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Optimization and Kinetics Extraction of Natural Dyes from Henna Leaves (*Lawsonia inermis* L.) with Ultrasonic Assistance

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Abstract

The Lawson dye contained in the leaves of *Lawsonia inermis* L. has a red-orange color, which can be used as a fabric dye. The solvent is ethanol because it can attract flavonoid compounds bound to Lawson. The ultrasonic-assisted extraction method is employed to enhance the extraction process by breaking down cell walls, thereby facilitating a more rapid extraction of the desired solute. This study investigated the effects of material-to-solvent ratio, ethanol concentration, and extraction time. The research results were analyzed using a UV-Visible spectrophotometer to determine the yield of Lawson extract. The Face-Centered Composite Design (FCCCD) method was applied to this study to obtain optimal analysis results and extraction conditions. The independent variables in this study were the ratio of ingredients to solvent (0.02-0.06 g/g), ethanol concentration (20-60%), and extraction time (5-15 minutes). The optimal extraction conditions were obtained at a ratio of 0.02 g/g, an ethanol concentration of 60%, and an extraction time of 15 minutes, with a predicted model yield of 15.417%. The actual yield under these conditions was found to be 15.4934%. Furthermore, the extraction kinetics model was analyzed to study and predict the optimal Lawson extraction results. Extraction kinetics calculations were carried out using first-order and second-order based on the Lagergren equation. The most suitable extraction kinetic model is second-order with a determinant coefficient value, or the value of R^2 is 1, which indicates that the order kinetic model equation represents the actual conditions.

1. Introduction

Synthetic dyes in the textile dyeing process have advantages and disadvantages. Synthetic dyes are widely used because they have a wide variety of colors and are more practical. However, the excessive use of synthetic dyes causes environmental problems with the heavy metal pollutants they contain. Synthetic dyes that are discharged into the waters will pollute the environment. Therefore, natural dyes are used to reduce the impact of these heavy metal pollutants. One of the plants that can be used as a natural dye is henna leaves (*Lawsonia inermis* L.) [1, 2].

Lawsonia inermis L. contain Lawson compounds, which can be used as yellow and orange dyes. Lawson's dyes can be applied to skin, nails, hair, silk, and wool. The conventional extraction of Lawson's dye typically involves maceration, which demands substantial amounts of solvent and time. The ultrasonic method aims to speed up the extraction process and increase the yield of the extraction results. The Response Surface Methodology (RSM) optimization technique is applied to elevate the yield of ultrasonic extraction results, aiming for maximum efficiency with minimized solvent usage and concentration. The RSM method was chosen using the Face-Centered Central Composite Design (FCCCD) to determine the points and the number of research variables to be carried out. Following the optimal conditions determined through the RSM analysis, a subsequent investigation into the extraction kinetics model was conducted. The study of extraction kinetics was used as one of the parameters to estimate the rate of the extraction process against time. The study of extraction kinetics was carried out using the first- and second-order approaches where the extraction rate obtained was used as a parameter when scale-up was carried out in the *Lawsonia inermis* L. leaves extraction process [3, 4, 5, 6].

2. Experimental

2.1. Equipment

The equipment used in this study was an ultrasonic bath, three-neck flask, thermometer controller, beaker glass, hotplate, and analytical balance. The arrangement of ultrasonic-assisted extraction tools is illustrated in Figure 1.

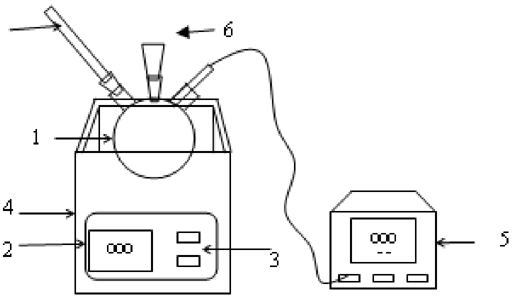

Figure 1. Schematic of the ultrasonic extraction device

2.2. Materials

The research material used was *Lawsonia inermis* L. (*Lawsonia inermis* L.). These *Lawsonia inermis* L. were obtained from the Middle East. The solvents used in this research were ethanol and distilled water.

