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Subcritical Water Extraction of Mango Seed Kernels and Its Application for Cow Ghee Preservation

Rambabu Krishnamoorthy *, Abdul Hai and Fawzi Banat

Department of Chemical Engineering, Khalifa University, Abu Dhabi P.O. Box 127788, United Arab Emirates; abdul.hai@ku.ac.ae (A.H.); fawzi.banat@ku.ac.ae (F.B.)

* Correspondence: rambabu.krishnamoorthy@ku.ac.ae

Abstract: Mango seed kernel (MSK) extract contains phytochemicals, bioactives, and fatty acids that are of interest to food and nutritional scientists. The subcritical water extraction process (SCWE) can be effective in extracting valuable bioactives from MSK. In this study, SCWE was investigated and optimized for the extraction of bioactives from MSK using Box–Behnken experimental design. The extract yield was examined as a function of various process variables, namely, solvent-to-feed (L/S) ratio, extraction temperature (T), and extraction time (t). Analysis of variance (ANOVA) for experimental results showed that extraction temperature was the most significant variable that impacted the extract yield. A maximum yield of 52.3% was obtained at optimized extraction conditions of L/S ratio = 20.7, T = 116.5 °C, and t = 45 min. Antioxidant assessment of the SCWE extract obtained at the optimized conditions showed higher total phenolic content (19.2 mg GAE/g), and DPPH and ABTS radical scavenging activity (>91%), than the extracts obtained by conventional hot water extraction and ultra-sound assisted extraction. Furthermore, an assessment of the MSK extract as a natural preservative showed that its inclusion (20% v/v) improved the oxidative stability of cow ghee with a par performance to synthetic butylated hydroxyanisole antioxidant (0.02% w/v). Thus, the study demonstrated SCWE as an effective green method for the production of MSK extract that could be applied for the preservation of oxidative food products.

Keywords: subcritical water extraction; mango kernel; Box–Behnken design; process optimization; antioxidant activity; ghee preservation

Citation: Krishnamoorthy, R.; Hai, A.; Banat, F. Subcritical Water Extraction of Mango Seed Kernels and Its Application for Cow Ghee Preservation. *Processes* **2023**, *11*, 1379. https://doi.org/10.3390/pr11051379

Academic Editors: Jaroslava Švarc-Gajić and Simone Morais

Received: 10 April 2023
Revised: 28 April 2023
Accepted: 30 April 2023
Published: 3 May 2023

1. Introduction

One of the most commonly consumed fruits in the world is the mango (*Mangifera indica* L.). Tropical and subtropical conditions are suitable for mango cultivation, and there is considerable variation among mango cultivars in terms of fruit size, color, shape, flavor, texture, and taste [1]. In the United Arab Emirates, mangoes have been imported from all around the globe, including India, Brazil, Mexico, Nigeria, Thailand, Egypt, etc. After dates and citrus, mangoes are becoming increasingly popular in UAE markets. In recent years, UAE cultivators have engaged in the production of mangoes through hybrid farming techniques. The nutritional and economic values of the fruit, as well as its delicate taste and flavor, have made mango cultivation popular in UAE agriculture. The FAO (2019) reports that the UAE has increased its mango cultivated area and number of mango trees significantly [2]. Epicarp (peel) and seeds are the main by-products of mango fruit processing. About 35–60% of the fruit's weight is made up of these by-products. As many as 75,000 tonnes/year of mango seeds are produced in UAE, making it a potential source of solid waste biomass without a sustainable disposal method currently available [2,3]. Remarkably, the polyphenols, phytosterols, and tocopherols found in mango seed kernels (MSK) make them a good source of natural antioxidants, lending great market value to this agro-waste stream [4].

Synthetic antioxidants are now present in almost all processed foods. For instance, the most commonly used synthetic antioxidants in the oil industry include butylated

hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), which were recently reported for their hazardous effects on human health [5]. A promising solution to this problem is to replace these synthetic antioxidants with natural antioxidants, such as those in MSK. The high fat and protein content, as well as the high antioxidant levels in MSK, make them a potential source of functional food ingredients. Research has shown that a wide range of phenolic compounds with exceptional antioxidant properties is present in MSK [6]. Thus, valorizing the MSK for natural antioxidant extraction and their application for food preservation would not only turn this waste into a valuable product, but would also define a new functionality for mango-based agro-industries.

The traditional technique for extracting valuable products from plant biomass is solvent extraction. It is, however, economically unfeasible to adopt solvent extraction on an industrial scale because of its low yield and solvent cost [7]. Furthermore, the extraction must also be followed by a rigorous solvent removal procedure for product separation and purification. Additionally, common solvents are toxic and poorly suited to the extraction of food or medical products due to their toxicity and unsustainable nature [8]. It is, therefore, necessary to develop more efficient extraction techniques that have higher extraction yields, are environmentally safe, economical, and do not require a solvent recovery facility. Several non-conventional techniques, such as ultrasonic extraction and microwave-assisted extraction, are emerging as alternatives to traditional solvent extraction [9]. It is, however, important to note that many of these techniques are energy and time intensive. Furthermore, suitable conditions are still lacking for the extraction of bioactive phenolic compounds using these methods [10].

One emerging green extraction method for bioactive compounds from plant-based biomatrices is pressured liquid extraction or accelerated solvent extraction. When water is used as the solvent, the process is called subcritical water extraction (SCWE). The process uses subcritical water as the extraction medium, which is liquid water at any temperature above 100 °C and just below its critical point [11]. In SCWE, temperature changes cause temperature-dependent variations in the solvent's dielectric constant affecting its density, polarity, and viscosity, therefore affecting the solubility of bioactive molecules and their migration into the solvent from biomass. Consequently, the solvent's selectivity and extraction efficiency are affected by altering the critical operating variables of the extraction [12]. Accordingly, SCWE seems to be a food-grade, tunable, eco-compatible, and non-toxic technique that employs a green and cost-effective solvent for recovery of bioactives. Additionally, SCWE has short extraction times and low energy consumption, resulting in high yields and high-purity products [13]. In the past, SCWE has been used successfully to solubilize sewage sludge and convert it into valuable products [14–16]. However, it is rarely used for the extraction of phenolic compounds. SCWE was recently reported to be effective for the extraction of phenolic compounds from onion skin [8] and date pits [10].

This study aims to evaluate SCWE as a green extraction technique for the production of MSK extract and to optimize the process to achieve maximum extract yield. Critical extraction variables, such as solvent-to-feed (L/S) ratio, extraction temperature (T), and extraction time (t), were investigated to understand and optimize the SCWE process based on Box–Behnken design (BBD) and Analysis of Variance (ANOVA) approaches. Additionally, the MSK extract obtained by the optimized SCWE process was compared with respect to its yield, physiochemical characteristics, fatty acid profile, total phenolic content, and antioxidant activities with extracts obtained using ultrasound-assisted extraction (USAE) and conventional hot water extraction (CHWE). Finally, the efficacy of MSK extract as a natural antioxidant preservative to extend the shelf-life of cow ghee against the synthetic BHA antioxidant is also demonstrated. The overall experimental procedure of the study is depicted in Figure 1.

