

GRASAS Y ACEITES 71 (4)
October–December 2020, e377
ISSN-L: 0017-3495
<https://doi.org/10.3989/gya.0788191>

Multi-target response surface optimization of the aqueous extraction of Macauba kernel oil

K.T. Magalhães^a, T.S. Tavares^a, T.M.C. Gomes^b and C.A. Nunes^{b, ✉}

^aDepartment of Chemistry, Federal University of Lavras, University Campus, Post Office Box 3037, 37200-000 Lavras, Minas Gerais, Brazil.

^bDepartment of Food Science, Federal University of Lavras, University Campus, Post Office Box 3037, 37200-000 Lavras, Minas Gerais, Brazil.

✉ Corresponding author: cleiton.nunes@ufla.br

Submitted: 01 July 2019; Accepted: 04 October 2019; Published online: 14 October 2020

SUMMARY: Macauba (*Acrocomia aculeata*) is a promising tropical palm for the production of vegetable oil for both the food and non-food sectors. In this work, a multi-target response surface optimization of the aqueous extraction of Macauba kernel oil aimed to maximize the oil yield and minimize the free acidity and peroxide value. High yield was achieved at a high pH, long extraction periods and moderate temperatures, but these conditions contributed to elevating the peroxide value of the oil. On the other hand, pH presented the only significant effect on the oil's acidity, which decreased with the increase in pH in the aqueous medium. Therefore, the multi-target response surface optimization based on a desirability approach showed that pH 11, room temperature (25 °C) and a 60 min agitation time was preferred to obtain high yield and low free acidity and peroxide values. These conditions resulted in 30% yield (63.1% of the yield obtained by solvent extraction), 0.3% free acidity, and a peroxide value of 2.9 meqO₂/kg. The oil from the optimized aqueous extraction had a higher saturated fatty acid content compared to that from solvent extraction, especially fatty acids with < 14 carbon atoms, which can make the oil harder and more useful for producing special fats for specific food applications.

KEYWORDS: Desirability; Fatty acid; Lipid; Palm

RESUMEN: *Optimización de superficie de respuesta de múltiples objetivos en la extracción acuosa de aceite de semilla de macauba.* La macauba (*Acrocomia aculeata*) es una prometedora palma tropical para la producción de aceite vegetal para los sectores alimenticio y no alimentario. En este trabajo, una optimización de superficie de respuesta de múltiples objetivos en la extracción acuosa de aceite de semilla de macauba tuvo como objetivo maximizar el rendimiento del aceite y minimizar el valor de acidez libre y peróxidos. Se logró un alto rendimiento a pH alto, tiempos prolongados y temperaturas moderadas, pero estas condiciones contribuyeron a elevar el índice de peróxido del aceite. Por otro lado, el pH presentó como único efecto significativo sobre la acidez del aceite, la disminución con el aumento del pH en el medio acuoso. Por lo tanto, la optimización de la superficie de respuesta de múltiples objetivos basada en un enfoque de idoneidad mostró que se prefería pH 11, temperatura ambiente (25 °C) y un tiempo de agitación de 60 minutos para obtener un alto rendimiento y bajos valores de acidez libre y peróxido. Estas condiciones dieron como resultado un rendimiento del 30% (63,1% del rendimiento obtenido por extracción con disolvente), un 0,3% de acidez libre y un índice de peróxido de 2,9 meqO₂/kg. El aceite de la extracción acuosa optimizada tenía un mayor contenido de ácidos grasos saturados en comparación con el de la extracción con solventes, especialmente de ácidos grasos con <14 átomos de carbono, lo que puede hacer que el aceite sea más duro y útil para producir grasas especiales para aplicaciones alimentarias específicas.

PALABRAS CLAVE: Ácidos grasos; Idoneidad; Lípidos; Palma

ORCID ID: Magalhães KT <https://orcid.org/0000-0001-7976-7148>, Tavares TS <https://orcid.org/0000-0002-2275-3113>, Gomes TMC <https://orcid.org/0000-0002-2956-8674>, Nunes CA <https://orcid.org/0000-0002-5147-7357>

Citation/Cómo citar este artículo: Magalhães KT, Tavares TS, Gomes TMC, Nunes CA. 2020. Multi-target response surface optimization of the aqueous extraction of Macauba kernel oil. *Grasas Aceites* 71 (4), e377. <https://doi.org/10.3989/gya.0788191>

Copyright: ©2020 CSIC. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International (CC BY 4.0) License.

1. INTRODUCTION

Acrocomia aculeata (known as macauba or bocaiuva) is a promising tropical palm for the production of vegetable oil for both the food and non-food sectors (Prates-Valério *et al.*, 2019). It grows in dry areas from Mexico and the Caribbean Islands to northern Argentina. The fruit of 3.0-5.0 cm in diameter has a mucilaginous fibrous mesocarp with a sweet taste. The endocarp strongly adheres to the mesocarp, and the seed shows a large endosperm. The fruits consist of approximately 20% hull, 40% pulp, 33% endocarp and 7% kernel (Colombo *et al.*, 2018). The kernel (seed) has about 50% of an oil which is rich in lauric acid (~30%) and oleic acid (~40%), in addition to bioactive compounds, such as phenolics, tocopherols and carotenoids, especially α -tocopherol, thus representing a valuable source of vitamins A and E (Coimbra and Jorge 2012).