2.3. Ultrasonic Extraction

Ultrasonic-assisted extraction is a renewable extraction method that speeds up and optimizes extraction. The parameters under investigation included the mass ratio of the material to the solvent, ethanol concentration, and extraction duration. Specifically, the material-to-solvent mass ratio ranged from 0.02 to 0.06 (g/g), ethanol concentrations varied between 20% and 60%, and the extraction time was 5-15 minutes. The fixed variable in this extraction was the extraction temperature at 60°C. Each extraction result with these variables was filtered using filter paper. As the target extract comprised solid compounds of Lawson, this filtration process was conducted utilizing a water bath set at a temperature of 70°C. The resulting dry solids were cooled and weighed to obtain the final yield. The resulting extract was analyzed using UV-Vis and an FTIR spectrophotometer.

2.4. RSM Optimization Study

Response Surface Methodology is an optimization method to help analyze and evaluate each variable's factor effects and interactions. This optimization was used to reduce the number of variations in research. The FCCCD optimization method was chosen to model and analyze the interactions and effects of the three variables studied: mass-to-mass ratio (g/g), ethanol concentration (%), and extraction time (minute). This RSM was used to assist researchers in increasing maximum research results with an efficient number of studies. The optimized response variable is the yield of Lawson extract from *Lawsonia inermis* L. leaves.

2.5. Extraction Kinetics Study

Modeling the kinetics of extracting *Lawsonia inermis* L. leaves with the help of ultrasonics was carried out using first-order and second-order kinetic models, where the kinetic models that fit the experimental results were later identified and analyzed.

The first-order kinetic Equation can be written as in Equation (1).

$$\frac{dC_t}{dt} = k_1(C_s - C_t) \quad (1)$$

where k_1 is the value of the extraction rate constant, and t is the extraction time.

Equation (1) is integrated with C_t = 0 at t = 0 and C_t = t at t = t, resulting in Equation (2) derivation.

$$\ln\left(\frac{Cs}{Cs - Ct}\right) = k_1 t \quad (2)$$

Equation (2) is converted into linear form, as stated in Equation (3).

$$\text{Log}\,(C_s - C_t) = \log\,(C_s) - \frac{k_1}{2.303}t \quad (3)$$

Next, a plot is made between $\log(C_s - C_t)$ vs t to get the slope and intercept values. The reaction rate constant (k_1) and extraction capacity (C_s) can be determined from the slope and intercept values.

The second-order kinetic Equation can be written as in Equation (4).

$$\frac{dC_t}{dt} = k_2(C_s - C_t)^2 \quad (4)$$

where k_2 is the extraction rate constant for the second-order. Equation (4) can be changed to Equation (5).

$$\frac{dC_t}{(C_s - C_t)^2} = k_2\, dt \quad (5)$$

Next, Equation (5) is integrated, and the limit value C_t = 0 is entered at t = 0 and C_t = C_t at t = t, resulting in Equation (6).

$$C_t = \frac{k_2 C_s^2 t}{1 + C_s k_2 t} \quad (6)$$

Equation (6) is converted into linear form, as expressed in Equation (7).

$$\frac{C_t}{t} = \frac{1}{\frac{1}{k_2 C_s^2} + \frac{t}{C_s}} \quad (7)$$

By substituting the value of k_2Cs_2 into h or incorporating the initial extraction rate value into Equation (6), the resulting Equation is formulated as Equation (7).

$$\frac{t}{C_t} = \frac{t}{C_s} + \frac{1}{h} \quad (8)$$

Next, a plot is carried out between t/C_t vs. t to determine the slope and intercept to obtain the extraction rate constant value k_2 and the extraction capacity value C_s.

3. Results and Discussion

3.1. RSM Optimization Study

The FCCCD method is applied in the research focused on the ultrasonic-assisted extraction of *Lawsonia inermis* L. leaves. A total of 15 trials were conducted in this study. Data were analyzed using Design-Expert 11 software by adjusting the second-order polynomial model as in Equation (9).

$$Y= \beta_0+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_{12}X_1X_2+\beta_{13}X_1X_3+\beta_{23}X_2X_3+\beta_{11}X_{12}+\beta_{22}X_{22}+ \beta_{33}X_{32} \quad (9)$$

where, Y is the response of the calculated model (yield value). The values x_1, x_2, and x_3 indicate the independent variables.

