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Kinetics of Extraction of Arabica Coffee Bean (*Coffea arabica*)

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Abstract. Coffee beans are the seeds of the coffee plant and a source of coffee beverages. Arabica coffee beans contain oil, which has many benefits. Extracting oil (solute) from coffee can be done through solvent extraction (leaching). The coffee bean oil extraction process uses n-hexane as a solvent because it can dissolve compounds with the same properties. This research aimed to study the extraction of essential oil from Arabica coffee beans and determine the kinetic model of extraction of essential oil from Arabica coffee beans by leaching. The process of separating coffee oil and solvent using thermogravimetric analysis with a temperature of 80 °C until the sample mass is constant. The variables used were temperature and time. The extraction time is 2 hours, with retrieval time every 10 minutes. The temperature used is 30, 40, and 50 °C with a ratio of material and solvent 1:10. The results showed that the kinetics of arabica coffee extraction followed the second-order extraction kinetics model. The second-order kinetic parameter values of arabica coffee essential oil extraction, namely extraction capacity (Cs) at 30, 40, and 50 °C were 5.45836, 5.46, and 5.46001 g L^{-1}, respectively, the rate of the initial extraction (h) was 0.00762718, 0,00756716, and 0,0104452 $gL^{-1}minute^{-1}$, the extraction rate constant (k) was 0.000256, 0.000254, and 0.00035 $g^{-1}L^{-1}minute^{-1}$, and determination values (R square) of 0.9965, 0.9967 and 0.9983.

Keywords: *coffee oil, extraction kinetics, and solvent extraction*

1. Introduction

Coffee is a reasonably high-value commodity among other plantations and is essential as a foreign exchange through exports. The taste and quality of coffee beans are determined by the processing method [1]. Coffee serves as the primary source of income for coffee farmers in Indonesia [2]. The success of coffee plantation agribusiness depends on coffee production, processing methods, and marketing strategy [3]. Indonesia has the most extensive coffee plantations, namely Arabica coffee beans and Robusta coffee beans [4][5]. Arabica coffee has a strong, slightly sour taste and distinctive aroma [6]. The oil content in fresh coffee beans ranges from 8% to 18%, depending on the type of coffee bean [7]. Arabica coffee beans contain

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oil that can be used as a source of triglycerides for biodiesel production, materials for making polyurethane membranes, antibacterial, anti-depressant, antioxidant, anti-cellulite, anti-hyperglycemic, anti-inflammatory, aromatherapy, relieve nausea, help the respiratory system, health soap, and others commercial things [8][9][10]. This is because coffee has complex chemical components such as caffeine, linoleic acid, palmitic acid, stearic acid, tocopherols, phosphatides, sterols, ceramides, and diterpenes which have been proven in biological activity. The content of roasted green coffee beans is 7-17% fat, consisting of 75% triacylglycerol and free fatty acids, similar to the composition of oils in other plants [11]. Green coffee bean oil contains a non-saponification fraction of phosphatides, sterols, ceramides, and diterpenes [12]. The two main diterpenes commonly observed in coffee are *kahweol* and *cafestol.* These two main diterpenes can increase Glutathione S-Transferase (GST) activity in rats' small intestine and liver. In animal models, these diterpenes have been shown to exert biological effects such as anticancer and chemo-preventive properties [13][14].

Extracting oil (solute) from coffee can be done through solvent extraction (leaching) [15][16][17]. Extracting oil from seeds using a solvent is preferred because the yield reaches 99% of the total oil content. Essential oils generally contain aromatic compounds such as terpenes (monoterpenes and sesquiterpenes), aldehydes, ketones, esters, alcohols, and phenols. Although diterpenes are a type of terpene, essential oils are typically richer in monoterpenes and sesquiterpenes than in diterpenes. The basic principle of extraction with solvents is that compounds with the same properties will dissolve with the properties of the solvent used. Extracts must have high solubility in solvents to obtain maximum extract content [18][19]. The selection of the type of solvent in the coffee oil extraction process needs to be considered because it affects the amount of oil and the yield of free fatty acids produced [20]. It is known that the highest extraction results with the highest amount of free fatty acids were obtained using hexane solvent compared to other non-polar solvents. The highest oil yield was produced in extraction with hexane solvent compared to ethanol and methanol solvents [21]. N-hexane, petroleum ether, carbon disulfide, carbon tetrachloride, benzene, and corn oil [22]are usually used to extract the nonpolar phase. Soxhletation is a type of extraction that uses solvents. The results obtained from this extraction are almost the same as the screw pressing technique since some of the polar fractions are also extracted [23] [24].