Macauba kernel oil (MKO) has played significant roles due to its particular composition. MKO showed hypoglycemic effects in an experiment in which type 2 diabetic rats fed with MKO had a reduction in blood glucose levels compared to the diabetic control group. Furthermore, a small fraction of total dietary medium-chain fatty acid was accumulated in the epididymal adipose tissue of the rats fed with MKO (Nunes *et al.*, 2018). An improvement in photoprotective activity in the development of a nanocarrier was achieved with the use of MKO, indicating that this oil can be a potentially superior alternative adjuvant and allows for the use of a renewable vegetable source (Dario *et al.*, 2018).

The screw press and solvent extraction are methods commonly used to obtain this kind of oil. A drawback in the screw press process is the temperature of the oil leaving the press. Due to friction, pressing is accompanied by the release of heat, which can degrade compounds of interest (Prates-Valério *et al.*, 2019; Rabrenović *et al.*, 2014). Although solvent extraction achieves high oil yield, inhalation exposure to large amounts of hexane is harmful to health and the explosive nature may jeopardize the safety of plants and humans (Li *et al.*, 2016). Extraction technology using pressurized fluids can also be used to recover oil from vegetable sources. Among the gases used as solvents in this kind of extraction, supercritical carbon dioxide (CO₂) stands out, but it requires the application of high pressure and long extraction time. Propane is an alternative to CO₂, but it is flammable, which necessitates the use of an explosion-proof extractor which uses local exhaust ventilation (Trentini *et al.*, 2018). Subcritical water extraction, which uses liquid water at 100–374 °C under pressurized conditions, attracted attention as an alternative technique to recover vegetable oils, but it also requires a special extraction apparatus to support the elevated pressure (about 5 MPa) (Wu *et al.*, 2018).

On the other hand, aqueous extraction is a process that can be used to recover vegetable oils with good quality. This process may be safer, environmentally friendly, and economical, mainly when compared to solvent extraction (Khoei and Chekin 2016; Mat Yusoff *et al.*, 2016). Also, it uses low pressure and temperature and does not require a special extraction apparatus as do supercritical and subcritical extraction processes.

In the aqueous extraction, the feedstock is milled and stirred with water under suitable conditions, which breaks the vegetable cells and allow the withdrawal of oil from plant tissues. This extraction procedure can produce oils with different characteristics from those extracted by others methods, such as less color imparting components, a lower free fatty acid content (Khoei and Chekin 2016) or a higher content of unsaturated fatty acids (Ghorbanzadeh and Rezaei 2017). Oils from different vegetable sources have been efficiently extracted by aqueous extraction, such as maize germ oil (Nikiforidis and Kiosseoglou 2009), soybean oil (Campbell *et al.*, 2011), and rice bran oil (Khoei and Chekin 2016).

Low yield is an inconvenience of aqueous extraction, which can be affected by some process variables, such as feedstock/water ratio, pH, time, temperature and agitation speed (Ghorbanzadeh and Rezaei 2017; Hanmoungjai *et al.*, 2000; Khoei and Chekin 2016). The optimal extraction conditions can vary among different feedstocks. High yield in the aqueous extraction of soybean oil was reached at pH above 8, while no relevant effect of the solid/water ratio was verified in this process (Rosenthal *et al.*, 1998). No influence of solid/water ratio or agitation speed was verified for the yield of rice bran oil in an aqueous extraction process, but a recovery of around 80% was reached at pH 12 with some increase with higher temperature and longer time (Hanmoungjai *et al.*, 2000).

Therefore, this work aimed to optimize a process for the aqueous extraction of macauba kernel oil using a five-level three-variable central composite design and response surface methodology. The multi-target optimization aimed to maximize oil yield and minimize free acidity and peroxide value. Also, the quality and the fatty acid composition of the oil from the optimized process of aqueous extraction were determined and compared to the oil extracted with organic solvent.

2. MATERIAL AND METHODS

2.1. Samples

Macauba fruits were collected directly from the ground. They were ripe, firm, and had no injuries. Whole fruits were dried at room temperature for 5 days. After drying, the kernel was separated from the

core with the aid of a vice. The moisture was determined immediately before each extraction process using a moisture determination balance (i-Thermo 163L – BEL Engineering) at 105 °C.

2.2. Aqueous extraction

The extraction method and the process parameter ranges were based on previous works (Hanmoungjai *et al.*, 2000; Rosenthal *et al.*, 1998). About 30 g of macauba kernels and 300.0 ml of distilled water were milled in a blender for 5 minutes. Afterward, the pH was adjusted according to factorial design using NaOH 1.0 mol·L⁻¹ or HCl 1.0 mol·L⁻¹. The mixture was agitated in a mechanical stirrer at 500 rpm in a water bath at temperature and time according to factorial design. The mixture was then centrifuged (relative centrifugal force of 2150 g) for 10 minutes. The upper phase was separated and cooled at -10 °C for 12 h to break the emulsion. The material was heated at 60 °C and centrifuged for 5 minutes. The oil was separated, weighed and stored in a closed bottle at -10 °C until analysis. The oil yield was calculated by gravimetric analysis on a dry basis.

2.3. Solvent extraction

The solvent extraction was carried out in a Soxhlet apparatus using ethyl ether as extractor solvent. After solvent evaporation, the oil was weighed and stored in a closed bottle at -10 °C until analysis.