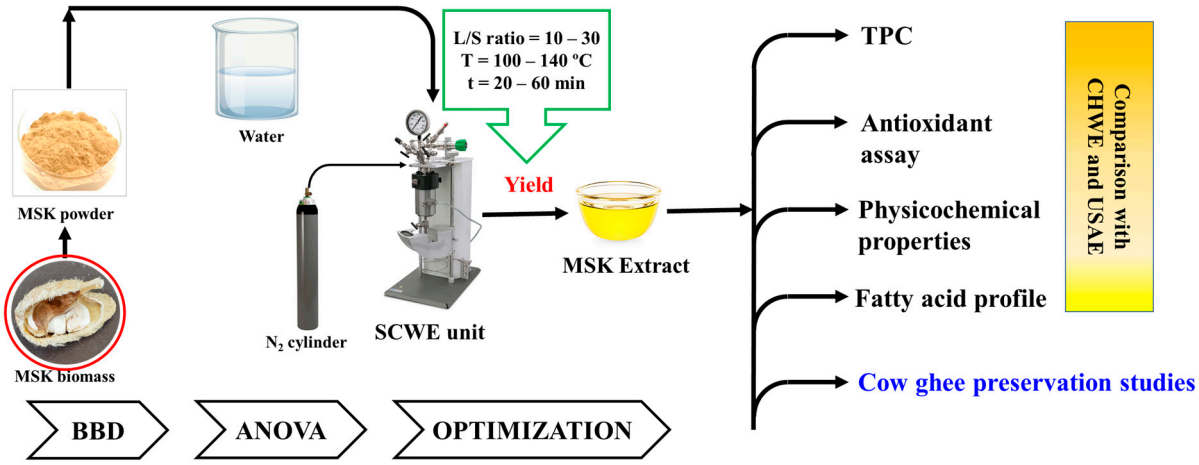

Figure 1. Schematic representation of the experimental study.

2. Materials and Methods

2.1. Mango Seed Sample

Mango seeds of the Alphonso (*Mangifera indica* L.) variant, one of the most popular mango types in the UAE, were obtained from a local fruit market. The seeds were washed and split into two halves. The kernels were manually removed from the seeds and subjected to sun-drying for an effective period of 8 h. Subsequently, the kernels were crushed using a hammer mill and forced through a #80 Tyler mesh (0.18 mm) to obtain MSK powder with a particle size <0.18 mm. The MSK powder was stored in air-tight containers for further study. All chemicals used in this study were of HPLC grade and procured from Sigma Aldrich, Germany.

2.2. Subcritical Water Extraction

A high-pressure 1 L Parr reactor (Model: 4520, Parr Instruments, Moline, IL, USA) was used for the subcritical water extraction of MSK extract. The reactor setup was equipped with adjustable speed impellers, thermocouples, external cooling jackets, internal cooling coils, pressure gauges, and a data logger. A homogenized aqueous feed mixture of 500 mL at a predetermined concentration was added to the reactor prior to each run. A pressure of 35 bar was then applied to the reactor using N_2 gas, and the temperature increased to the desired level. An impeller was used to continuously mix the aqueous mixture at 500 rpm throughout the experiment. The extraction was carried out for different time lengths. At the end of each run, the extract yield was determined by collecting the liquid product from the reactor and filtering it through a glass microfiber filter (0.7 mm). The value ranges of the critical extraction variables, namely solvent-to-feed (L/S) ratio, temperature (T), and time (t), examined in this study, are presented in Table 1. Based on preliminary experiments and process conditions reported for similar SCWE works on plant bioactive recovery [8,10], the conditions or ranges for the extraction variables were selected. Equation (1) was used to determine the extract yield (%) for each run.

$$\text{Extract yield (EY)} = \frac{Wt.of\ the\ extract}{Wt.of\ the\ MSK\ feed} \times 100 \quad (1)$$

2.3. Experimental Design

Optimization of the SCWE conditions for the MSK extract production was conducted using the response surface methodology. Extraction experiments were designed using the Box–Behnken experimental design (BBD) with three factors and three levels. Table 1 shows the coded and uncoded levels of independent variables, viz., solvent-to-feed (L/S) ratio, temperature (T), and time (t). A randomized design of 15 experiments with three replicates at the central point was generated, as shown in Table 2. The optimization study used

extract yield (EY, %) as the response variable. Based on the Analysis of Variance (ANOVA) approach, a second-order regression model (as shown in Equation (2)) was developed using the experimental data that described the individual and interrelated effects of the independent variables (L/S ratio, T, and t) on the response variable (EY).

$$Y = C_t + \sum L_i X_i + \sum Q_i X_i^2 + \sum_{i \neq j} I_i X_i X_j + \epsilon \quad (2)$$

where C_t is the correlation constant; L_i, Q_i, and I_i are the linear, square, and interaction effect coefficients for the independent variable X (namely L/S ratio, T, and t); and ϵ is the random error. The optimum conditions for maximum extract yield were determined using the model equation and the optimization algorithm. Validation of the predicted maximum was then performed using additional SCWE experiments.

Table 1. Operating variables and their level ranges for MSK extract production.

Operating Variables	Code	Levels		
		−1	**0**	**1**
Solvent-to-feed ratio	A	10	20	30
Temperature (°C)	B	100	120	140
Time (min)	C	20	40	60

Table 2. Box–Behnken design for SCWE of MSK extract.

Run Number	Solvent-to-Feed Ratio [A]	Temperature (°C) [B]	Time (min.) [C]	MSK Extract Yield (%)	
				Experimental	Predicted
1	30	120	20	35.84	36.75
2	20	100	60	45.96	46.81
3	10	100	40	39.85	39.91
4	20	120	40	52.16	51.57
5	30	100	40	35.88	34.68
6	20	140	60	33.67	33.38
7	30	140	40	36.71	36.65
8	20	100	20	36.38	36.67
9	10	120	60	37.61	36.71
10	10	120	20	44.94	44.59
11	20	120	40	50.89	51.57
12	10	140	40	28.52	29.72
13	20	120	40	51.65	51.57
14	30	120	60	45.91	46.26
15	20	140	20	42.73	41.88

2.4. Ultrasound-Assisted Extraction and Conventional Hot Water Extraction

The yield and extract quality of the SCWE were compared with ultrasound-assisted extraction (USAE) and conventional hot water extraction (CHWE). Both extractions were performed at the optimum solvent-to-feed ratio and extraction time, as identified from the optimization studies of SCWE. The maximum permissible temperature of 95 ± 2 °C (according to the equipment limits) for the liquid phase of the solvent (at the ambient conditions) was used for the extraction. A bath sonicator (USC 2100 THD, VWR, Lutterworth, UK) was used to perform the USAE in a batch mode at a frequency of 45 kHz and

a power density of 12 W/L. The CHWE study was conducted in a 1000 mL glass beaker that was conditioned in a hot water bath and magnetically stirred at 400 rpm throughout the extraction. A vacuum filter was used to separate the extract from the biomass at the end of both batch runs, and the product was further purified by filtering it through a glass microfiber filter (0.7 mm).