The kinetics of extracting essential oils from plants has been studied several times. According to the researchers, the mathematical model of steam extraction of basil essential oil

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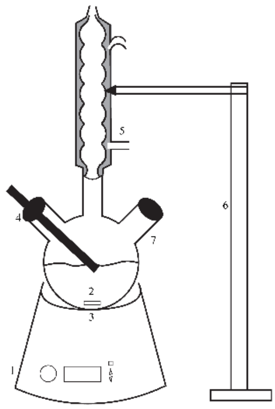
is based on the diffusion transfer and simultaneous convection of the vapor phase. The kinetics of essential oil extraction uses the first-order kinetics**.** However, the kinetic model for sandalwood oil extraction uses a second-order equation. The rapidly increasing amount can be seen in the second-order characteristics of essential oil at the beginning, and it will decrease slowly if the time is longer. Kinetic studies are critical studies that need to be done in the coffee bean extraction process. This study aims to determine the steps of the reaction rate controller and its kinetic model. In solvent extraction, it is important to remember that knowledge of the kinetics of oil extraction is essential as it helps determine the highest oil yield in the time interval studied. Therefore, it is necessary to conduct extensive studies on oil extraction kinetics from Arabica coffee beans [25] [26]. During the oil extraction process, the rate of extraction (the rate at which equilibrium is reached) is affected by several factors, such as the diffusing capacities of the solute and solvent, size, shape, internal structure of the seed particles (matrix), and the rate of dissolution of the solvent to the oil-soluble substance (solute). In other words, the extraction kinetics involves releasing oil from the porous or cellular matrix into the solvent through a mass transfer mechanism. The oil (solute) that binds to the solid matrix of the kernel particles both physically and chemically must be transferred to the solvent phase through the dissolution process [27]. The novelty of this study compared to previous research lies in its focus on the kinetic study of essential oil extraction from Arabica coffee beans. This topic has yet to be extensively explored in prior studies. Most previous research has concentrated on coffee oil's chemical composition and biological benefits. Still, it has yet to profoundly investigate the kinetic models of extraction that could be used to improve the efficiency of the extraction process. This study compares first-order and second-order kinetic models in the extraction process, providing a better understanding of the extraction rate mechanism and selecting the most appropriate model to describe the coffee oil extraction process. This approach differs from previous studies, which typically used only one kinetic model without a comprehensive comparison.

2. Materials and Methods

2.1 Materials

The materials used in this study were arabica coffee beans from Andungsari Village, Pakem District, Bondowoso Regency, and n-hexane PA.

2.2 Equipment



1. Heating mantle+stirrer
2. Three neck flasks
3. Stirrer
4. Thermometer
5. Ball condenser
6. Stative
7. Stopper

Figure 1. One Set of Leaching Extraction Tools

The tools used in this study were one set of leaching extraction equipment, oven (Samsung), measuring cup, measuring pipette, pipette, beaker glass, analytical balance, ball pipette, 80-mesh size sieve, glass funnel, watch glass, spoon, Erlenmeyer, rotary evaporator (IKA RV 8), membrane filtration.

2.3 Variables

Variables used in this study were time and temperature. The oil extraction in this process was done every 10 minutes for 2 hours with temperature variations of 30, 40, and 50 °C.