2.4. Oil characterization

The obtained oils were characterized according to the following parameters:

Free acidity. Expressed as the percentage of free oleic acid, according to the AOCS method Ca 5a-40.

Peroxide value. Expressed in milliequivalents of active oxygen contained in 1 kg of oil, according to the AOCS method Cd 8b-90.

Iodine value. Expressed as the amount of iodine absorbed by 100 g of sample, calculated using the fatty acid composition according to the AOCS method Cd 1c-85.

Saponification value. Defined by the amount in milligrams of potassium hydroxide needed to saponify 1 g of oil or fat, calculated using the fatty acid composition in the AOCS method Cd 3a-94.

Fatty acid composition. Samples were transesterified into methyl esters using potassium hydroxide in methanol and n-hexane, according to the AOCS method Ce 2-66. The methyl esters were analyzed by gas chromatography (GC-2010 - Shimadzu) equipped with a flame ionization detector and an SPTM-2560 capillary column (100 mm x 0.25 mm x 0.2 µm) according to the conditions recommended by Supelco for 37-Component FAME Mix analysis on the 100 m SP-2560. The standard used was a

mixture of 37 methyl esters (Supelco 37 Component FAME Mix). The following operational parameters were used: split injection mode, split ratio 1:100; 1 µL injection volume; 260 °C detector temperature; 260 °C injector temperature; oven temperature program: held at 60 °C for 1 minute; ramp of 4 °C·min⁻¹ to 140 °C, held for 5 minutes; ramp of 4 °C·min⁻¹ to 240 °C, held for 30 minutes. Peak identification was resolved by comparing the retention times of the fatty acid methyl ester standards to the retention times of the observed peaks. Quantification was done by area normalization (%).

2.5. Statistical analysis

The effect of the agitation speed (500–2000 rpm), solid/water ratio (1:10–1:5), pH (4–10), temperature (25–70 °C) and time (15–60 min.) over the oil yield was initially evaluated by a Plackett Burman design. Afterward, an optimization process considering those significant factors was carried out using a five-level central composite design and response surface methodology (RSM). The multi-target optimization aimed to maximize the yield and minimize free acidity and peroxide value based on a desirability function (*d*) was computed by:

$$d = \left(\frac{\hat{y} - L}{U - L} \right)^r \quad (1)$$

for yield with the desirability power (*r*) of 1.2, and

$$d = \left(\frac{\hat{y} - U}{L - U} \right)^r \quad (2)$$

for free acidity and peroxide value with desirability power (*r*) of 1.0, where \hat{y} is the experimental response, *U* is the upper and *L* is the lower value of the response (Costa *et al.*, 2011). A higher desirability power for yield (*r* = 1.2) in comparison with free acidity and peroxide value (*r* = 1.0) prioritizes the maximization of the yield over the minimization of the free acidity or peroxide value, *i.e.*, it is more important to increase the yield than decrease the free acidity or the peroxide value in the optimization process.

The global desirability (*D*) used in the RSM model was computed by the geometric mean of the individual desirability (*d*) for yield, free acidity and peroxide value (Costa *et al.*, 2011).

The RSM models were fitted using codified variables and only significant (*p* ≤ 0.05) regression coefficients were considered. Linear and quadratic models were tested by variance analysis (ANOVA) to check the best fit. All calculations and graphs were made with Chemoface software (Nunes *et al.*, 2012).

The optimum condition was found using the response surface model by computing the desirability from the combinations of the significant factors.

3. RESULTS AND DISCUSSION

The effect of agitation speed, solid/water ratio, pH, temperature and time over the oil yield was initially evaluated by a Plackett Burman design, which indicated no significant effect of agitation speed or solid/water ratio (Table 1). Agitation speed and solid/water ratio had no substantial effect on the aqueous extraction of rice bran oil, while time, pH, and temperature influenced yield (Hanmoungjai *et al.*, 2000). The aqueous extraction process is based more on the insolubility of oil in water than on the dissolution of oil, *i.e.*, the water-soluble components of oil crops diffuse in the water rather than in oil, thereby releasing the oil which was previously bound in the original structure. Therefore, the non significant effect of the solid/water ratio in this experiment can indicate that the amount of water used sufficed to adequately dissolve the soluble components and release the oil. It was verified that despite the solid/water ratio not being relevant for yield, high ratios resulted in a mixture which was difficult to agitate properly. Thus, the agitation speed was fixed at 500 rpm and the solid/water ratio at 1:10. Moreover, extractions at pH below 7 resulted in low yield, and therefore the experimental design considered a pH range above 7.

Under the conditions of the central composite design, the yield of MKO in the aqueous extraction process varied from 22 to 29% (Table 2), which is equivalent to 46.3 to 61.1% of the yield obtained by solvent extraction (47.5 g·100g⁻¹).

