Kinetic and Mass Transfer for the Extraction of Peanut Oil Using Soxhlet Extraction

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Abstract: This project focused on the extraction of peanut oil by using Soxhlet extraction. The main objective of this research is to determine the optimum condition for the Soxhlet extraction process in order to produce the highest extraction yields. Apart from that, this research is also to study about the mass transfer rate and kinetic to obtain the suitable diffusion coefficient and rate constant based on Fick's law and kinetic studies. The experiments were conducted with few manipulated variables which are particle sizes, solvent to solid ratio and extraction contact time. The optimum condition for the peanut oil extraction was found at 0.6 mm of particle size, 15:1 solid to solvent ratio with an extraction time of 8 hours. Besides, the calculated effective diffusivity is 4.3258 x 10^{-14} m^2/s. The extraction rate constant, k was found increase when the ratio of solvent to solid ratio increase due to higher amount of solvent facilitates the extraction process.

Keywords: Soxhlet extraction, Diffusion coefficient, Kinetic st

1. Introduction

Extraction is a technique of separating one or more desired substances from a liquid or solid mixture depending on their solubility and other physical properties. It usually occurs between two phases. Extraction is often used to extract natural product. Oil can be extracted either from a fleshy fruit such as palm and olives or from the plant seeds such as almond, sunflower, soybean, kenaf and peanut. In 2010 - 2013 an estimated 42 MMT (million metric tons) of peanuts were utilized annually in the world which was an increase of approximately 134 % from 18 MMT in the 1970s (Varshney, 2017). In Malaysia, peanut plantation only available in few states such as Perak, Kelantan, Johor, Terengganu, Sabah and Sarawak (Varshney, 2017). For a whole peanut, the shell accounts for approximately 28 - 32% and the kernel accounts for approximately 68 - 72% of the peanut (Wang et al., 2016). The peanut kernel is very nutritious, containing 38 - 60% fat, 24 - 36% protein, 10 - 23% carbohydrate, about 3% minerals, as well as bioactive components, such as vitamins, polyphenols, phytosterols, active polycarbohydrates, phospholipids and dietary fiber (Wang et al., 2016).

There are few techniques for the extraction process such as supercritical carbon dioxide extraction, heat reflux extraction, ultrasonic extraction, microwave-assisted extraction and few other techniques (Hung et al., 2014). The efficiency of the solvent extraction can be enhanced by employing microwaves, ultrasound and electrical field and charges into the extraction system (Hung et al., 2014). By using microwave, it is proven to shorten the extraction time due to the improvement of heating efficiency in the system. Ultrasound creates a bubble effects in the liquid which leads to cavitation hence it can provide better penetration of solvent and increase the mass transfer area within the system. Electrical field work with the same concept as ultrasound where the electrical breaks the cell structure and form cavitation which results in particle fragmentation. This also will lead to the increase in the mass transfer area.

Soxhlet extraction is one of the well-established and widely used extraction methods (Chen et al., 2015). The Soxhlet extractor was invented by Franz Ritter von Soxhlet in 1879 (Chen et al., 2015). One of the advantages of Soxhlet extraction is that the system is operating at high temperature by the heat applied to the distillation flask, this will increase the efficiency of the extraction. Furthermore, it also uses a simple methodology where only minimum training is required to perform the process. The main objective of this research is to determine the optimum condition for the Soxhlet extraction process in order to produce the highest extraction yields. Apart from that, this research objective is also to study about the mass transfer rate and kinetic to obtain the suitable diffusion coefficient and rate constant based on Fick's law and kinetic studies.

2. Materials and Methods

2.1 Peanut Seeds and General Chemical

For this research purpose, around 10 kg whole dehulled peanut was purchased from local supermarket. The peanut was placed in an oven at constant temperature of 100^{o}C for few hours to remove extra moisture. Further grinding and sieving process was done to get few different sizes of peanut sample. The ground peanut was sieved to the size of 0.6mm, 2.0mm and 2.4 mm. Around 10 liters of n-hexane (Pharmo-Aaper, 95 wt%) was used to be the extraction solvent for this research.