2.4 Methods

2.4.1 Determination of Soxhlet Extraction

The experiment in this study used arabica coffee beans. The first step was to roast Arabic coffee beans in an oven at 225 °C for 15 minutes. Roasting at 225 °C causes the change in color of the coffee beans, accompanied by the release of a distinctive coffee aroma. The color of coffee beans turns dark brown (blackish brown), accompanied by a powerful coffee aroma typical. This temperature produces maximum coffee bean oil. Then, it was cooled, mashed, and sieved using an 80-mesh sieve. When coffee beans are heated, the volatile compounds responsible for the aroma and taste of coffee are released. If coffee beans are ground directly without cooling, these compounds can evaporate quickly and reduce the quality of the aroma and taste of the coffee. Cooling helps stabilize these compounds, so they remain intact during extraction. High temperatures can cause thermal degradation of several essential compounds in coffee beans. This degradation process can be reduced by cooling the coffee beans so that the quality of the resulting extract remains optimal. From a practical perspective, cooling the coffee beans after heating will make subsequent handling easier and safer. Coffee beans that are still hot can cause equipment such as grinders or sieves to become damaged or compromise user safety. Cooling also helps ensure that the coffee beans can be crushed and sifted consistently, resulting in uniform particle sizes. This is important to ensure the extraction process runs effectively and efficiently. Next, the materials and solvents were prepared with a 1:10 ratio for each, namely 20 grams of material and 200 mL of solvent. Furthermore, setting up the extraction tools. The extraction method used was the Soxhlet method. The extraction was carried out until the results of the solvent inside the round flask became apparent, with a total time of 20 hours. The results were then put into the rotary evaporator to separate the solvent and oil to obtain the total oil yield in the arabica coffee beans. The operating conditions when using a rotary evaporator are as follows: the temperature is between 40-60 °C because n-hexane has a boiling point of approximately 69 °C at atmospheric pressure. The water bath temperature is typically between 40-60 °C to ensure efficient evaporation without approaching the standard boiling point. The vacuum pressure is maintained between 100-150 mbar to lower the boiling point of n-hexane, allowing the solvent to evaporate at a lower temperature. The rotation speed is set between 100-200 rpm to increase the surface area contact between the solvent and the water bath, thereby accelerating evaporation. The coolant must have a sufficient flow rate to effectively condense the n-hexane vapor, with the coolant temperature usually set around 0-10 °C to ensure effective condensation. The operational requirements for the rotary evaporator include ensuring no leaks in the vacuum system before starting. Any leaks can cause the solvent to evaporate inefficiently, requiring higher temperatures and increasing risk. It is essential to continuously monitor the water bath temperature and vacuum pressure during operation. Uncontrolled fluctuations in temperature or pressure can lead to inconsistent evaporation results or even damage to the sample.

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2.4.2 Determination of Extraction Kinetics

Studies by researchers on the kinetics of essential oil extraction are brought closer by two simultaneous processes, diffusion and convection, which represent the first-order and second-order extraction kinetics models. First-order kinetics of extraction can be interpreted by the change in the concentration of essential oils each time between the concentration of essential oils in a saturated state (Cs) and the concentration of essential oils in the material (Ct) when 't' is time (minutes) which is expressed in the equation below:

$$\frac{\mathrm{dCt}}{\mathrm{dt}} = \mathrm{k_1(Cs - Ct)} \tag{1}$$

Where k_1 is the first-order essential oil extraction rate constant (min^{-1}), Cs is the oil concentration in a saturated state. It is the extraction capacity (gL^{-1}), and Ct is the concentration of essential oil (gL^{-1}) when t (minutes). The value of the rate constant and extraction capacity of first-order essential oils is obtained by integrating equation (1) in the boundary conditions Ct = 0 when t = 0 and Ct = Ct when t = t, so the following equation is obtained:

$$\ln \frac{\mathrm{Cs}}{\mathrm{Cs - Ct}} = \mathrm{k_1 t} \tag{2}$$

Equation (2) can be stated if the values of the extraction rate constants and first-order extraction capacities, namely k_1 and Cs are obtained from the linear regression equation between log data (Cs-Ct) to t.