An effect analysis (Figure 1-A) of the process variables revealed that temperature and time had a high antagonistic interaction effect (X2*X3) on oil yield, while time had a positive and significant effect (X3). The effect of pH (X1) was also significantly positive, while its interaction with time (X1*X3) was synergistic, but antagonistic with temperature (X1*X2). As a result, high oil yields were achieved

with high pH, long time periods and moderate temperatures, corroborating the extraction under pH 11, at 34 °C for 51 min. (experiment 6, Table 2), which yielded 29% oil. Concerning the time effect, the driving force for extraction is initially high because the oil concentration gradient between the solid surface and the bulk of the solution is high. However, the driving force is low after the initial period, and the oil has to diffuse from the interior of the solid (Khoei and Chekin 2016), which can be overcome by the increase in the solubilization of cell wall components with the rise in extraction time. Regarding the temperature effect, its increase contributed to decrease the oil viscosity and favor the withdrawal of oil from plant tissues, but excessive temperatures may have caused protein coagulation and the oil could be trapped in these structures, decreasing the extractability (Ghorbanzadeh and Rezaei 2017). Regarding pH, it has been reported that its variation does influence extractability in an aqueous extraction process. The solubility of the proteins depends on its isoelectric point in the oil source, which is influenced by pH and affects the withdrawal of oil from the particles. The pH also affects the stability and solubility of the oleosins that surround the oil droplets and the oleosins in the membrane of fatty tissues. Thus, the suitable pH for aqueous extraction of oils from different sources can vary due to the different proteins in their structures (Ghorbanzadeh and Rezaei 2017; Nikiforidis and Kiosseoglou 2009). Most aqueous extraction processes reached high yield at high pH due to protein solubility being highest at basic pH (Campbell *et al.*, 2011; Khoei and Chekin 2016; Rosenthal *et al.*, 1998), but for some oil sources the suitable pH for extraction can be low (Ghorbanzadeh and Rezaei 2017).

The effect of pH was only significant in the free acidity of the MKO from aqueous extraction (Figure 1-B), for which the negative value indicated that free acidity decreased with an increase in pH. This behavior can be verified by the regression of pH against free acidity (Table 2), resulting in an R² of 0.9. As reported for aqueous extraction of other oils, this effect can be a consequence of the neutralization of free fatty acids on the alkaline medium of extraction (Hanmoungjai *et al.*, 2000; Khoei and Chekin 2016).

All main effects of pH, time, and temperature were significantly synergistic on the peroxide value, but the interaction between pH and time (X1*X3) had an antagonistic effect (Figure 1-C). Therefore, lower peroxide values were obtained under moderate conditions of pH, time and/or temperature. Some works have reported that lipooxygenase activity increases with an increase in pH, thereby contributing to oil oxidation (ASBI *et al.*, 1989), but this enzyme can be inactivated after a few minutes at high temperatures (50-70 °C) (Ludikhuyze *et al.*, 1998).

TABLE 1. Effect of pH, temperature, time, solid/water ratio, and agitation speed on the oil yield determined by a Plackett Burman design.

	Effect	Error	p
pH	5.6	1.4	0.002
Temp. (°C)	-3.2	1.4	0.046
Time (min)	3.7	1.4	0.023
Solid/water	2.3	1.4	0.123
Agitation (rpm)	-0.1	1.4	0.923

TABLE 2. Yield, free acidity (FA) and peroxide value (PV) of the Macauba kernel oil from aqueous extraction according to a central composite factorial design.

Assay	pH	Temperature (°C)	Time (min)	Yield (%)	FA (%)	PV (meqO ₂ ·kg ⁻¹)
1	8	34	24	22.0	3.9	2.9
2	8	34	51	25.0	4.6	5.7
3	8	61	24	26.5	4.9	3.4
4	8	61	51	22.9	4.7	6.8
5	11	34	24	23.0	0.3	5.0
6	11	34	51	29.0	0.3	4.0
7	11	61	24	24.5	0.3	6.9
8	11	61	51	25.9	0.4	6.6
9	7	47.5	37.5	24.0	6.6	6.0
10	12	47.5	37.5	26.9	0.0	8.3
11	9.5	25	37.5	25.1	1.0	3.9
12	9.5	70	37.5	25.5	2.4	5.9
13	9.5	47.5	15	24.0	1.4	1.9
14	9.5	47.5	60	26.8	3.4	3.9
15	9.5	47.5	37.5	24.4	2.8	3.0
16	9.5	47.5	37.5	23.9	2.4	2.9
17	9.5	47.5	37.5	24.1	1.9	2.3

Furthermore, the presence of hydroxide ions (OH⁻) can accelerate triacylglycerol hydrolysis, producing free fatty acids, monoacylglycerols, and diacylglycerols, which are amphiphilic and can accelerate the rate of lipid oxidation. This rate acceleration is due to the formation of association colloids, since the interface between oil and water is a possible location for lipid oxidation (Chaiyasit *et al.*, 2007; Kim *et al.*, 2016).