2.2 Peanut Oil Extraction

For this research project, there were three manipulated variable that need to be taken into consideration. First was the size of particle which is 0.6 mm, 2.0 mm and 2.4 mm. Solvent to solid ratio (8:1; 12: 1 and 15:1) and the duration for the extraction process (2-8 hours) were also considered in this experiment. The experiment started with the use of the tiniest particle size which is 0.6 mm with the smallest solvent to solid ratio which is 8 to 1 and the extraction time was set to be at 2 hours. The amount of solid which is the peanut use in this experiment was set constant at 30 g. For the 8 to 1 solvent to solid ratio, the amount of solvent used is around 250 ml. The 250 ml of n-hexane was poured into the receiving flask and 30 g of 0.6 mm size grounded peanut was filled into the cellulose thimble. The cellulose thimble was placed into the extraction chamber. The extraction chamber was assembled on top of the receiving flask and the tube for water flow was connected to the condenser. The temperature of the Soxhlet extractor was set at 70 ^{o}C. The experiment was started and the volume of the n-hexane in the receiving flask was checked from time to time to prevent it from drying. Once the time reached 2 hours, the Soxhlet extractor switch was turned off and it was allowed to cooled down for few minutes.

The product collected in the receiving flask was a mixture of peanut oil and the n-hexane. This liquid mixture was placed in the evaporator flask to be equipped in the rotary evaporator. The evaporator flask was rotated in a water bath which was set at a temperature of 100 ^{o}C. At this temperature, n-hexane exceeded its boiling point and vaporized. The vaporized n-hexane was condensed and collected through a pipe connecting the evaporator flask to the other flask. The evaporating process was set about half an hour or until the n-hexane was fully vaporized and condensed. The liquid which left in the evaporator flask was the pure peanut oil. The peanut oil was then transferred to a beaker and the mass was measured by the weighing scale. The mass of oil collected was recorded and the percentage of oil extracted was calculated by using equation in 1.1.

The experiment was repeated by using other particle sizes, solvent to solid ratios and different range of extraction period. All the result was recorded and tabulated in Table B.1.

2.3 Percentage of Oil Extracted

The oil yield extracted was calculated by using the equation below (Sulaiman ,2013):

$$\text{Percentage oil extracted (\%)} = \frac{oil\ collected\ (g)}{mass\ of\ peanut\ sample\ (g)}\ x\ 100 \qquad (1.1)$$

2.4 Kinetic Study

The mechanism and kinetics of extraction process have been reported in various studies. The equation for the oil dissolution rate which described by second order of kinetic is given by (Saxena et al.,2011):

$$\frac{dC_t}{dt} = k(C_e - C_t)^2 \qquad (1.2)$$

Where:

K = The second order extraction rate constant (L/g.min)

C_e = The oil concentration at equilibrium (g/L)

C_t = The oil concentration at time t (g/L)

After integrating and rearranging equation 3.2, the equation for the oil dissolution rate written as

$$\frac{C_t}{t} = \frac{kC_e{}^2}{1+C_e kt} \qquad (1.3)$$

At t = 0, the LHS of equation 2.3 will be the initial extraction rate, E_i. Hence the equation can be further reduced to

$$E_i = kc_e^2 \qquad (1.4)$$

Combining equation 3.3 and 3.4, the linear form of equation can be form in equation 3.5

$$\frac{t}{C_t} = \frac{1}{E_i} + \frac{t}{C_e} \qquad (1.5)$$

By plotting a graph of t/C_t vs time, the initial extraction rate, E_i, the oil concentration at equilibrium, C_e and the second order extraction constant was recorded and tabulated.

2.5 Mass Transfer Rate

The effective diffusivity, D_{eff} can be calculated by using Fick's second law by assuming the effective diffusivity is constant with ratio of concentration of oil at time t and the initial oil concentration,Y by the following equation (Sulaiman, 2013).

$$\ln Y = \ln\left(\frac{6}{\pi^2}\right) - \frac{\pi D_{eff}}{r^2} T \qquad (1.6)$$

Where

R = Particle radius in mm

Y = ratio of concentration of oil at time t and the initial oil concentration

Graph of ln Y versus time was plotted and the slope was used to determine the effective diffusivity.