2.5. Characterization of MSK Extract

2.5.1. Physicochemical Characterization

Physicochemical analyses were performed for all MSK extracts prepared using SCWE, USAE, and CHWE. Standard testing procedures were followed for the determination of various physicochemical properties of the extracts. According to the procedures established by the European Committee for Standardization (2003) and UNE-EN-ISO (1999), the peroxide value (EN 14112) and density (EN ISO 3675) of the extracts were determined. Furthermore, standard testing procedures based on AOAC (2005) were used for the determination of refractive index (AOAC 921.08), free fatty acid content (AOAC 969.33), saponification value (AOAC 920.160) and iodine value (AOAC 993.20) of the extracts. Additionally, the acid value analysis of the extracts was carried out according to the ASTM D-974 standard. Additionally, the extracts were tested for their viscosities at 30 °C using an Oswald kinematic viscometer [17]. All tests were performed in triplicate, and the average values with their error bands were recorded.

2.5.2. Analytical Characterization

A Shimadzu gas chromatography coupled with mass spectrometry device (GC-MS, Model QP2010, USA) was used for the estimation of the fatty acid profile of the extracts. Briefly, the temperature of the gas chromatography (GC) injector was maintained at 250 °C for 15 min, while that of the oven was kept at 190 °C. Following that, the oven was heated at 5 °C/min until a maximum temperature of 230 °C was reached. The carrier fluid was pure nitrogen gas at 500 kPa pressure. The average weight area (%) of each fatty acid was calculated by repeating the analysis in triplicates. The chemical functional groups of the extracts were analyzed using Fourier-transform infrared (FT-IR) spectroscopy (Shimadzu IRAffinity-1S, Duisburg, Germany). The extract was mixed with KBr powder (spectroscopic grade), pressed into pellets, and subjected to analysis. Analysis was performed within the wavenumber range of 4000 to 400 cm^{-1} at a scan resolution of 2 cm^{-1}. KBr background correction was applied to the acquired spectra.

2.5.3. Total Phenolic Content and Antioxidant Activity

The Folin–Ciocalteu reagent reduction method was used to estimate the total phenolic content (TPC) of the MSK extracts [11]. Briefly, about 3 mL of the extract was mixed with 0.3 mL of Folin–Ciocalteu reagent (10% v/v) and 2 mL of sodium carbonate solution (7.5% v/v) to prepare the reaction mixture. A UV-vis spectrophotometer (UV-2700, Shimadzu, Duisburg, Germany) at 750 nm was used to measure the absorbance of the mixture after 15 min of incubation. The TPC of the extracts was expressed as milligram gallic acid equivalent (mg GAE) per 100 g of the extract. Internal calibration using the gallic acid (GA) standard was performed using solutions of known concentrations prior to the TPC analysis of the extracts.

ABTS and DPPH radical scavenging assays were used to assess the antioxidant capacity of the MSK extracts. For the ABTS method, the required amount of the reagent was diluted with demineralized water to prepare a 0.007 M ABTS solution. To this, 2.45 M $K_2S_2O_8$ solution was mixed in a 1:1 (v/v) ratio for 8 h. The mixture was diluted with ethanol to an absorbance value of 0.7 at 730 nm. About 20 µL of the MSK extract was added to 1980 µL of this diluted solution and conditioned in a dark environment for 15 min. A

UV-vis spectrophotometer at 730 nm was used to measure the final solution's absorbance. The extract's ability to scavenge ABTS radicals was calculated using Equation (3).

$$\text{ABTS Radical scavenging} = \frac{R_0 - R_1}{R_0} \times 100 \quad (3)$$

where R_0 and R_1 are the absorbances of the sample without extract (control) and with the extract.

For the DPPH assay, 0.5 mL of ethanolic DPPH solution with a concentration of 0.1 mM was mixed with 1.5 mL of MSK extract. At 515 nm, the UV-vis spectrophotometer was used to measure the absorption of the solution after 30 min of incubation. A blank DPPH solution was also measured for its absorbance at the same incident wavelength, and the extract's ability to scavenge DPPH radicals was calculated using Equation (4).

$$\text{DPPH Radical scavenging} = \frac{\text{BlankDPPH}_{abs} - \text{Sample}_{abs}}{\text{BlankDPPH}_{abs}} \times 100 \quad (4)$$

2.6. Cow Ghee Preservation Studies

Cow ghee preservation studies were conducted using a method described by Taha et al. [18] with some modifications. The cow butter was heated to produce ghee, and the product was divided into five equal portions on a volume basis. The first portion was used as a control specimen (without any additives inclusion), while 0.02% w/v of BHA was added as the synthetic antioxidant to the second portion [19]. The remaining three portions of ghee were loaded with 5, 10, and 20% (v/v) of MSK extract, respectively, and subjected to the storage study. Sterile test tubes were used to fill all the samples (equal volumes) and then incubated in an oven (Venticell 111, Munich, Germany) at 80 °C (±2 °C). The peroxide values of the samples were monitored at definite time intervals using a titration-based procedure as described elsewhere [20]. The study by Puravankara et al. [19] determined that ghee samples with a peroxide value of 5 have completely degraded. Thus, a peroxide value of 5 was used in this accelerated storage study at 80 ± 2 °C to determine the ghee deterioration due to autoxidation.

2.7. Software

Minitab software (version 19.1, Minitab Inc., State College, PA, USA) was used for the design of experiments, response surface analysis, and optimization studies. Predictor variables were set to a 0.05 significance level ($p < 0.05$). Moreover, all experiments were performed in triplicate, and mean values of the yield are reported.

3. Results and Discussions

3.1. Statistical Analysis of MSK Extract Production

3.1.1. Regression Analysis

A summary of the various experimental conditions for the SCWE of the MSK extract with the corresponding experimental yields is presented in Table 2. According to the results, MSK extract yields ranged from 28.52% to 52.16%. It was observed that the extract yields were very stable for runs 4, 11, and 13, which corresponded to the center points of the predictor variables. The repeatability and validity of the experiments were confirmed by these observations [11]. Furthermore, ANOVA and regression analyses were conducted on the extraction experiments, and the best mathematical model that related the SCWE variables (predictors) with the MSK yield (response) was selected. The relationship between the SCWE variables (Table 1) and the MSK extract yield was described by a second-order polynomial, as shown in Equation (5).

$$\begin{aligned} EY = {} & -300.7 + 0.336A + 5.374B + 1.588C - 0.0747A^2 - 0.0222B^2 - 0.0076C^2 \\ & + 0.0152AB + 0.0218AC - 0.0117BC \end{aligned} \quad (5)$$

where A, B, and C are the uncoded values of the solvent-to-feed ratio, temperature (°C), and time (min), respectively. The obtained regression model had a very high correlation coefficient (R^2) value of 0.99. In general, the higher the R^2 value, the better the fit between the model's predictions and reality. Furthermore, a value of 97.2% for the adjusted correlation coefficient (Adj. R^2) showed that the predicted model fits the actual data well [21].