The global desirability (D) was computed to optimize a suitable condition for obtaining MKO by aqueous extraction, aiming to maximize the yield and minimize the free acidity and peroxide value. Therefore, the pH, temperature and time values from the factorial design (Table 2) were regressed against the respective global desirability using least square regression. A quadratic model had the best fit (Equation 2), with R² of 0.88, Adjusted R² of 0.80, significant regression (p < 0.05) and non-significant lack of fit (p > 0.05). The linear term for time, as well as the quadratic terms for temperature and time, was not significant (p > 0.05). The regression coefficients (Equation 2) indicated that the pH (X1) had the greatest influence over the desirability, with higher desirability at high pH, but with a maximum due to the significance of its negative quadratic term (X1²). In fact, pH had high influence on all the evaluated responses (yield, acidity, and peroxides) as previously discussed (Figure 1),

i.e., the increase in pH contributed to increasing the yield, decreasing the acidity and increasing the peroxide value, with significant interactions with time and temperature (except for free acidity). The interaction effects (Equation 2) of pH with temperature (X1X2) and time (X1X3), as well as of temperature with time (X2X3), indicated that higher desirability could be reached by the combinations of high pH for long periods and moderate heat. This trend can be confirmed by the response surfaces (Figure 2), in which high desirability at pH 11-12, time of 51-60 min., and temperature of 34-25 °C were detected. These conditions resulted in a higher yield and better oil quality (low acidity and acceptable peroxide value).

$$D = -8.574 + 1.604X_1 + 0.055X_2 - 0.004X_1X_2 + 0.003X_1X_3 - 0.001X_2X_3 - 0.078X_1^2 \quad (3)$$

A multi-target numerical optimization based on the desirability model (Equation 3) was carried out and considered the following ranges: pH from 7 to 12 in increments of 0.5; temperature from 25 to 70 °C in increments of 1 °C; and time from 15 to 60 min. in increments of 1 min. After computing the global desirability for all variable combinations, the predicted condition that would result in high yield and low free acidity and peroxide value was found to be an extraction at pH 11, 25 °C for 60 min.

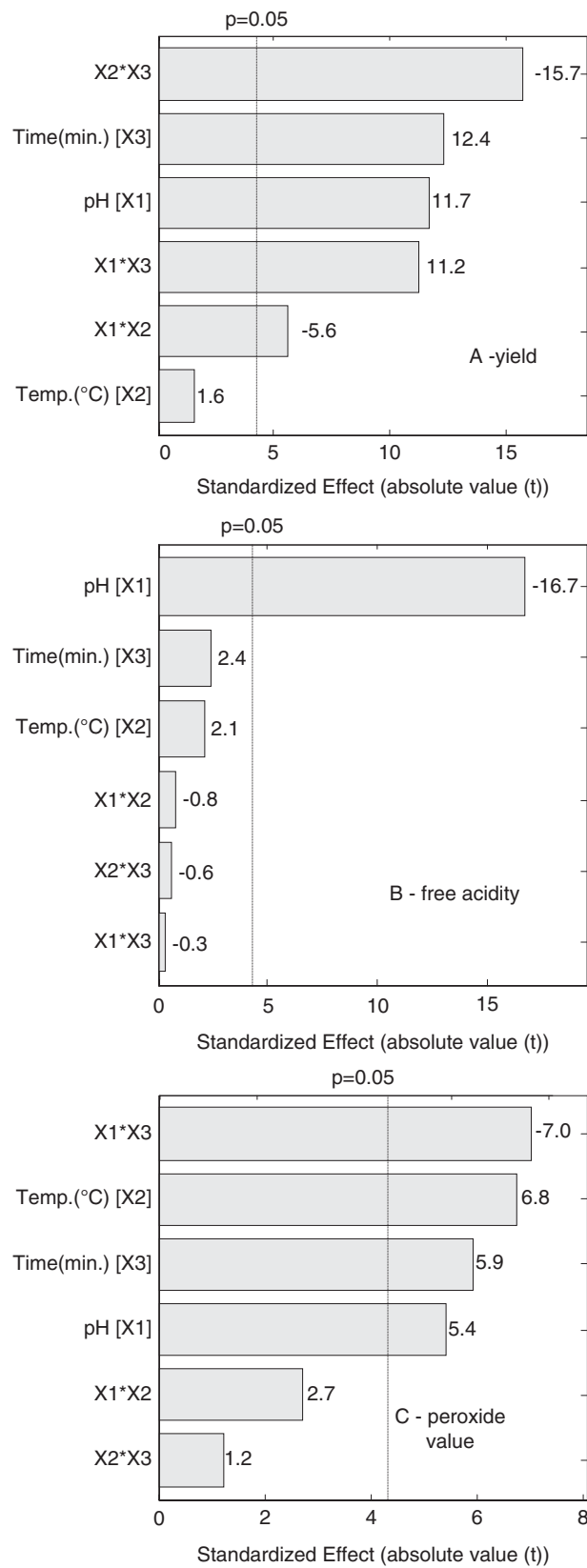


FIGURE 1. Effects of pH (X1), temperature (X2) and time (X3) on yield (A), free acidity (B) and peroxide value (C) of the Macauba kernel oil from aqueous extraction.