3. Results and Discussion

The peanut oil extraction was done for the range of 2 hours to 8 hours period for each solvent to solid ratio and particle sizes. The amount of peanut sample was kept constant at 30 g for each experiment, which means for the 8 to 1 solid to solvent ratio, the solvent which is the n-hexane used for the extraction process is roughly about 250 ml and it follows similarly for the other two ratios.

3.1 Effects of Particle Sizes

The peanut oil extraction was conducted with 3 different particle sizes which is 0.6 mm, 2.0 mm and 2.4 mm using the same maximum amount of solvent to solid ratio which is 15 to 1 and constant extraction time which is for 8 hours**.** **Figure 1** below shows the trend for the graph of percentage of oil yield against particle sizes.

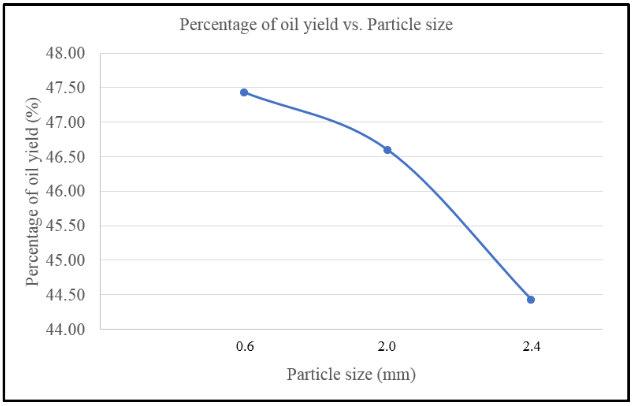

Figure 1. Graph of Percentage of Oil Yield vs Particle Size.

As shown by graph in **Figure 1**, the peanut sample of size 0.6 mm, 2.0 mm and 2.4 mm have an oil yield percentage of 47.43 %, 46.60 % and 44.43

% respectively. The result shown follows as expected whereby peanut with smaller particle size was expected to produce higher percentage of oil extraction as the surface area per unit weight of these particle will be higher. Also, bigger size particle will have a higher extraction resistance as the solvent require to travel through longer path to leach out the oil compared to the smaller size particle (Saxena et al., 2011).

3.2 Effect of Solvent to Solid ratio

To determine the effect of solvent-solid ratio, 8:1, 12:1 and 15:1 of the solvent-solid ratio were prepared and extraction process was conducted at a constant time which is 8 hours by using the smallest particle size which is 0.6 mm for the whole experiments. This particle size was chosen as it gave the maximum yield in the previous experiment in determining the best particle size for an optimum extraction rate. **Figure 2** below shows the trend for the graph of solvent to solid ratio vs % oil extracted.

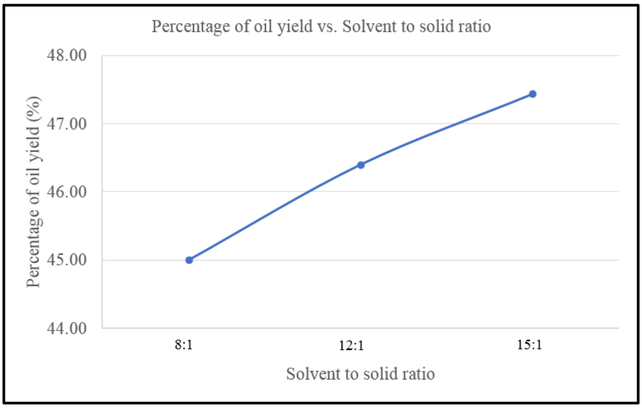

Figure 2. Graph of Percentage of Oil Yield vs Solvent to Solid Ratio.