The results of the ANOVA study are shown in Table 3 for the experimental results obtained using BBD. Significant linear, square, and interaction effects were evident from the results ($p < 0.05$). As far as the linear influence of the independent variables was concerned, the temperature was the only significant variable. Conversely, the extract yield was significantly influenced by quadratic effects (both square and interaction effects) of all independent variables. Interestingly, the square effects dominated the interaction effects in determining extract yield, which was evident from their higher F-values [11]. Additionally, from the predicted model (Equation (5)), the positive coefficients of the linear terms, namely A, B, C, and interaction terms AB, and AC showed that all these terms had a positive correlation on the extract yield. Likewise, MSK extract yield was negatively affected by the square effects and the interaction term BC, which was confirmed through their negative coefficients in the regression model. The Pareto chart in Figure 2a identifies the regression terms that are significant and insignificant, as identified from the ANOVA study. As a result, $B^2 > A^2 > BC > AC > AB > B > C^2$ are the significant terms that influence MSK extract yield, in order of dominance. From the ANOVA results, it was clear that the extraction temperature was the most influential variable that impacted the extract yield. Figure 2b shows the distribution between the actual and predicted MSK extract yields. There was a close correlation between the predicted and actual yields of the extract along the 45° line. This proved the validity of the regression model that predicted MSK extract yield as a function of the SCWE reaction variables. Furthermore, it is evident from Figure 2c that the scatter of the yield residuals was linear, which confirmed the analytical hypothesis and the non-requirement of response transformation [22]. Figure 2d shows an externally studentized residual plot against predicted yield data. Data points were distributed randomly along the reference line in the plot. As a result, the regression model proved to be extremely efficient in relating the SCWE variables with the extract yield [23].

Table 3. ANOVA results for MSK extract production by BBD.

Source	DF	Adj SS	Adj MS	F-Value	*p*-Value
Model	9	709.794	78.866	54.90	0.000
Linear	3	36.575	12.192	8.49	0.021
A	1	1.462	1.462	1.02	0.359
B	1	33.784	33.784	23.52	0.005
C	1	1.328	1.328	0.92	0.380
Square	3	473.700	157.900	109.93	0.000
A^2	1	205.942	205.942	143.37	0.000
B^2	1	289.736	289.736	201.70	0.000
C^2	1	33.750	33.750	23.50	0.005
Two-Way Interaction	3	199.519	66.506	46.30	0.000
AB	1	36.966	36.966	25.73	0.004
AC	1	75.690	75.690	52.69	0.001
BC	1	86.862	86.862	60.47	0.001
Error	5	7.182	1.436	-	-
Lack-of-Fit	3	6.365	2.122	5.19	0.166
Pure Error	2	0.817	0.408	-	-
Total	14	716.976	-	-	-

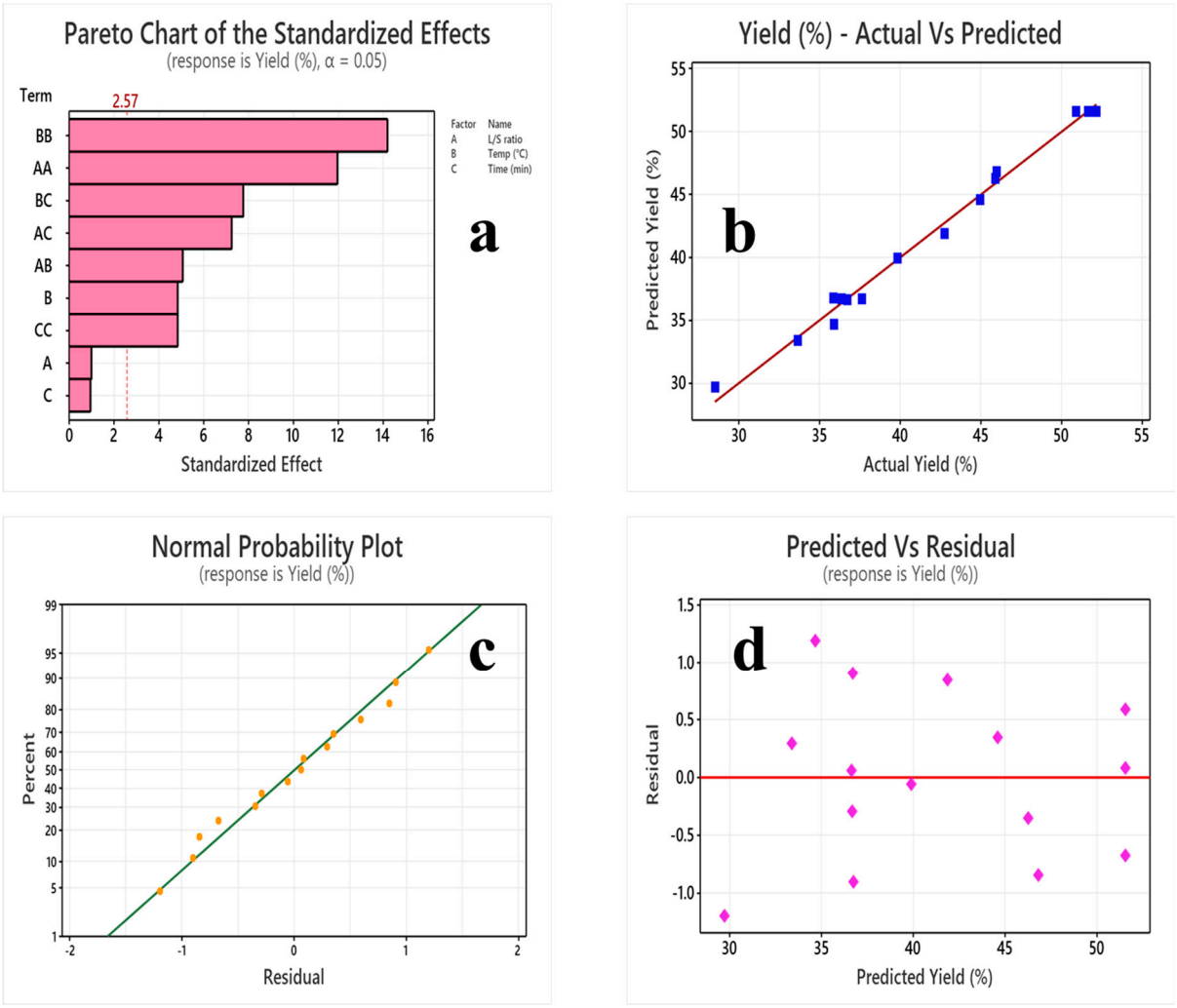

Figure 2. ANOVA analysis: (**a**) Pareto chart; (**b**) actual vs. predicted yield comparison; (**c**) normal probability plot of residuals; (**d**) predicted yield vs. residuals.

3.1.2. Single-Factor Effects

Statistical analysis allows for a limited number of experiments to be conducted in order to interpret the impact of the input variables on the response variables. Figure 3a illustrates the effect of solvent-to-feed (L/S) ratio variations on the extract yield. The yield is plotted between a lower level (−1) and a higher level (+1) of the L/S ratios, while other variables are held at their central levels (0). The results showed that the extract yield increased by increasing the L/S ratio from 10 to 20. An increase in the L/S ratio led to an increase in concentration gradient attributable to an increase in the solvent amount in the mixture, resulting in greater extraction efficiency. Onyia et al. [24] reported that increasing the L/S ratio increased the amount of leachable oil during extraction. The manifestation of this phenomenon is illustrated in Figure 3a, with a maximum yield occurring around an L/S ratio of 20. However, a further increase in the L/S ratio resulted in a decrease in the extract yield. It is not unusual for this phenomenon to occur because, based on Jisieike and Betiku [25], an L/S ratio beyond its optimum point causes diffusion difficulties and decreased extraction efficiency. Other researchers have made similar observations, corroborating these findings [11,26]. The maximum yield of the MSK extract by SCWE was achieved at an L/S ratio of 20.7. It is worth specifying that, with SCWE, it is possible to achieve good extract yields with a lower L/S ratio. This is due to the fact that the extraction is intensified by the dissolution potential of the analytes and the external film transfer diffusion in the SCWE process [27].