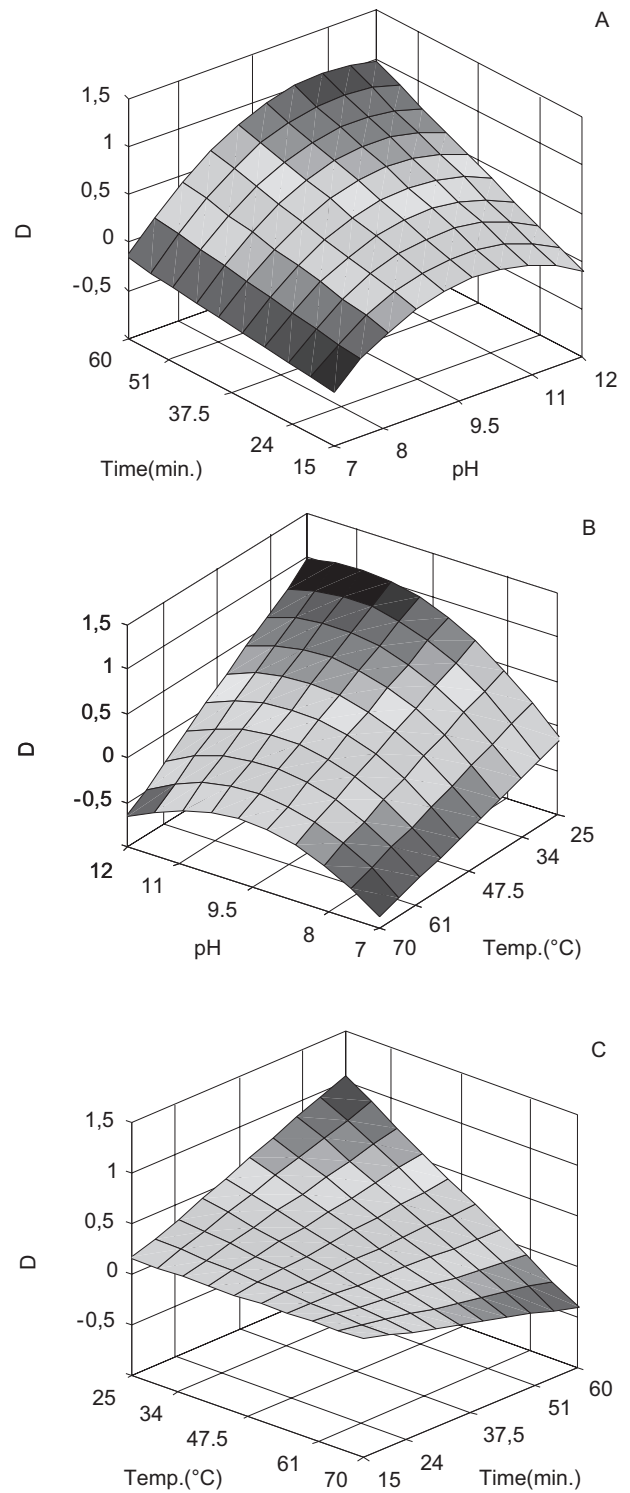


FIGURE 2. Surface responses for pH, temperature, and time against the desirability (combination of yield, free acidity, and peroxide value) for the aqueous extraction of Macauba kernel oil.

Thus, a new aqueous extraction of the MKO was carried out under those conditions, which resulted in a yield of 30%, free acidity of 0.3% and peroxide value of $2.9 \text{ meqO}_2 \cdot \text{kg}^{-1}$, which was close to the predicted values for yield (29%), free acidity (0%) and peroxide value ($1.9 \text{ meqO}_2 \cdot \text{kg}^{-1}$), considering maximal global desirability of 1 in the desirability functions (Equations 1 and 2). This yield was comparable to that reported for the aqueous extraction of Pomegranate Seed Oil (Ghorbanzadeh and Rezaei 2017). The yield achieved under the optimum condition (30%) was 63.1% of the yield obtained by solvent extraction. It is believed that the efficiency of the aqueous extraction of MKO can be improved with auxiliary techniques, such as the use of proteases and cellulases or ultrasonication, as reported for other aqueous extraction processes (Khoei and Chekin 2016; Mat Yusoff *et al.*, 2016).

The oil from the optimized aqueous extraction process was analyzed for fatty acid content. The oils from solvent extraction and aqueous extraction had a predominance of lauric acid (C12:0) and oleic acid (C18:1) (Table 3), corroborating previous works (Coimbra and Jorge 2011; Moreira *et al.*, 2013). The oil from aqueous extraction had a higher proportion of saturated fatty acids when compared to the oils extracted with hexane (Table 3). The increase in the saturated portion was mainly due to the higher proportion of short- and medium-chain saturated fatty acids (C8:0-C14:0). On the other hand, the proportions of long-chain saturated fatty acids (C16:0 and C18:0) were slightly lower,

in addition to a lower proportion of unsaturated fatty acids (C18:1 and C18:2). Consequently, the oil from aqueous extraction had a higher saponification value, since this oil had a lower average fatty acid molecular weight when compared to the oil from solvent extraction, as well as a lower iodine value because of its lower proportion of unsaturated fatty acids. These differences can be explained by the different affinity of fatty acids for the aqueous medium, which is influenced by chain length. It was reported that even when low, the solubility of saturated fatty acids in water increased with the decrease in the hydrocarbon chain length (Khuwijitjaru *et al.*, 2003). Therefore, the migration from vegetable tissue to the aqueous medium would be favored by triacylglycerols with short- and medium-chain saturated fatty acids, which can explain the higher proportions of these fatty acids in the oil from aqueous extraction. The increase in saturated fatty acid content in lauric oils, such as MKO, can play an essential role in the change of its thermal properties, especially by making the oil harder and more useful as a specialty fat such as chocolate-type coating fats and fats for margarine, as reported for fractions of coconut oil (Sonwai *et al.*, 2017).