$$\mathrm{log(Cs - Ct) = logCs} - \frac{\mathrm{k_1}}{2{,}303}\mathrm{t} \tag{3}$$

Second-order kinetics of extraction involves two simultaneous processes, beginning with an increase in the amount of essential oil in the extraction process quickly and with a decrease in the rate of formation of essential oil when an equilibrium state is reached in the volume of essential oil produced. Second-order kinetics can be shown in the equation below:

$$\frac{dCt}{dt} = k_2(Cs - Ct)^2 \tag{4}$$

With k_2 being the second-order essential oil extraction rate constant (g^{-1} L $menit^{-1}$). Equality (4) integrated with the boundary conditions Ct = 0 when t = 0 and Ct = Ct when t = 0, so it is obtained:

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

The initial rate of extraction can be stated by h, namely k_2Cs^2 where Cs is the extraction capacity of the essential oil (gL^{-1}). The h, k_2, and C values are obtained from the slope and intercept values of the linear regression line between the t and t/Ct data [28].

The experiment used arabica coffee beans. The coffee beans were roasted in an oven at 225℃ for 15 minutes. Then, it was cooled, mashed, and sieved using an 80-mesh sieve. Next, prepared materials and solvents with a ratio of 1:10 for each, namely 20 grams of material and 200 mL of solvent. After that, the extraction equipment was set up. The extraction was done for 2 hours, using coffee bean oil every 10 minutes. The extraction results were then analyzed using thermogravimetry to see the amount of oil produced. This analysis aimed to determine the presence of solvents in the oil. The solvent in the extracted oil must be removed to obtain pure coffee bean oil. This analysis was carried out using an oven at 80 ℃ until the mass obtained was constant.

3. Result and Discussion

3.1 The Total Oil Yield

The total oil obtained from Bondowoso Arabica coffee beans was 5.46 grams. The yield at the end of the extraction of arabica coffee bean essential oil was 27.3%. The yield value of Bondowoso arabica coffee bean essential oil is higher than that of Aceh and Lampung, respectively, at 3.43% and 18.69% [10][23]. The yield of essential oils is influenced by plant species, planting location, harvesting age, and distillation method. In addition, the operating conditions used in this study differed from those for Arabica coffee beans from Aceh and Lampung. Research conducted by Lamona and Numan (2018) used arabica coffee from Aceh. It implemented the soxhlet extraction method, using 40 grams of material and 200 mL n-hexane at a temperature of 80 ℃ for 180 minutes. Research on the extraction of arabica coffee beans was also carried out by Berghuis and Maulana (2023) with arabica coffee from Lampung using the soxhlet extraction method, which used 10 grams of material and 250 mL of n-hexane at a temperature of 60 ℃ for 6 hours.

The influence of different conditions in this study can be observed through the variables used to extract essential oil from Arabica coffee beans. Differences in plant species, cultivation location, harvest age, and distillation methods significantly impact the extraction results.

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Operational conditions such as temperature and extraction time also play an important role in different studies, such as those conducted by Lamona and Numan (2018) and Berghuis and Maulana (2023). Variations in temperature and extraction duration yielded different results. The experimental results showed that the essential oil yield from Bondowoso Arabica coffee beans was higher (27.3%) compared to those from Aceh (3.43%) and Lampung (18.69%). This difference is attributed to the varying extraction conditions, such as the higher temperature and longer extraction time used in the Bondowoso Arabica coffee beans study. Increasing the extraction temperature can cause the diffusion rate of the solvent into the cell walls to rise. As a result, the cell walls will rupture, resulting in the release of essential oils. In addition, the extraction time also influences the results obtained. The longer the extraction time, the greater the results obtained until it reaches equilibrium [25]. Increasing the extraction temperature can affect the extraction yield by enhancing the diffusion rate of the solvent into the cell walls, resulting in the release of more essential oil. Therefore, operational conditions, particularly temperature and extraction time, significantly impact the yield of essential oil obtained.