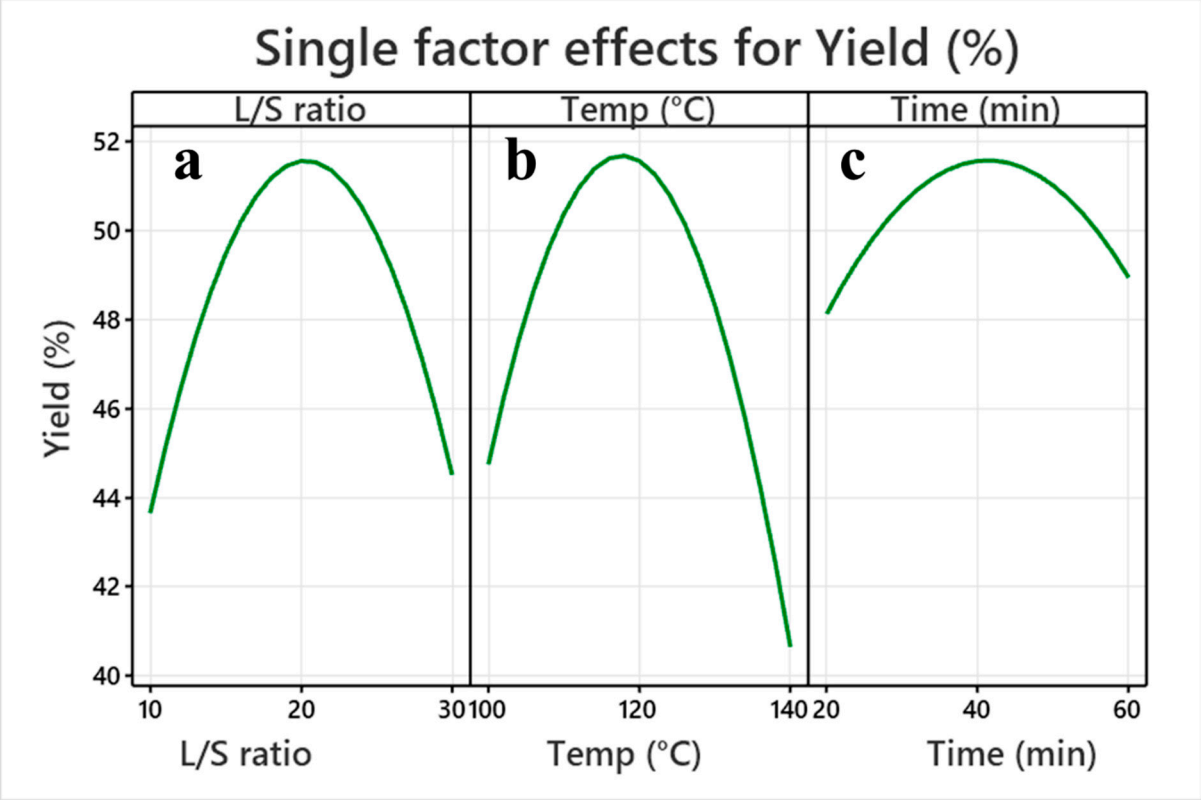

Figure 3. Single-factor analysis: (**a**) L/S ratio; (**b**) temperature; (**c**) extraction time.

Figure 3b illustrates the impact of temperature on the production of MSK extract using an SCWE approach. The yield is plotted between a lower level (−1) and a higher level (+1) of the extraction temperature, while other variables are held at their central levels (0). Initially, the extract yield increased when the temperature was raised from 100 °C to 116 °C, and then it showed a progressive decrease till 140 °C. Solvent diffusivity into the biomass matrix increased with the initial incremental phase of the SCWE operating temperature. As a result, bioactive components were more likely to migrate into the solvent [27]. Additionally, low-polar analytes of the biomatrix were more readily soluble in the solvent at high temperatures because of the altered dielectric constant and reduced polarity of subcritical water. In addition, the solvent's viscosity and surface tension decreased at elevated temperatures, which improved extraction performance [11]. Furthermore, target analytes were less bound to the biomatrix phase during extraction with rising extraction temperatures, allowing them to move easily into the solvent phase. A similar pattern of behavior was observed when phenolic compounds were extracted from watermelon [28] and peach palm [29] using SCWE. Nevertheless, high extraction temperatures (>120 °C) resulted in low yields of the MSK extract due to the thermal degradation of bioactives present in the MSK. The results of previous studies on SCWE were also similar for high-temperature extraction [8,30].

Figure 3c shows the dependency of the extract yield on the extraction time. The yield is plotted between a lower level (−1) and a higher level (+1) of extraction time, while other variables are held at their central levels (0). Results show that the extract yield was mildly impacted by extraction time compared to the L/S ratio and temperature. The figure shows a gradual decrease in yield with increasing or decreasing extraction time either side of the intermediate level (t = 45 min). The initial increase in extraction time from 20 to 45 min ensured adequate pressurization of the biomass, allowing the cell walls to break and improving the contact between biomatrix and solvent [11]. Moreover, a longer retention time allowed the solvent to diffuse deeper into the MSK matrix and effectively recover the bioactive components contained therein [31]. As a result of these effects, the mass transfer rate of analytes to solvent improved, resulting in higher extract yields. However, longer

extraction times decreased the extract yield due to possible degradation of bioactives and loss of their chemical stability. Additionally, a longer extraction time in an SCWE process can result in excessive free radical formation, which can lower the extract yield and its bioactivities by affecting the biomass structure [32]. Similar results have been reported for mangiferin extraction from Mahkota Dewa [33] and phenolics extraction from cereals distillery stillage [34].

3.1.3. Interaction Effects of the Extraction Variables

While single-factor analyses can be used to evaluate the extract yield, a holistic approach for determining the variations in yield is not yet possible. Consequently, contour plots are needed to analyze the interaction effects among the proven variables. The contour plots shown in Figure 4 demonstrate how the interaction effects of the SCWE variables synergistically impact the MSK extract yield. The plots show the variation in the extract yield for changes in two variables while keeping the third at its central (0) value. An optimal MKO extraction process can be designed using the isolines seen in the contour plots [35]. Additionally, the geometric features of the isolines show the degree of interaction between the two factors (under consideration) on the response yield. Accordingly, circular isolines characterize the combination conditions of the factors that are less influential on MSK yield, while elliptical contours indicate the strong influence of the combination conditions of the factors [36]. Thus, by observing the results in Figure 4, it can be concluded that the interaction effects of T and t (Figure 4c) and L/S ratio and t (Figure 4b) more strongly impacted the extract yield of the SCWE process than L/S ratio and T (Figure 4a). The F-values stated in Table 3 for the individual interaction effects agree closely with this result. As shown in Figure 4, the lowest extract yield is found in the red/brown region depicting the widest incomplete elliptical region, while the highest yield is found in the magenta region depicting the narrowest complete elliptical region.