4. CONCLUSIONS

The aqueous extraction was effective for extracting macauba kernel oil. Key factors affecting aqueous extraction of macauba kernel oil were identified. Both the yield and peroxide value of the macauba kernel oil were influenced by pH, time, and temperature in the aqueous extraction process. The highest yield was achieved at high pH, long extraction times, and moderate temperatures, but this condition contributed to elevating the peroxide value. On the other hand, pH presented the only significant effect on the oil's acidity, which decreased with the increase in pH in the aqueous medium. Therefore, the ideal condition for obtaining a higher oil yield was not the same for achieving better oil quality. The multi-target response surface optimization based on a desirability approach showed that pH 11, room temperature (25°C) and agitation time of 60 min was preferred to obtain high yield and low free acidity and peroxide value. Despite lower yield, the oil from the optimized aqueous extraction had a higher saturated fatty acid content compared to that from solvent extraction, especially in fatty acids with < 14 carbon atoms, which can make the oil harder and more useful for producing special fats for specific food applications. The improvement in the extraction efficiency by using proteases and cellulases or ultrasonication, as well as the use of a less expensive method for breaking the emulsion, are future works to be considered.

TABLE 3. Fatty acid composition of the Macauba kernel oil from solvent and aqueous extraction.

Fatty acid	Solvent extraction	Aqueous extraction
C6:0	0.4±0.1	0.4±0.1
C8:0	4.6±0.4	5.6±0.3
C10:0	3.5±0.2	4.1±0.3
C12:0	41.5±0.3	45.7±0.3
C14:0	8.9±0.5	9.2±0.3
C16:0	6.6±0.4	6.3±0.3
C18:0	2.3±0.2	2.1±0.2
C18:1n9c	29.1±0.3	24.1±0.5
C18:2n6c	3.4±0.1	2.8±0.1
Σsaturated	67.5±0.6*	73.1±0.7*
Σunsaturated	32.5±0.1*	26.9±0.5*
Iodine value ($\text{gI}_2 \cdot 100\text{g}^{-1}$)	30.9±0.0*	25.5±0.5*
Saponification value ($\text{mgKOH} \cdot \text{g}^{-1}$)	230.0±0.5*	235.4±3.0*

Mean ± standard deviation (n = 2). * Calculated from fatty acid compositions.

ACKNOWLEDGMENTS

This Study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (Capes) Finance Code 001 (Magalhães K. T.) and by the Fundação de Amparo à Pesquisa de Minas Gerais (FAPEMIG, Brazil, APQ-00638-14, PPM-00498-16 and Tavares T. S. scholarship). The authors would like to thank the Center for Analysis and Chemical Prospecting of the Federal University of Lavras, Finep and Capes for supplying the equipment and technical support for experiments involving chromatographic analyses.