3.2 The Extraction Kinetics

Based on the research results shown in Table 1, the yield of arabica coffee bean essential oil increased rapidly in the 30th to 60th minute and slowed down after the 60th minute of the extraction process. In Table 1, it can be seen that the higher the temperature and the longer the extraction time, the yield of arabica coffee bean essential oil will increase and be constant when it reaches equilibrium.

Table 1. The Results of Arabica Coffee Bean Essential Oil Weight at Different Temperature and Time

Time (minutes)	Weight (gram) at		
	30 °C	40 °C	50 °C
10	0.049	0.051	0.057
20	0.050	0.052	0.059
30	0.051	0.055	0.062
40	0.054	0.058	0.065
50	0.058	0.063	0.068
60	0.061	0.066	0.070
70	0.063	0.068	0.072
80	0.064	0.069	0.074
90	0.065	0.070	0.074
100	0.066	0.071	0.075
110	0.066	0.072	0.076
120	0.066	0.072	0.076

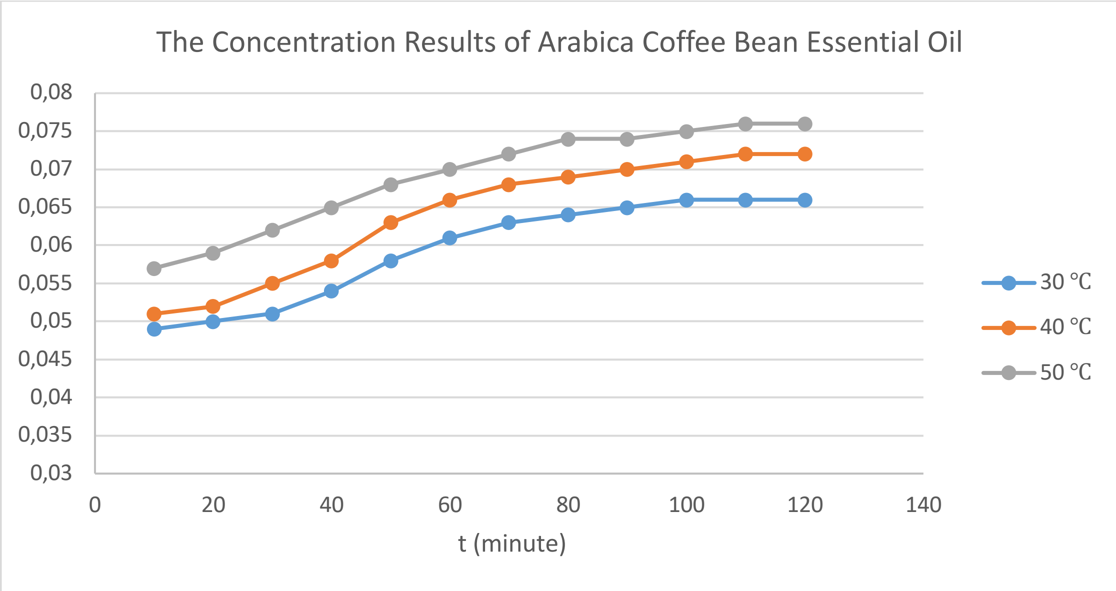

Figure 2. The Results of Arabica Coffee Bean Essential Oil Weight (gram)

Arabica coffee bean essential oil reached its maximum value at 120 minutes, as shown in Figure 2; this indicates that the essential oil reached a saturated state. The phenomenon of high extraction rates at the beginning of the process, followed by the diffusion of essential oils from the interior to the surface of the solid, is a characteristic of the extraction of essential oils from plants. The results of the coffee bean essential oil above are by the Arrhenius equation below:

$$k = A.e^{\frac{-E}{RT}} \tag{6}$$

$$k = 27{,}287.e^{-1520{,}9/T} \tag{7}$$

Information:

k = extraction rate constant

A = collision factor $((L/mol).s)$

E = activation energy (J/mol)

R = gas constant $(8{,}314\ Jmol^{-1}K^{-1})$

T = temperature (K)

From Figure 2 and Equation 7, it can be seen that the relationship between k and temperature is that the higher the temperature, the greater the value of k and the yield of arabica coffee bean essential oil, and with increasing time, the extraction rate increases.