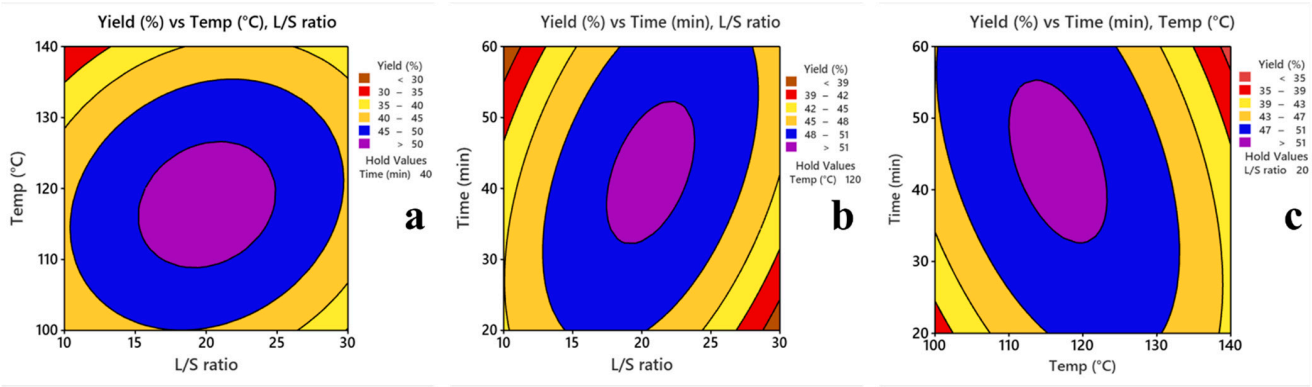

Figure 4. 2-D contour plot for interaction effects—(**a**) L/S ratio and T; (**b**) L/S ratio and t; (**c**) T and t.

3.1.4. Process Optimization and Validation

Statistical analysis involves investigating the optimal response conditions through the standard error of the regression model [37]. The MiniTab software was used to optimize the MSK extract yield while maintaining the reaction variables within their examined ranges. According to the regression model in Equation (5), it was projected that the SCWE process comprising of a solvent-to-feed ratio of 20.7, operating temperature of 116.5 °C, and extraction time of 45 min would result in an optimized MSK extract yield of 51.8%. Furthermore, to validate the computed optimum of MSK extract yield, SCWE experiments were repeated three times at predicted optimum values of the extraction variables. The optimal extraction conditions resulted in a 52.3% extract yield, which was not significantly different from the predicted value of 51.8%. Once again, this supported the validity of the regression model and demonstrated its effectiveness for optimizing MSK extract production using the BBD-based experimental design.

3.2. Comparison with Ultrasonication and Conventional Hot Water Extraction

A comparison of the SCWE approach with USAE and CHWE techniques for MSK extract production was carried out to demonstrate the advantages of the former over the latter approaches. The extraction time and solvent-to-feed ratios for USAE and CHWE techniques were maintained at 45 min and 20.7, to match the optimized conditions for SCWE. Additionally, the extractions were performed at a temperature of 95 ± 2 °C, which is the maximum permissible for the liquid phase of the solvent. The extract yields obtained from these techniques and their varying characteristics are discussed in the following sections.

3.2.1. Extract Yield, TPC, and Antioxidant Activity

Based on the results of the comparison study of different extraction methods, Table 4 shows the overall extract yield, TPC values, and the antioxidant properties of the extracts based on DPPH and ABTS assay. It is evident from the results that SCWE had a distinct advantage over the USAE and CHWE approaches in MSK extract production. The MSK extract yield obtained with SCWE was 1.25 and 1.44 folds higher than with USAE and CHWE, respectively, under optimized conditions. The SCWE method produced higher extract yields than USAE and CHW due to improved mass transfer rates of the active components, deeper penetration of solvent into the fruit matrix, and the higher solubility of the bioactives [11]. Furthermore, the TPC concentration in the extracts was determined using the Folin–Ciocalteu reagent method, and the results are presented as GAE. The SCWE extract contained 33.7% and 75.3% more TPC than the USAE and CHWE extracts, respectively, indicating the effective phenolic redemption of the MSK biomass by SCWE. Water is generally a good solvent for recovering phenolic compounds from biomass [38]. Subcritical water's reduced polarity improved the solubility of the phenolics in the solvent, enabling them to be effectively removed from the MSK biomatrix [11]. The TPC values of the MSK extracts obtained in this study were significantly higher than those reported by Buelvas-Puello et al. [39], regardless of the extraction method studied. The MSK extract produced in this study by the SCWE technique showed a nearly 1.27-fold higher TPC than the extract obtained using Soxhlet extraction. Additionally, the TPC of the present study's extract was far higher than the extract obtained from Ataulfo variant kernels [40].

Table 4. Comparison of SCWE, USAE, and CHWE techniques for MSK extract production.

Extraction Method	MSK Extract Yield (%)	TPC (mg GAE/100 g)	DPPH Radical Scavenging (%)	ABTS Radical Scavenging (%)
SCWE [a]	52.3 ± 0.6	79.2 ± 1.4	91.2 ± 0.9	97.3 ± 1.1
USA [b]	41.9 ± 1.3	52.5 ± 1.9	82.3 ± 1.2	86.4 ± 0.8
CHW [b]	36.2 ± 2.1	19.6 ± 1.5	70.6 ± 0.6	72.6 ± 1.3

[a]—Extraction performed at the optimum operating conditions; [b]—Extraction performed at L/S ratio = 20.7, T = 95 °C and t = 45 min.

Analysis of antioxidant activities using the DPPH and ABTS assays showed that all MSK extracts exhibited good antioxidant activities (Table 4). It was also observed that the extracts showed a better scavenging efficiency for ABTS radicals than the DPPH radicals. Importantly, the SCWE-derived MSK extract was more effective at scavenging the DPPH and ABTS radical cations than the USAE and CHWE extracts. The high concentration of phenolic compounds in the SCWE extract compared to the other two extracts explained the significant variation in antioxidant activity. CHWE extract had relatively low antioxidant activities due to its low phenolic content. According to Marcillo-Parra et al. [41], phenolic content is positively correlated with antioxidant activity. In general, there are numerous therapeutic and pharmacological activities attributed to phenolic components in mango kernels, including antioxidant, antimicrobial, anti-aging, anti-carcinogenic, and hepatic/cardioprotective properties [42]. Consequently, the SCWE method produced an MSK extract rich in natural antioxidants and nutritional bioactives by maximizing the recovery of phenolics and phytochemicals from the kernels.

3.2.2. Physicochemical Characteristics and Fatty Acid Profile

Table 5 presents the results of physicochemical properties and fatty acids profile for all the MSK extracts prepared using different techniques. MSK extract's physicochemical quality is mostly determined by its saponification, peroxide, iodine, and acidity values [36]. Combined with all the fatty acids that contribute to the glyceride molecules, the acid value gives a measure of the total lipid acidity. The results of the acid value studies showed that the SCWE-derived extract displayed the lowest tendency to undergo hydrolytic rancidity from lipases, making it suitable for direct use without any undergoing pre-treatment such as neutralization. The peroxide value measures the concentration of peroxides and hydroperoxides formed during the early stages of lipid oxidation. Oil samples are often examined for oxidative rancidity using the peroxide value. It was observed that the peroxide value of the extracts ranged between 2.25 and 4.82 mg/g, with the SCWE extract being the least. In general, peroxide values <10 mg/g are acceptable for natural extracts and oils [42]. Thus, SCWE-derived MSK extract seemed to be more stable than other extracts in terms of both peroxide and acid values.