The resulting response variation modeling was analyzed using Mean vs. Total, Linear vs. Mean, 2FI (2-factor interaction) vs. Linear, Square vs. 2FI, and Cubic vs. Quadratic. The analysis shows that modeling quadratic functions or second-order polynomials is most appropriate (Table 1). Based on ANOVA analysis of the RSM model based on responses, the R^2 value of 0.90-0.99 shows results close to the actual experimental value (Table 2). The average predicted yield is determined using Equation (10).

$$Y= 19.02930 - (195.70497 \times F/S) - (0.113040 \times \text{Ethanol Concentration}) - (0.050036 \times \text{Extraction time}) + (0.335202 \times F/S \times \text{Ethanol Concentration}) - (2.44328 \times F/S \times \text{Extraction time}) + (0.003310 \times \text{Ethanol Concentration} \times \text{Extraction time}) + (1.626.10147 \times F/S^2) + (0.000922 \times \text{Ethanol Concentration}^2) + (0.004068 \times \text{Extraction time}^2) \quad (10)$$

The ANOVA results in Table 3 using a quadratic model are generally significant. Analysis of variance in ANOVA (Table 3) for the quadratic model typically has a p-value <0.05, indicating that the model is logical and valid. The F-value of the model is 28.33, meaning that this model is significant [7, 8]. Variables influencing the yield response encompass the mass ratio of material to solvent (F/S, g/g), ethanol concentration (%), and extraction time (minute). Notably, all variables, except for ethanol concentration, exhibit values with a noteworthy impact on the yield response. The ethanol concentration variable, indicated by a p-value exceeding 0.05, suggests a lesser influence on the yield response value [9, 10].

In addition, quadratic models can provide evaluation and analysis of the interactions of each variable. The interactions between the F/S ratio and ethanol concentration (AB), the F/S ratio with extraction time (AC), and the ethanol concentration with extraction time (BC) are not significant (p> 0.05), which indicates that these specific interactions have a minimal influence on the Lawson dye extraction process from *Lawsonia inermis* L. leaves. In the quadratic interaction analysis, it is observed that the variable values exert less effect on the yield response, except for the quadratic variable F/S ratio, which demonstrates a p-value below 0.05. This signifies that the F/S ratio variable significantly influences the extraction process of *Lawsonia inermis* L. leaves [11].

Table 1. Selection of approach models

	Yield (%)				
Source	Sum of Squares	df	Mean Square	F-value	p-value
Mean vs Total	2369.11	1	2369.11		
Linear vs Mean	33.86	3	11.29	21.41	<0.0001
2FI vs Linear	1.50	3	0.4993	0.9283	0.4702
Quadratic vs 2FI	3.54	3	1.18	7.73	0.0252
Cubic vs Quadratic	0.7197	4	0.1799	4.18	0.3496
Residual	0.0430	1	0.0430		
Total	2408.77	15	150.58		

Table 2. ANOVA of the FCCCD model based on response variables

Fit Statistics	Mean	Std. dev	CV %	R^2	Adjusted R^2
Yield (%)	12.57	0.3906	3.11	0.9808	0.9462

Table 3. ANOVA and Regression Coefficient of the RSM Model

Response	Source	Sum of Square	df	Mean Square	F-value	p-value
Yield (%)	Model	38.90	9	4.32	28.33	0.0009
	A-F/S	32.09	1	32.09	210.34	<0.0001
	B-Concentration of Ethanol	0.2884	1	0.2884	1.89	0.2276
	C-Time	1.49	1	1.49	9.75	0.0262
	AB	0.1438	1	0.1438	0.9428	0.3762
	AC	0.4776	1	0.4776	3.13	0.1371
	BC	0.8765	1	0.8765	5.75	0.0619
	A^2	2.56	1	2.56	16.79	0.0094
	B^2	0.8241	1	0.8241	5.4	0.0677
	C^2	0.0626	1	0.0626	0.4104	0.5500

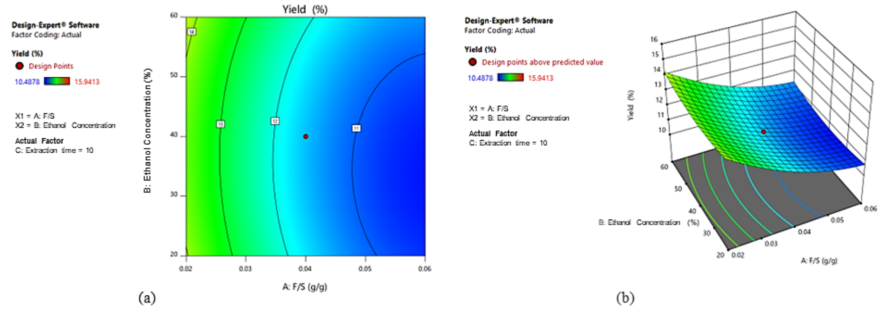

Figure 2. Contour and plot between F/S ratio and ethanol concentration to yield; a) 2 dimensions, b) 3 dimensions