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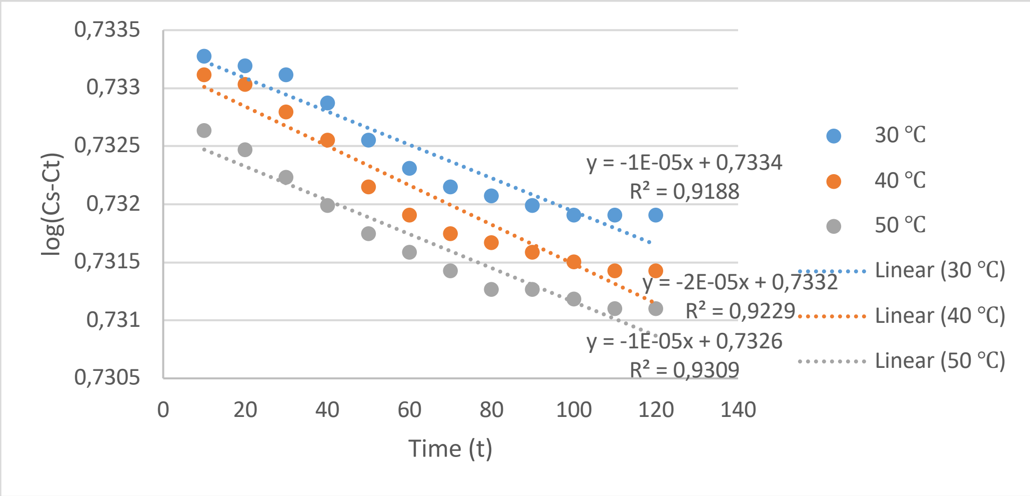

Figure 3. The Kinetic Model Curve of First-Order Coffee Bean Oil Extraction

Extraction kinetics is a combination of extraction and diffusion rates. A first-order and second-order kinetic model can approximate the extraction rate. The results of the log plot (Cs-Ct) against t, as shown in Figure 3, and using a first-order reaction using equation (3), the intercept value is obtained, which states the magnitude of the log Cs value, with Cs being the extraction capacity. The extraction rate constant value is obtained from the slope value of the graph in Figure 3. The extraction rate values at temperatures of 30, 40, and 50 ℃ are 0.00002303, 0.00004606, 0.00002303, respectively, and the first-order extraction capacity is 5.41253, 5.41003, and 5.40256 ($g.L^{-1}minute^{-1}$) with the R-square values at temperatures of 30, 40, and 50 ℃ are 0.9188, 0.9229, and 0.9309 respectively.