Table 5. Physicochemical characteristics and fatty acids profile of the MSK extracts.

Property	SCWE	USAE	CHWE
Density (kg/m^3)	920 ± 2	899 ± 3	862 ± 3
Refractive index at 20 °C	1.36 ± 0.02	1.31 ± 0.03	1.28 ± 0.01
Viscosity at 20 °C (mPa s)	15.4 ± 0.2	16.1 ± 0.2	15.9 ± 0.2
Peroxide value (mg/g MSE)	2.25 ± 0.03	3.67 ± 0.09	4.82 ± 0.14
Acid value (mg KOH/g)	12.32 ± 0.12	16.58 ± 0.32	19.36 ± 0.41
Iodine value (g I_2/100 g)	21.36 ± 1.36	24.12 ± 1.04	25.27 ± 0.63
Saponification index (mg KOH/g MSE)	126.45 ± 3.73	157.49 ± 2.61	170.38 ± 1.92
Free fatty acid (%)	5.92 ± 0.31	8.36 ± 0.27	10.41 ± 0.19
Fatty acid profile (in wt.%)			
Lauric acid (C12:0)	2.41	3.32	4.38
Myristic acid (C14:0)	19.64	16.67	14.38
Palmitic (C16:0)	42.11	36.74	38.19
Palmitoleic (C16:1)	1.53	2.49	3.85
Stearic (C18:0)	10.69	11.93	9.72
Oleic acid (C18:1)	15.56	16.82	14.76
Linoleic acid (C18:2)	2.19	3.65	4.92
Others	5.87	8.38	9.8
Saturated content	~74.85	~68.66	~66.67
Unsaturated content	~19.28	~22.96	~23.53

Iodine value refers to how much iodine it would take to saturate 100 g of the MSK extract with iodine (g). It reflects the resistance of the extract to oxidation and correlates directly with the number of covalent bonds found in long-chain fatty acid monoesters [36]. As seen from the results, the extract produced by the SCWE technique showed the lowest iodine value compared to extracts produced by USAE and CHWE approaches. Similarly, the saponification value that ascertains the molecular weight of the fatty acids contained in the extract, was found to be low for SCWE-derived MSK extract. This signified the presence of more low-molecular-weight triacylglycerols in this extract than in the other two extracts. The low iodine value and saponification index uphold the SCWE-derived

MSK extract for its better oxidation resistance and application for food preservation than the other MSK extracts [38].

The quality of the MSK extract is greatly determined by the fatty acid profile. Table 5 shows the major fatty acid components detected in the MSK extract and their respective composition computed from their chromatographic area. All extracts showed similar profiles and contained significant amounts of saturated fatty acids (myristic, palmitic, and stearic) ranging between 66 and 75%. Consequently, the MSK extract can primarily be used as reaction intermediates to produce alkali salts that can be used as emulsifiers, emollients, or lubricants in a wide variety of industrial applications [36]. Additionally, the high palmitic acid content in the extract indicated its suitability for cosmetics production. There was a significant presence of myristic acid (tetradecanoic acid) in SCWE-derived MSK extract. Accordingly, this MSK extract can be used as a precursor for the production of myristic acid, an industrially important substance used in a wide variety of applications, including detergents and soaps, perfumes, food flavoring, etc. Moreover, myristic acid also strengthens the human immune system proteins by stabilizing them [43]. The higher composition of the saturated fatty acid in SCWE-derived extract clearly indicated the pronounced stability of this extract than the USAE and CHWE extracts. Conclusively, the extract produced by the SCWE approach showed better physicochemical properties and fatty acid profile owing to its superiority in recovering the natural antioxidants and other essential bioactives from the MSK biomass than USAE and CHWE techniques.

3.2.3. Chemical Functionality of the Extracts

The various chemical functionalities present in the MSK extracts were examined by means of FT-IR studies. The FT-IR spectra for the different extracts, as shown in Figure 5, showed close similarities with respect to their functional groups. High-range vibrational peaks felt in the region of 3300 to 3400 cm^{-1} can be ascribed to the O-H functionality of extract and adsorbed water. The bands detected around 2750 cm^{-1} can be related to the C–H asymmetric and symmetric stretching vibrations of the CH_2 and CH_3 groups [44]. Characteristic prominent peaks pertaining to the carbonyl groups of the triglycerides were detected around 1735, 1737, and 1742 cm^{-1} for the SCWE, USAE, and CHW extracts, respectively [45]. As discussed earlier, these observations are consistent with the saponification results. There were several distinctive peaks observed for all the extracts in the fingerprint region of 1650 to 650 cm^{-1}. The majority of the CH_2 bending vibrations occurred between 1460 and 1450 cm^{-1}, which can be ascribed to the acyl chain packing and conformation. The scissors bands between 1366 and 1372 cm^{-1} observed for the extracts indicated the asymmetric deformation modes of the CH_3 group [11]. The presence of saturated esters C-C(=O)-O in the extracts was confirmed from their vibrational peaks detected between 1220 and 1130 cm^{-1}, while the peaks present at lower frequencies (600–700 cm^{-1}) indicated the unsaturated esters in the extracts [45]. The results obtained for the fatty acid profiles were consistent with these findings.

3.3. Cow Ghee Preservation

Cow ghee generally deteriorates faster due to oxidative damage, so antioxidant inclusion ensures a long shelf life for this dairy product [20]. In this study, the MSK extract prepared using the SCWE technique was examined for its potential as a green antioxidant for cow ghee preservation studies. The performance of the SCWE-derived MSK extract was compared with open control (no antioxidant inclusion) and a ghee sample fortified with synthetic BHA ((0.02% w/v). Ghee deterioration due to autoxidation under the accelerated storage study at 80 $\pm$ 2 °C was measured in terms of peroxide value. An oil or lipid's peroxide value indicates the extent of its primary oxidation. This is the amount of active oxygen (mg) contained in 1 g of lipid [19]. Peroxide values of various ghee samples subjected to accelerated storage studies are tabulated in Table 6.

