced as reaction occurs faster. The final concentration also increases with temperatures due to the thermodynamic effect of temperature on solubilization of oil inside the solid.

The extraction rate is fast at the beginning of the extraction but gets slow gradually. The reason is that when the meal is exposed to the fresh solvent, the free oil on the surface of seeds is solubilized and oil gets extracted quickly inducing a fast increase in the extraction rate. Furthermore, since the oil concentration is low in the solvent at the beginning of the extraction process, the oil diffuses quickly from the meal to the liquid phase due to the mass transfer effect. As the time passing by, the concentration of oil increases in the solvent resulting in a decrease in the diffusion rate. When the maximum amount of extractable oil is obtained, the oil yield level remains invariable even by

extending the reaction time. The saturated extraction capacity, C_s , the extraction rate constant, k and the initial extraction rate, h , all increased with temperature. The extraction temperature has a direct effect on all the three variables.

The straight line curve as shown in Fig. 7 implies a good agreement of the second order extraction model with the experimental results. This agreement confirms the assumptions that solid liquid extraction of *Jatropha* seeds takes place in two subsequent stages.

According to the results achieved from Eq. 8, it can be concluded that solid liquid extraction of *Jatropha* seeds is an endothermic process since the activation energy is positive.

CONCLUSION

Five main operating parameters affecting the solid liquid extraction of *Jatropha* seeds were optimized based on the maximum oil yield extracted from the seeds. The optimum conditions for the lab scale solid liquid extraction were obtained at temperature near the boiling point (68°C), extraction time of 8 h solid to solvent ratio of 6:1, coarse size meal and hexane as a solvent. Hexane gives slightly better oil yield compared to petroleum ether. The kinetics of the extraction was developed based on the assumption of a second order extraction mechanism. The experimental data agrees well with the second order model and kinetics parameters namely the initial extraction rate, the rate constant of extraction, the saturation capacity of extraction and the activation energy were calculated using the model.

REFERENCES

1. Nobrega, W. and A. Sinha, 2007. Riding the Indian Tiger: Understanding India-the World's Fastest Growing Market. John Wiley and Sons, ISBN: 10: 0470183276, pp: 272.
2. Juan, L., Y. Fang, T. Lin and C. Fang, 2003. Antitumor effects of curcin from seeds of *Jatropha curcas*. Acta Pharmacol. Sin., 24: 241-246. <http://www.ncbi.nlm.nih.gov/pubmed/12617773>
3. Gubitz, G., M. Mittelbach and M. Trabi, 1999. Exploitation of the tropical oil seed plant *Jatropha curcas* L. Bioresour. Technol., 67: 73-82. <http://cat.inist.fr/?aModele=afficheN&cpsid=1624276>
4. Henning, R., 1997. Fuel Production Improves Food Production: The *Jatropha* Project in Mali. Proceedings from the symposium *Jatropha 97*, Managua, Nicaragua. http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19970201_gen-132.pdf
5. Vasudevan, P.T. and M. Briggs, 2007. Biodiesel production-current state of the art and challenges. J. Ind. Microbiol. Biotechnol., 35: 421-430. DOI: 10.1007/s10295-008-0312-2
6. Tiwari, A.K., A. Kumara and H. Raheman, 2007. Biodiesel production from *jatropha* oil (*Jatropha curcas*) with high free fatty acids: An optimized process. Biomass Bioenergy, 31: 569-575. DOI: 10.1016/j.biombioe.2007.03.003.
7. Forson, F.K., E.K. Oduro and E. Hammond-Donkoh, 2004. Performance of *jatropha* oil blends in a diesel engine. Renew. Energ., 29: 1135-1145. DOI: 10.1016/j.renene.2003.11.002.
8. So, G.C. and D.G. Macdonald, 1986. Kinetics of oil extraction from Canola (rapeseed). Can. J. Chem. Engin, 64: 80-86. [http://72.14.235.132/search?q=cache:3AE7xdKJm dUJ:grasasyaceites.revistas.csic.es/index.php/grasasyaceites/article/download/34/33+Kinetics+of+oil+extraction+from+Canola+\(rapeseed&cd=1&hl=en&ct=clnk&gl=pk](http://72.14.235.132/search?q=cache:3AE7xdKJm dUJ:grasasyaceites.revistas.csic.es/index.php/grasasyaceites/article/download/34/33+Kinetics+of+oil+extraction+from+Canola+(rapeseed&cd=1&hl=en&ct=clnk&gl=pk)
9. Wiese, K.L. and H.E. Snyder, 1987. Analysis of the oil extraction process in soybeans: A new continuous procedure. Am. Oil Chem. Soc., 64: 402-406. DOI: 10.1007/BF02549304
10. Meziane, S., H. Kadi and O. Lamrous, 2006. Kinetic study of oil extraction from olive foot cake. Grasasy Aceites, 57: 175-179. <http://cat.inist.fr/?aModele=afficheN&cpsid=18216571>
11. Meziane, S. and H. Kadi, 2008. Kinetics and thermodynamics of oil extraction from olive cake. Am. Oil Chem. Soc., 85: 391-396. <http://www.highbeam.com/doc/1P3-1461016971.html>
12. Rakotondramasy, R.L., J.L. Havet, C. Porte and H. Fauduet, 2007. Solid-liquid extraction of protopine from *fumaria officinalis* L-Analysis determination, kinetic reaction and model building. Separat. Purificat. Technol., 54: 253-261. <http://cat.inist.fr/?aModele=afficheN&cpsid=18626242>
13. Richardson, J.F. and J.H. Harker, 2002. Coulson and Richardson's Chemical Engineering-Particle Technology and Separation Processes. Butterworth-Heinemann, ISBN: 0750644451, pp: 502-542
14. Tzia, C. and G. Liadakis, 2003. Extraction Optimization in Food Engineering. CRC Press, USA., ISBN: 10: 0824741080, pp: 170-171.