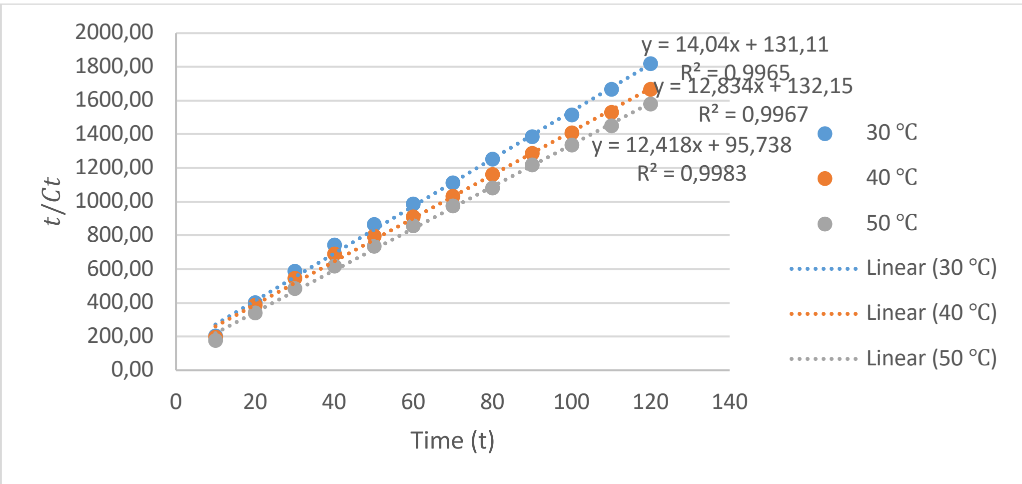

Figure 4. The Kinetic Model Curve of Second-Order Coffee Bean Essential Oil Extraction

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From equation (5), the extraction capacity of Arabica coffee bean essential oils obtained using the second-order kinetic model is 5.45836, 5.46, and 5.46001 gL^{-1}, respectively. Meanwhile, the initial extraction rate (h), namely k_2Cs^2, was obtained from the intercept values 0.00762718, 0.00756716, and 0.0104452 g $L^{-1}menit^{-1}$. The value of the second-order extraction rate constant (k_2) at temperatures of 30, 40, and 50 °C is 0.000256, 0.000254, and 0.00035 g^{-1} $L^{-1}minute^{-1}$, respectively, and the R-square values are 0.9965, 0.9967, and 0.9983 respectively.

Table 2. Kinetic Parameters for First-Order and Second-Order Reactions at Different Temperatures

Temperature (°C)	Order Reaction	Extraction Capacity (Cs) ($g.L^{-1}$)	Extraction Rate (k) ($g.L^{-1}.minute^{-1}$)	Initial Rate (h) ($g.L^{-1}.minute^{-1}$)	R-square
30	First Order	5.41253	0.00002303	-	0.9188
	Second Order	5.45836	0.000256	-	0.9965
40	First Order	5.41003	0.00004606	-	0.9229
	Second Order	5.46	0.000254	0.00762718	0.9967
50	First Order	5.40256	0.00002303	0.00756716	0.9309
	Second Order	5.46001	0.00035	0.0104452	0.9983

Based on Table 2, it is evident that the R^2 values for the second-order kinetic model (0.9965, 0.9967, 0.9983) are higher than those for the first-order kinetic model (0.9188, 0.9229, 0.9309) at all temperatures tested. This indicates that the second-order kinetic model is more appropriate for the data in this study, suggesting that the extraction rate of Arabica coffee bean essential oil is better described by the second-order kinetic model than the first-order model.

Table 3. Kinetics of Essential Oil Extraction of Various Plants

Plants	Methods	Order	Cs (gL^{-1})	k	h ($gL^{-1}min^{-1}$)	R^2	Ref.
Sandalwood	*Microwave Hydrodistilation*	2	0.6015	0.0642	0.0232	0.9597	[29]
Vertiver	*Microwave Hydrodistilation*	2	6.2189	0.0007	0.029	0.9427	[30]
Black Pepper	*Hydrodistilation*	2	4.9	0.0086	0.206	0.997	[25]
Arabica Coffee	*Leaching*	2	5.46001	0.00035	0.0104452	0.9983	The present study

Table 3 shows the kinetics of the extraction of essential oils from several plants by following the second-order kinetic model. The plant species influence the extraction rate constant (k) and the concentration of essential oils in the saturated state (Cs). The k value in the extraction of Arabica coffee beans using the leaching method has the smallest k value because the temperature used in this study is lower than in other studies. The higher the temperature, the greater the k obtained [25][29][30].

4. Conclusion

The extraction of Bondowoso arabica coffee bean essential oil using the solvent extraction (leaching) method produced an experimental yield of 27.3% with the extraction kinetics following the second-order kinetics model. The kinetic parameters of the essential oil extraction of Bondowoso arabica coffee beans, namely extraction rate constants, k was 0.000256, 0.000254, and 0.00035 g^{-1} $L^{-1}minute^{-1}$, with determination values (R square) of 99.65%, 99.67%, and 99.83% and using second order reactions.

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