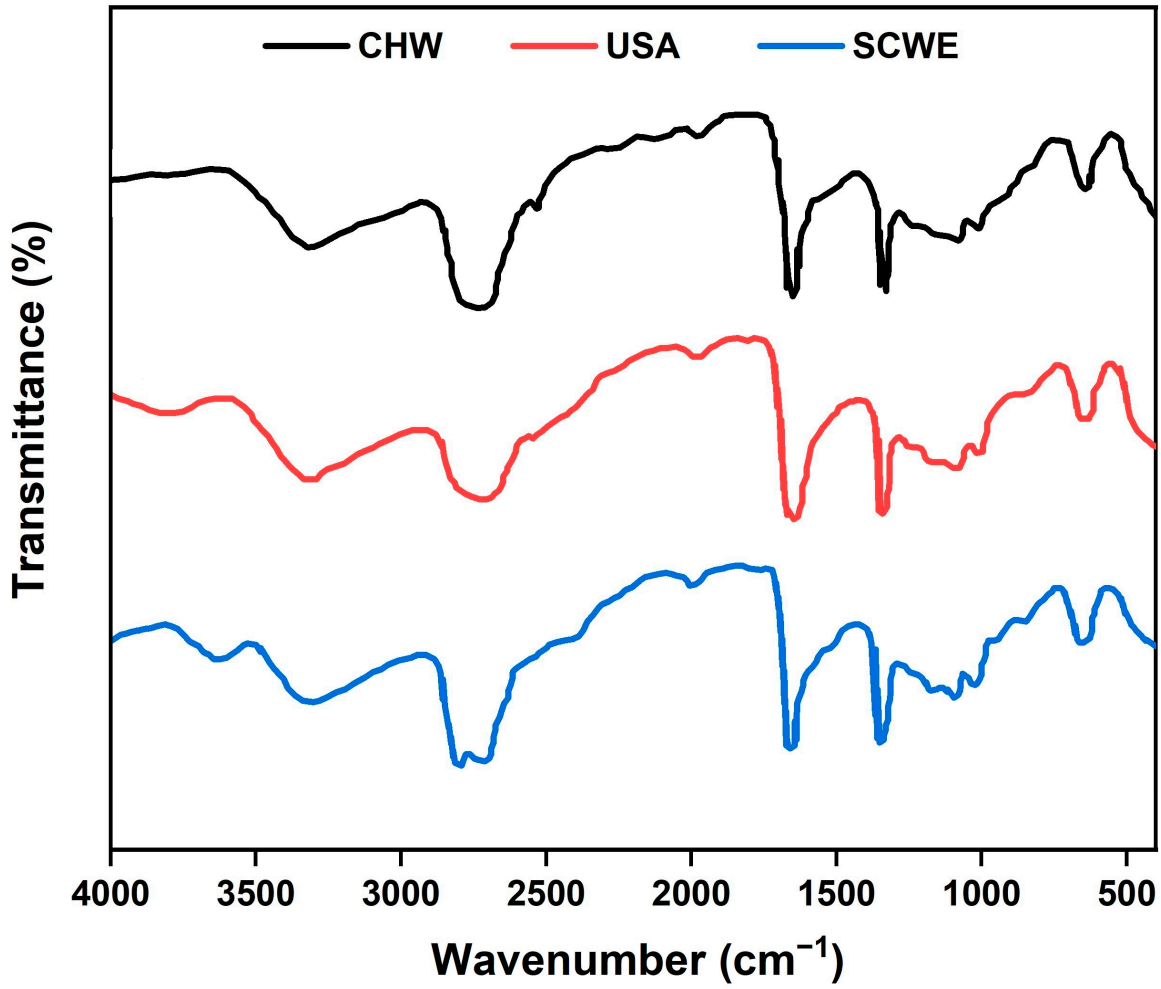

Figure 5. FT-IR spectra of the MSK extracts.

Table 6. Peroxide values (mM/g of fat) of cow ghee preservation studies.

Samples	Day 1	Day 5	Day 10	Day 15	Day 20
Control	2.08 ± 0.05	4.91 ± 0.12	10.2 ± 0.06	14.36 ± 0.3	21.38 ± 0.54
BHA loaded	0.86 ± 0.07	1.03 ± 0.09	1.93 ± 0.08	2.45 ± 0.15	2.97 ± 0.23
5% MSK extract	1.27 ± 0.03	1.62 ± 0.08	2.96 ± 0.11	4.29 ± 0.21	8.13 ± 0.29
10% MSK extract	1.03 ± 0.06	1.41 ± 0.05	2.37 ± 0.09	3.54 ± 0.29	5.83 ± 0.31
20% MSK extract	0.81 ± 0.04	1.15 ± 0.07	2.02 ± 0.1	2.68 ± 0.18	4.37 ± 0.27

From the results, it is clear that the open control (without any antioxidant inclusion) showed a rapid deterioration and reached the threshold peroxide value of 5 on Day 5 [20]. On the other hand, the ghee loaded with 0.02 w/v% of BHA showed a very slow degradation and still reminded stable with a peroxide value <5 on Day 20. Ghee samples loaded with the SCWE-derived MSK extracts showed an improved shelf life compared to the open control. The results showed that the performance of MSK extracts in improving the ghee stability increased with its increment levels incorporated into the samples. Within the samples preserved with the MSK extracts, it was observed that the rate of oxidation decreased with the increasing concentration of the extract. The ghee sample modified with 5% MSK extract showed an acceptable peroxide value (4.29 mM/g) on Day 15, while the sample containing 10% MSK extract with a peroxide value of 5.83 mM/g showed a marginal quality loss on Day 20. Nevertheless, the cow ghee fortified with 30% MSK

extract showed a good inhibitory effect on oxidation and had an acceptable peroxide value of 4.37 mM/g at Day 20. Interestingly, this sample showed a performance on par with the BHA-loaded ghee sample till Day 15 induction, proving its competitiveness with the synthetic BHA antioxidant at its permitted level [20]. Thus, the use of MSK extract obtained using the SCWE approach is promising for application as a natural and green antioxidant for food preservation and to replace hazardous synthetic antioxidants.

4. Conclusions

This study showcased the production of MSK extract using the SCWE technique and its application as a natural antioxidant for food preservation applications. The effect of critical variables of the SCWE, namely solvent-to-feed (L/S) ratio, operating temperature (T), and extraction time (t), on the MSK extract yield was studied using a Box–Behnken experimental design and ANOVA. The results showed that extraction temperature (T) was the most significant SCWE variable that impacted extraction yield. Furthermore, the extraction was optimized to have a maximum extract yield of 52.3% at extraction conditions of L/S ratio = 20.7, T = 116.5 °C, and t = 45 min. Comparison studies with CHWE and UAEU extraction techniques showed that the SCWE outperformed these techniques, with a yield that was 1.25 and 1.44 folds higher than these techniques, respectively. Furthermore, the extract obtained by the SCWE process possessed higher phenolic content and demonstrated better antioxidant activity than the other extracts. The physicochemical properties and fatty acid profile of SCWE-derived MSK extract proved its further suitability as an antioxidant preservative. Accordingly, cow ghee preservation studies established the potential of the SCWE-derived MSK extract as a natural antioxidant with a performance on par with that of synthetic BHA. A 20 w/v% concentration of MSK extract showed comparable performance with BHA at its permitted level (0.02 w/v%) for preserving cow ghee. Thus, the results from this study can be adapted to optimize the extraction and subsequent use of MSK extract as a natural and green food preservation agent.

Author Contributions: R.K.: Conceptualization, Validation, Resources, Data Curation, and Writing—Original Draft. A.H.: Methodology, Data Curation, and Writing—Original Draft. F.B.: Validation, Writing—Review and Editing, Supervision, and Funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Project 8474000471 under an internal grant of Khalifa University.

Data Availability Statement: Data available on request due to privacy/ethical restrictions.

Acknowledgments: Project 8474000471, under an internal grant of Khalifa University, is greatly acknowledged for supporting this research work.

Conflicts of Interest: The authors declare no conflict of interest.

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