As shown in graph in **Figure 2**, the percentage of oil yield increase as the amount of solvent used in the extraction increase and this proves that the expected result was highly acceptable. At solvent to solid ratio of 8 to 1, the percentage of oil yield is at 45.00%. This considered the lowest among all 3 yield for the solvent to solid ratio. This amount of oil yield was affected by the solubility of oil in the solvent which is n-hexane. Hence, it will prevent further extraction process occurring as it reaches near the saturation point of oil in n-hexane (Saxena et al., 2011). While for the solvent to solid ratio of 15 to 1, it yields around 47.43% of oil where at this point, the amount of solvent acting for the extraction mechanism was enough or in excess for the cycle of extraction to occur repeatedly. Hence yielding high amount of peanut oil

3.3 Effect of Extraction Time

This study was carried out for a period range of 2 to 8 hours maximum. For the effect of percentage of oil yield with extraction period, the size of particle and amount of solvent to solid ratio was set at constant value which is at size of 0.6 mm and 15 to 1 ratio. This particle size and solvent to solid ratio was chosen as it gave the maximum yield in the previous experiment in determining the best particle size and solvent to solid ratio for an optimum extraction rate. **Figure 3** below shows the trend for the graph of extraction time vs % oil extracted.

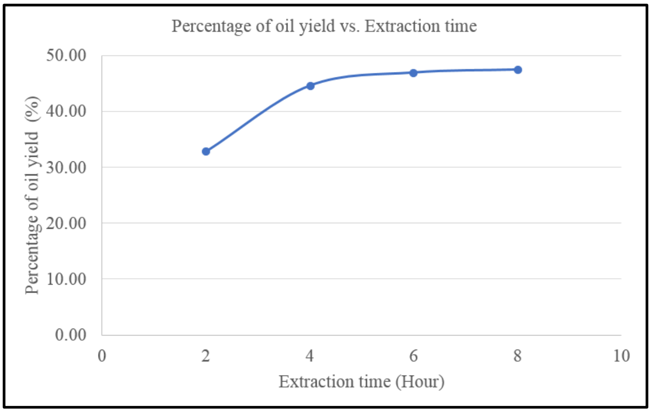

Figure 3. Graph of Extraction Time vs % Oil Extracted

As referred to **Figure 3**, the percentage of oil yield at an extraction time of 2 hours, 4 hours, 6 hours and 8 hours is 42.52 %, 44.53 %, 46.90 % and 47.43 % respectively. At the extraction time of 2 hours and 4 hours, there are an increment of 2.01 % of oil yield percentage. While 2.37 % increment from extraction time of 4 hours to 6 hours. At the extraction time of 6 hours and 8 hours, the increment in the percentage of oil yield was at 0.53 % where it is clearly the smallest increment among the other extraction time range. The result produced by this experiment match accordingly with the expected result where the extraction rate is expected to be high in the first hour and tapers off near the end. The rate of extraction is initially high during the first few hours because of the scrubbing of oil which presence on the peanut surface and the reduction of extraction rate in the end cause by the diffusion of the remaining oil into the solution (Rakotondramasy et al., 2007). This diffusion of the oil into the solution hence reduce the effectiveness of the extraction process. When the extractable oil reaches its maximum amount, the yield of oil will remain unchanged even after exceeding the time of extraction (Sulaiman et al., 2013).

3.4 Kinetic Study

There are few different studies which have been reported describing the kinetic and mechanism of this extraction process. Most of the researchers proposed a second order reaction kinetic for the solid-liquid extraction (Saxena et al, 2011). Typically, second order process takes place in two stages. First is the most important part which giving high impact on the extraction yield which is the scrubbing of oil surface influenced by the driving force of the solvent. While for the next stage, the diffusion of oil is lowered or slowed down hence reducing the extraction rate of the remaining peanut oil. The diffusion rate of the oil can be described by Equation 1.2.

$$\frac{dC_t}{dt} = k(C_e - C_t)^2 \tag{1.2}$$

Where:

K = The second order extraction rate constant (L/g.min)

C_e = The oil concentration at equilibrium (g/L)

C_t = The oil concentration at time t (g/L)

The equation was reduced and rearranged to the final equation which is Equation 1.5 as follow:

$$\frac{t}{C_t} = \frac{1}{E_i} + \frac{t}{C_e} \tag{1.5}$$

Graph of t/C_t against t was plotted. The gradient and intercept of the graph was obtained. Hence, the second order extraction constant, k, the concentration of solution at equilibrium, C_e, and the initial extraction rate, E_i can be calculated and tabulated in **Table 1.**

Table 1. Tabulated Result for Kinetic of Peanut Oil Extraction.