REFERENCES

- Asbi BA, Wei LS, Steinberg MP. 1989. Effect of pH on the Kinetics of Soybean Lipoxigenase-1. *J. Food Sci.* **54**, 1594–1595. <https://doi.org/10.1111/j.1365-2621.1989.tb05167.x>
- Campbell KA, Glatz CE, Johnson LA, Jung S, Moura JMN, Kapchie V, Murphu P. 2011. Advances in Aqueous Extraction Processing of Soybeans. *J. Am. Oil Chem. Soc.* **88**, 449–465. <https://doi.org/10.1007/s11746-010-1724-5>
- Chaiyasit W, Elias RJ, McClements DJ, Decker EA. 2007. Role of physical structures in bulk oils on lipid oxidation. *Crit. Rev. Food. Sci. Nutr.* **47**, 299–317. <https://doi.org/10.1080/10408390600754248>
- Coimbra MC, Jorge N. 2011. Characterization of the Pulp and Kernel Oils from *Syagrus oleracea*, *Syagrus romanzoffiana*, and *Acrocomia aculeata*. *J. Food Sci.* **76**, C1156–61. <https://doi.org/10.1111/j.1750-3841.2011.02358.x>
- Colombo CA, Berton LHC, Diaz BG, Ferrari RA. 2018. Macauba: a promising tropical palm for the production of vegetable oil. *Oilseeds Fats Crops Lipids* **25**, D108. <https://doi.org/10.1051/ocl/2017038>
- Costa NR, Lourenço J, Pereira ZL. 2011. Desirability function approach: A review and performance evaluation in adverse conditions. *Chemom. Intell. Lab. Syst.* **107**, 234–244. <https://doi.org/10.1016/j.chemolab.2011.04.004>
- Dario MF, Oliveira FF, Marins DSS, Baby AR, Velasco MVR, Löbenberg R, Bou-Chacra NA. 2018. Synergistic photoprotective activity of nanocarrier containing oil of *Acrocomia aculeata* (Jacq.) Lodd. Ex. Martius—Arecaceae. *Ind. Crops Prod.* **112**, 305–312. <https://doi.org/10.1016/j.indcrop.2017.12.021>
- Ghorbanzadeh R, Rezaei K. 2017. Optimization of an Aqueous Extraction Process for Pomegranate Seed Oil. *J. Am. Oil Chem. Soc.* **94**, 1491–1501. <https://doi.org/10.1007/s11746-017-3045-4>
- Hanmoungjai P, Pyle L, Niranjan K. 2000. Extraction of rice bran oil using aqueous media. *J. Chem. Technol. Biotechnol.* **75**, 348–35. [https://doi.org/10.1002/\(SICI\)1097-4660\(200005\)75:5<348::AID-JCTB233>3.0.CO;2-P](https://doi.org/10.1002/(SICI)1097-4660(200005)75:5<348::AID-JCTB233>3.0.CO;2-P)
- Khoei M, Chekin F. 2016. The ultrasound-assisted aqueous extraction of rice bran oil. *Food Chem.* **194**, 503–507. <https://doi.org/10.1016/j.foodchem.2015.08.068>
- Khujwitijaru P, Adachi S, Matsuno R. 2002. Solubility of saturated fatty acids in water at elevated temperatures. *Biosci. Biotechnol. Biochem.* **66**, 1723–6. <https://doi.org/10.1271/bbb.66.1723>
- Kim JY, Bora Y, Chankyu L, Seo-Yeong G, Mi-Ja K, Jaehwan L. 2016. Effects of pH on the rates of lipid oxidation in oil-water system. *Appl. Biol. Chem.* **59**, 157–161. <https://doi.org/10.1007/s13765-015-0146-3>
- Li P, Gasmalla MAA, Zhang W, Liu J, Bing R, Yang R. 2016. Effects of roasting temperatures and grinding type on the yields of oil and protein obtained by aqueous extraction processing. *J. Food Eng.* **173**, 15–24. <https://doi.org/10.1016/j.jfoodeng.2015.10.031>
- Ludikhuyze L, Indrawati I, Van Den Broeck C, Weemaes C, Hendrickx M. 1998. Effect of Combined Pressure and Temperature on Soybean Lipoxigenase. 1. Influence of Extrinsic and Intrinsic Factors on Isobaric–Isothermal Inactivation Kinetics. *J. Agric. Food Chem.* **46**, 4074–4080. <https://doi.org/10.1021/jf980256c>
- Mat Yusoff M, Gordon MH, Ezeh O, Niranjan K. 2016. Aqueous enzymatic extraction of *Moringa oleifera* oil. *Food Chem.* **211**, 400–408. <https://doi.org/10.1016/j.foodchem.2016.05.050>
- Moreira MAC, Payret Arrúa ME, Antunes AC, Fiuza TER, Costa BJ, Weirich Neto PH, Antunes SRM. 2013. Characterization of *Syagrus romanzoffiana* oil aiming at biodiesel production. *Ind. Crops. Prod.* **48**, 57–60. <https://doi.org/10.1016/j.indcrop.2013.04.006>
- Nikiforidis CV, Kiosseoglou V. 2009. Aqueous Extraction of Oil Bodies from Maize Germ (*Zea mays*) and Characterization of the Resulting Natural Oil-in-Water Emulsion. *J. Agric. Food Chem.* **57**, 5591–5596. <https://doi.org/10.1021/jf900771v>
- Nunes AA, Buccini DF, Jaques JAS, Portugal, LC, Guimarães, RCA, Favaro SP, Caldas RA, Carvalho CME. 2018. Effect of *Acrocomia aculeata* Kernel Oil on Adiposity in Type 2 Diabetic Rats. *Plant Foods Hum. Nutr.* **73**, 61–67. <https://doi.org/10.1007/s11130-017-0648-8>
- Nunes CA, Freitas MP, Pinheiro ACM, Bastos SC. 2012. Chemoface: a novel free user-friendly interface for chemometrics. *J. Brazil. Chem. Soc.* **23**, 2003–2010. <https://doi.org/10.1590/S0103-50532012005000073>
- Prates-Valério P, Celayeta JMF, Cren EC. 2019. Quality Parameters of Mechanically Extracted Edible Macauba Oils (*Acrocomia aculeata*) for Potential Food and Alternative Industrial Feedstock Application. *Eur. J. Lipid Sci. Technol.* **121**, 1800329. <https://doi.org/10.1002/ejlt.201800329>
- Rabrenović BB, Dimić EB, Novaković MM, Tešević VV, Basić ZN. 2014. The most important bioactive components of cold pressed oil from different pumpkin (*Cucurbita pepo* L.) seeds. *LWT - Food Sci. Technol.* **55**, 521–527. <https://doi.org/10.1016/j.lwt.2013.10.019>
- Rosenthal A, Pyle DL, Niranjan K. 1998. Simultaneous Aqueous Extraction of Oil and Protein from Soybean: Mechanisms for Process Design. *Food Bioprod. Process.* **76**, 224–230. <https://doi.org/10.1205/096030898532124>
- Sonwai S, Rungprasertphol P, Nantipipat N, Tungvongcharoan S, Laiyankoon N. 2017. Characterization of Coconut Oil Fractions Obtained from Solvent Fractionation Using Acetone. *J. Oleo Sci.* **66**, 951–961. <https://doi.org/10.5650/jos.ess16224>
- Trentini CP, Cuco RP, Cardozo-Filho L, Silva C. 2019. Extraction of macauba kernel oil using supercritical carbon dioxide and compressed propane. *Can. J. Chem. Eng.* **97**, 785–792. <https://doi.org/10.1002/cjce.23236>
- Wu H, Li C, Li Z, Liu R, Zhang A, Xiao Z, Ma L, Li J, Deng S. 2018. Simultaneous extraction of oil and tea saponin from *Camellia oleifera* Abel. seeds under subcritical water conditions. *Fuel Process. Technol.* **174**, 88–94. <https://doi.org/10.1016/j.fuproc.2018.02.014>