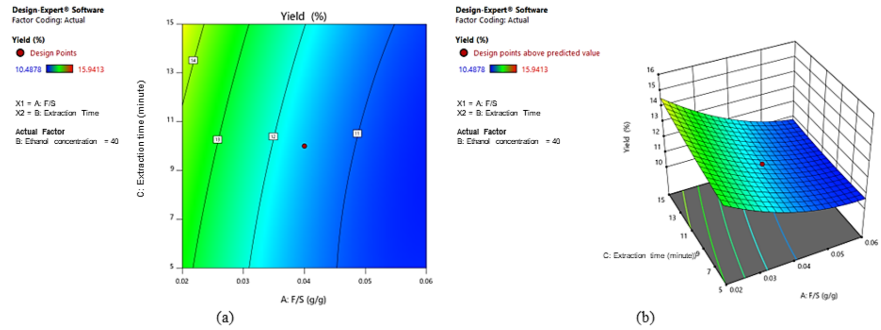

Figure 3. Contours and plots between F/S ratio and extraction time against yield in a) 2 dimensions, b) 3 dimensions

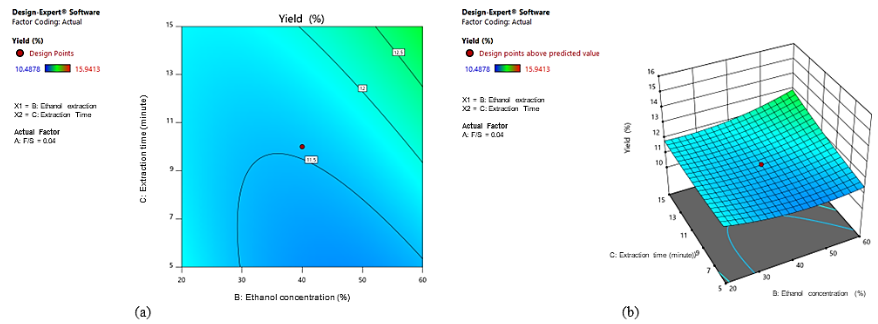

Figure 4. Contours and plots between ethanol concentration and extraction time on yield in a) 2 dimensions, b) 3 dimensions

Aligned with the analysis of variance, which highlights significant interactions between variables, an optimization study on *Lawsonia inermis* L. leaves extraction was conducted to identify the variables influencing the extraction process. In addition, RSM provides an overview of the analytical model of the research. This plot is represented and given by the model equation, where the contour plot and the model equation affect the optimization results of constant values [4].

Figures 2, 3, and 4 depict contours and 3D plots illustrating the relationships between the mass ratio of material-to-solvent and ethanol concentration, the mass ratio of material-to-solvent and extraction time, and the ratio of ethanol mass to extraction time, respectively. Figures 2 and 3 illustrate that the extract yield decreases as the mass ratio of material-to-solvent (F/S ratio) increases. This trend is attributed to a higher F/S ratio, implying less solvent usage. However, when more solvent is employed for extraction, the solvent load diminishes, maximizing the extract yield. The decrease in extraction results when the value of the mass ratio of material-to-solvent increases is due to the large mass of material during the extraction of dye from *Lawsonia inermis* L. leaves. The large mass of raw material with a fixed solvent volume of 200 mL results in low extraction. Each type of solvent has a maximum capacity for extracting Lawson content [4, 10, 12].

Figures 3 and 4 further underscore the significance of extraction time as a crucial factor influencing the extraction process, supported by a p-value of 0.0262 or below 0.05. This substantiates that a prolonged extraction time correlates with a higher extract yield. Longer ultrasonic extraction durations facilitate extended contact between the solvent and the material, leading to a more frequent occurrence of the cavitation process, thereby enhancing the extraction efficiency. The cavitation process and prolonged contact time between the solvent and *Lawsonia inermis* L. leaves can increase the yield of the extract. The cavitation process is initiated by introducing ultrasonic waves into the solvent medium, inducing unstable pressure changes that form bubbles. This dynamic process results in a phase change within the solvent, contributing to enhanced extraction efficiency. The bubbles formed during cavitation will expand and undergo explosive collapse, generating significant energy capable of breaking down the cell walls of *Lawsonia* *inermis* L. leaves. The continuous cavitation process over a long period facilitates the more effective extraction of Lawson compounds [2, 5, 13, 14]. Figures 2 and 4 illustrate the impact of variations in solvent concentration on the yield parameters of the resulting extract. During the extraction process, the yield increases as the solvent concentration increases. Figures 2 and 4 show that the ethanol solvent with a concentration of 60% gives the highest extraction yield. This is because the ethanol concentration can affect the solvent's polarity and the amount of dissolved compounds in the extraction process.