Solvent to solid ratio/ Size / Parameter		8:1	12:1	15:1
0.6 mm	C_e (g/L)	54.9451	40.3226	31.8471
	K (L/g.min)	1.6237 x 10^{-3}	1.9341 x 10^{-3}	3.5723 x 10^{-3}
	E_i (g/L.min)	4.9020	3.6232	3.1447
	R^2	0.98	0.99	0.99
2.0 mm	C_e (g/L)	54.3478	40.0000	31.5457
	K (L/g.min)	1.6122 x 10^{-3}	1.7960 x 10^{-3}	2.4273 x 10^{-3}
	E_i (g/L.min)	4.7619	2.8736	2.4155
	R^2	0.99	0.99	0.99
2.4 mm	C_e (g/L)	53.7634	38.7597	30.0300
	K (L/g.min)	1.6959 x 10^{-3}	2.0171 x 10^{-3}	4.2003 x 10^{-3}
	E_i (g/L.min)	4.9020	3.7879	3.0303
	R^2	0.99	0.99	0.99

Based on results above, for all 9 cases the regression coefficient, R^2 lies in range of 0.98 to 0.99. This proves that all the results are successfully described as the second order kinetic as suggested in Equation 1.2.

The concentration of oil at equilibrium, C_e, for particle size 0.6 mm calculated is 54.9451 g/L, 40.3226 g/L and 31.8471 g/L for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. This concentration of oil at equilibrium decreases with the increase of solvent to solid ratio. As shown in **Figure 4**, the result for the effect of solvent to solid ratio with extraction time, the oil yield percentage increases as the solvent to solid ratio increases. Theoretically, the concentration should follow the same trend as the oil yield percentage. But the result produced was the other way around. This is influence by the amount of solvent used for each experiment. The amount of solvent used was increase about 100 ml for each experiment. Since the increment in solvent amount was high compared to the increment in the mass of oil produced for each experiment, the concentration of oil at equilibrium decrease linearly with the increase of solvent to solid ratio. This theory was proven by the results of the other two particle sizes used in the experiment. For a particle size of 2.0 mm, the concentration of oil at equilibrium, C_e, is 54.3478 g/L, 40.00 g/L and 31.5457 g/L for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. For the last particle size which is 2.4 mm, the concentration of oil at equilibrium, C_e, is 53.7634 g/L, 38.7597 g/L and 30.03 g/L for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. For all 3 particle sizes used, the concentration of oil at equilibrium, C_e decreases when bigger volume of solvent is used. This result was strongly supported by a study conducted by Saxena et al. (2011) which also shows a decrease in the concentration of oil result as the solvent amount was increased.

3.5 Mass Transfer Rate

For the determination of mass transfer rate, the effective diffusion coefficient needs to be obtained. The following equation was used to determine the effective diffusivity, D_{eff}:

$$\ln Y = \ln\left(\frac{6}{\pi^2}\right) - \frac{\pi D_{eff}}{r^2}\, t \tag{1.6}$$

Where:

R = Particle radius in mm

Y = Ratio of concentration of solvent at time, t and the initial solvent concentration

Based on this equation, the graph of ln Y against time was plotted and the slope obtained was used to determine the effective diffusivity, D_{eff}. **Figure 4** shows the graph of ln Y against time plotted. Referring to graph, the gradient obtained is -0.5436 h^{-1} and the effective diffusivity calculated is 4.3258 x 10^{-14} m^2/s.

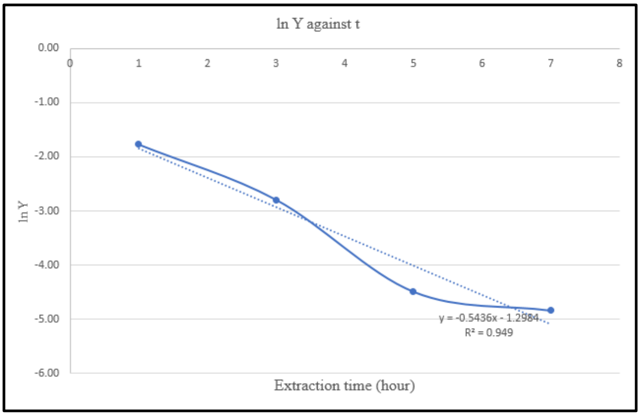

Figure 4. Graph of ln Y Against Time

Literature study conducted in by Mosca et al. (2018) stated a range of value for the effective diffusivity in between 1.15 x 10^{-11} m^{2}/s to 2.10 x 10^{-11} m^{2}/s for the extraction of antioxidant compound from seeds of *Sterculia apetala* plant. While the other literature study gave a range between 13.26 x 10^{-14} m^{2}/s to 105.49 x 10^{-14} m^{2}/s for the extraction of antioxidant from grape byproducts (Pinelo, 2006). The value of effective diffusivity is influenced by different raw material used, the surrounding condition for the extraction process to take place, size of particle used and also the extraction time (Mosca et al., 2018). The effective diffusivity shows how fast the extraction process occurs. The higher the effective diffusivity results in higher extraction rate (Petrovick et al., 2011). Determining the extraction rate is important as it is the major influential factor in designing a solvent extractor with a large-scale system. Literature study done by Seth et al. (2007) stated that a solid particle such as flaxseed, cottonseed and peanut which were cracked could be extracted more efficiently than flakes of equivalent thickness.

Initial concentration rate, E_i shows the instantaneous rate at the beginning of the experiment. For a result of the initial concentration rate, E_i shown in the research done by Saxena et al. (2011), the initial concentration rate, E_i increases as the solvent to solid ratio increases. The results trend produced and tabulated by this extraction of peanut oil experiment follows similarly as the research done by Saxena et al. (2011). In this case, for a particle size of 0.6 mm, the initial concentration rate, E_i is 4.9020 g/L.min, 3.6232 g/L.min and 3.1447 g/L.min for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. The justification for the decrease in the initial concentration rate can be related to the ratio of the amount of oil produced to the solvent amount used in each experiment. The amount of solvent for each experiment is set constant where the mass of oil produced increase but with just a small increment. Therefore, the initial concentration rate decreases linearly with the increase of solvent to solid ratio. For the other two particle sizes, the same results were obtained. The initial concentration rate, E_i for the particle size of 2.0 mm is 4.7619 g/L.min for a solid to solvent ration of 8:1, 2.8736 g/L.min for the solid to solvent ratio of 12:1 and 2.4155 g/L.min for the solid to solvent ratio of 15:1. While for the last particle size which is 2.4 mm, the initial concentration rate is 4.9020 g/L.min, 3.7839 g/L.min and 3.0303 g/L.min for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively.

The second order extraction rate constant, k, was calculated and tabulated in table for each experiment. For the particle size of 0.6 mm, the second order extraction rate constant, k is 1.6237×10^{-3}, 1.9341×10^{-3} and 3.5723×10^{-3} for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. While for particle size of 2.0 mm, the second order extraction rate constant, k is 1.6122×10^{-3}, 1.7960×10^{-3} and 2.4273×10^{-3} for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. For the last particle size which is 2.4 mm, the second order extraction rate constant, k, is 1.6959×10^{-3}, 2.0171×10^{-3} and $4.2003 \times 10^{-3\ 3}$ for the solvent to solid ratio of 8:1, 12:1 and 15:1 respectively. For all 3 particle sizes used, the second order extraction rate constant, k, shows an increase when bigger volume of solvent is used. This shows that the extraction rate is faster at a high solvent to solid ratio. Solubility of oil plays a great impact on the value of second order extraction rate constant for each of the solvent ratios. Saturation of oil and n-hexane occurs with the solvent to solid ratio of 8:1 hence reducing the rate of extraction. This result was strongly supported by previous literature study by Saxena et al. (2011) which also

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