Ethanol is commonly used to extract phenolic compounds from natural sources. Introducing a small amount of water into the ethanol mixture enhances the solvent's polarity. When appropriately balanced, ethanol-water mixtures prove more effective in extracting the phenolic compound composition than pure water or pure ethanol solvents. A mixture of ethanol and water used as a solvent to extract the components of Lawson's compound in *Lawsonia inermis* L. leaves is better than a mixture of methanol and water [2, 5, 15]. Figure 5 shows the relationship between the predicted yield obtained by the FCCCD method with the design expert and the yield of the actual extraction results. The linear line shows the level of agreement between predicted and actual yields. Closer proximity to the linear line suggests that the equation employed effectively represents the actual results.

As shown in Table 4, the optimal conditions involve a material-to-solvent mass ratio of 0.02, an ethanol concentration of 60%, and an extraction time of 15 minutes. The predictive model is estimated to have a maximum extraction yield of 15.417%. Meanwhile, the actual value of extraction yield under the same variable conditions is 15.4934%. The residual value between the actual and predicted values is 0.0764%. This small value indicates a proximity between the predicted and actual extraction yields. Thus, the optimum conditions for the extraction process of *Lawsonia inermis* L. leaves using ultrasonics are a mass-to-solvent ratio of 0.02, an ethanol concentration of 60%, and an extraction time of 15 minutes.

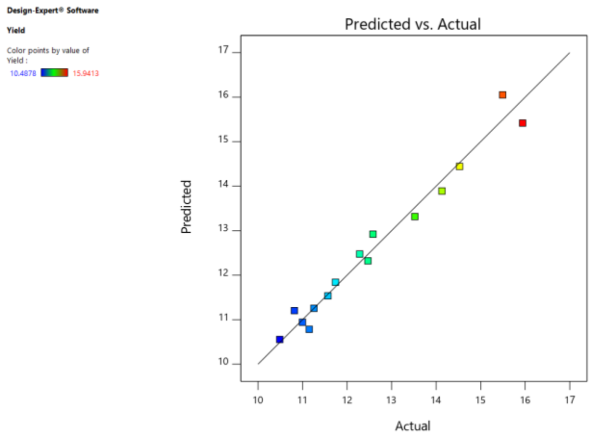

Figure 5. The relationship between predicted yield and actual yield

Table 4. Comparison of predicted yield with actual yield on optimal conditions

F/S (g/g)	Ethanol concentration (%)	Time (minute)	Predicted yield (%)	Actual yield (%)	Residual (%)
0.02	60	15	15.417	15.4934	0.0764

3.2. Extraction Kinetics Study

The kinetics model used in this study is kinetics first-order and second-order. Analysis of the kinetics model is used to observe the mechanism of extraction. Kinetic analysis was performed under the optimum conditions described in Table 4 to monitor changes in the response variable to the extraction time from 0 to 60 minutes. As depicted in Figure 6, there is a notably significant increase in yield from 0 to 5 minutes. The extraction rate in this condition is very high due to the maximum solute uptake by 60% ethanol solvent. In addition, ultrasonic waves accelerate cell wall breakdown, leading to an increased extraction of solutes. In the 5 minutes to 10 minutes, there was an increase in yield but not too significant because the 60% ethanol solvent had almost reached the maximum extract limit that could be extracted. Subsequently, from 10 to 60 minutes, there is no further increase, and the yield stabilizes. It is worth noting that Lawson's compound may undergo degradation due to excessive ultrasonic intensity, with continuous firing of ultrasonic waves causing slight damage. Additionally, degradation may occur at 70°C [2, 5].

Table 5. Extraction rate constants of first-order and second-order

Materials	Extraction Kinetics Model			
	First-order		Second-order	
Lawsonia inermis L.	Slope*	-0.1245	Slope*	3.5294
	k_1 (min^{-1})	0.2867	k_2(mL/g.min)	19.8885
	Intercept*	-0.5482	Intercept*	0.6263
	C_S (g/mL)	0.2830	C_S (g/mL)	0.2833
	R^2*	0.8970	R^2*	1
	RSME	1.0688	RSME	0.0589

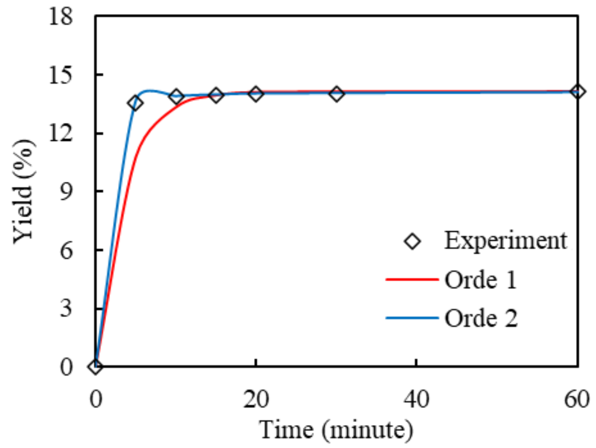

Figure 6. Comparison of model kinetics with experimental results

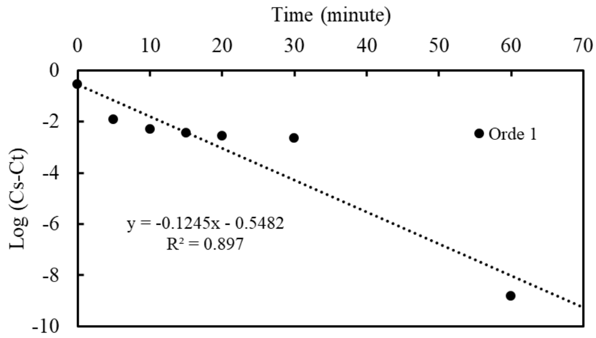

Figure 7. The kinetics of the first-order extraction model

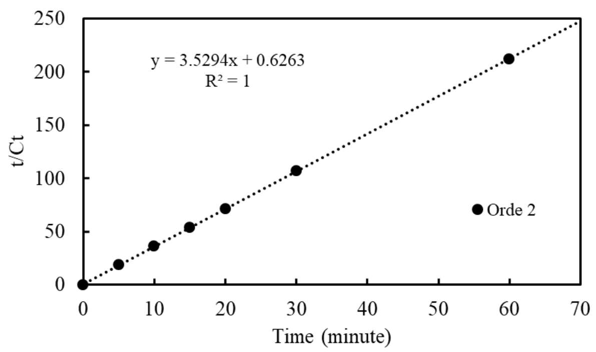

Figure 8. The kinetics of the second-order extraction model

Figures 7 and 8 show plots between Log (Cs-Ct) vs time and t/Ct vs time plots. The first-order kinetic model represents a process with one well-defined mechanism occurring. Meanwhile, the second-order kinetics model represents the existence of 2 mechanisms that occur in extracting *Lawsonia inermis* L. leaves. From both Figures 7 and 8, it can be seen that the corresponding linear regression is second-order. The mechanism of this second-order model is seen by the presence of Lawson's extract from *Lawsonia inermis* L. leaves increasing rapidly at the beginning of time until a certain time. Then, the Lawson extract increases slowly until it stabilizes [5, 6, 16, 17].

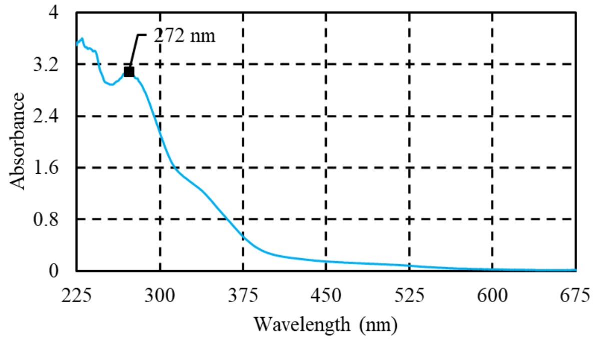

Figure 9. UV-Vis spectrophotometry analysis of *Lawsonia inermis* L. extract

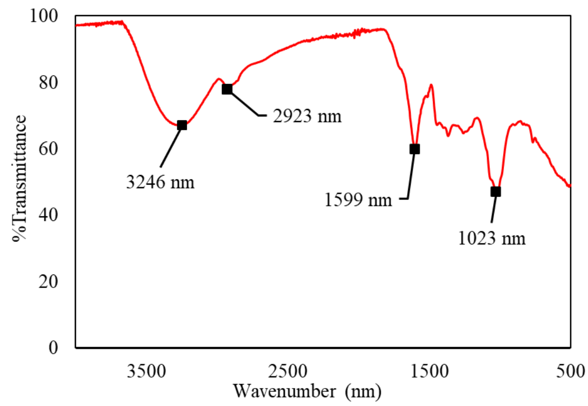

Figure 10. FT-IR analysis of *Lawsonia inermis* L. leaves extract

In Table 5, it can also be seen that the second-order kinetic model for the extraction of Lawson dyes from *Lawsonia inermis* L. leaves obtained by the ultrasound-assisted extraction method has a coefficient of determination ($R^2 = 1$), which is higher when compared to the first-order model which has an R^2 of 0.8970. This shows that second-order Lawson dye extraction of *Lawsonia inermis* L. leaves has a better R^2 value than first-order. The R^2 value of 1 represents that the Equation represents the actual event. So, it can be said that for modeling the kinetics of extracting *Lawsonia inermis* L. leaves with 60% ethanol solvent, it is more suitable to use a second-order equation with a maximum extraction capacity value (Cs) obtained of 0.2833 mg/mL and an extraction rate constant value (k_2) of 19.8885 mL/g.min. In addition, the selection of an appropriate kinetic model can be seen by the RSME value. The RSME value shows the error or magnitude of error between the kinetic model value and the actual value. The smaller the RSME value, the smaller the difference between the actual and kinetic model values [17, 18].

Figure 9 shows the results of the analysis of *Lawsonia inermis* L. leaves extract using a UV-Vis spectrophotometer. The absorbance from the UV spectrophotometer shows the level of absorption of Lawson extract compounds. The increase in absorbance at a wavelength of 272 nm indicates the presence of the main compound in the *Lawsonia inermis* L. extract in the form of 2-hydroxy-1,4 naphthoquinone (HNQ) or Lawson. The absorbance at a wavelength of 272 nm increases due to the presence of benzene and quinone with π-π^* electron transitions [19].

Figure 10 shows the results of Fourier transform infrared spectroscopy (FTIR) analysis. This FTIR analysis was used to identify the functional groups of Lawson compounds obtained from the extraction process of *Lawsonia inermis* L. leaves. The FTIR spectrum of *Lawsonia inermis* L. leaves is mostly hydroxyl (OH) and carbonyl (C=O) groups. Lawson's compound (2-hydroxy, 1,4-naphthoquinone) is indicated by the hydroxyl group found in the extract. The wavelength of 3276 cm^{-1} indicates the stretching vibration of the hydroxyl group, which can be found in the Lawson aromatic ring. The extent of absorbance is caused by intramolecular hydrogen bonds between OH groups and adjacent oxygen atoms. Quinone compounds are usually indicated at wavelengths between 1655-1690 cm^{-1}. The absorption that appears at a wavelength of 1599 nm is due to unsaturated carbonyl groups. The presence of hydroxyl or oxidation processes in C=O produces a decrease in frequency, which causes the compound to turn into a hydroquinone complex compound. The peak at a wavelength of 1023 nm indicates the presence of the C-O-C ester group [19, 20, 21, 22, 23, 24].

4. Conclusion

In this research, experimental data was optimized by observing variable interactions between the independent variables used in RSM. The FCCCD method makes research efficient and obtains more accurate predicted values. The independent variables were the F/S ratio, ethanol concentration, and extraction time. The extraction results show that the optimum conditions for Lawson extraction from *Lawsonia inermis* L. leaves are a material-to-solvent ratio of 0.02, an ethanol concentration of 60%, and an extraction time of 15 minutes. Under these conditions, the predicted yield was 15.417%, and the actual yield was 15.4934%. The predicted yield results using the FCCCD optimization method are close to the actual results with a residual value of 0.0764%. Using ultrasonics can increase the process of mass and heat transfer in extraction. Modeling of the extraction kinetics in the extraction of *Lawsonia inermis* L. was also carried out and it was found that the second-order kinetics were more suitable than the first-order because the coefficient of determination (R^2) had a higher value and was closer to 1 compared to the value of the first order coefficient of determination.

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