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Effect of process variables on the oil extraction from passion fruit seeds by conventional and non-conventional techniques

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ABSTRACT. The effects of process variables on the oil extraction from passion fruit seeds by three techniques, ultrasound shaker, and soxhlet, and of environment-friendly solvents are evaluated. Ratio variables of seed weight, solvent volume (R), time of extraction (T), and type of solvent (S) were evaluated. The significant variables for oil extraction from passion fruit seeds were R and S by ultrasound and shaker techniques and T for soxhlet extraction. Comparison of the three techniques showed that the soxhlet technique had the highest yield with 65% of total oil in the initial matrix.

Keywords: solvent, passion fruit, extraction, oil, ultrasound, soxhlet.

Efeito das variáveis de processos na extração do óleo das sementes de maracujá por técnicas convencional e não convencional

RESUMO. Os efeitos das variáveis de processo sobre a extração do óleo das sementes de maracujá por três técnicas ultrassom, shaker, e soxhlet e também os efeitos do tipo de solventes menos impactantes ao ambiente foram avaliados nesse trabalho. As variáveis razão massa de semente por volume de solvente (R), tempo de extração (T) e tipo de solvente (S) foram avaliados. As variáveis significativas para a extração do óleo das sementes de maracujá foram de R e S para as extrações conduzidas com ultrassom e T para extrações conduzidas em soxhlet. A comparação das três técnicas demonstrou que a técnica soxhlet obteve o maior rendimento com 65% do total de óleo presente na matriz inicial.

Palavras-chave: solvente, maracujá, extração, óleo, ultrassom, soxhlet.

Introduction

Brazil is the world's largest producer of passion fruit. The yellow passion fruit (*Passiflor aedulis f. flavicarpa*) represents about 97% of the planted area and of the commercialized volume in all of Brazil. An estimated 60% of the Brazilian production is sold in fruit and vegetable markets and supermarkets or consumed *in natura.* The remainder is industrially processed for juice as a main product. According to Ferrari et al. (2004), the seeds represent between 6 and 12% of the fruit weight.

Extraction with solvents is a single-step solid-liquid operation in which one or more soluble constituents present in the solid mixture are extracted with a liquid solvent. Although several solvents have been investigated, hexane is a favorite due to the advantageous energy balance which directly affects industrial costs. However, according to the literature (AQUINO et al., 2011; BROSSARD-GONZÁLEZ et al., 2010; GALLEGOS-INFANTE et al., 2003), new solvents, such as ethanol, acetone, acetic acid and others, have been recently tested. These solvents have been used because they pollute less and are less toxic than hexane. This fact meets the principles of green chemistry proposed by Lenardão et al. (2003). The authors emphasized that the chemical processes that bring about environmental problems can and must be replaced with less polluting or even non-polluting alternatives.

Several extraction techniques have been used to obtain vegetable oils, including extraction with solvent, by pressing, with supercritical fluid, ultrasound, pressurized liquid and others. The first two techniques are classical extraction processes. Many of the analytical studies involving oil extraction in the last years have investigated new extraction methodologies and compared them to classical techniques.

Current assay compares the extraction yields of passion fruit seed oil using (i) non-conventional extraction techniques (ultrasound and shaker) and a conventional technique (soxhlet) and (ii) solvents fitting the green chemistry category.

Material and methods

Crude material and characterization

Yellow passion fruit seeds (*Passiflora edulis* f. *flavicarpa*), obtained from a local industry, were employed in current assay. In the laboratory, the seeds were placed in a bowl and washed with light friction to eliminate the aril. Seeds were then dried in a forced convection drier at 60ºC, with air flow of 4.54 m^3 s^{-1} and ground with a Marconi Tecnal grinder (model T345) for 30 s.

A seed lot sample was characterized by physical-chemical analysis – moisture, ash, crude fiber, total lipids and crude protein – according to the procedures by Adolfo Lutz Institute (IAL, 2008). Analyses were performed in triplicate and their means are presented in current study. The sample underwent granulometric analysis of solid particles with a set of standard sieves.

The fatty acid profile of the oil and the quantification of the ethyl esters were done by gas chromatography with Varian model CP-3800 coupled with a flame ionization detector (FID) and a 30 m x 0.25 mm specific capillary column, particle size 0.25 μm for fatty acid separation, BP-X70. Carrier gas was helium at a split rate of 1:10. The analysis was performed with a column temperature program starting at 140°C, heating up to 250 at 5°C $min.^{-1}$. The detector temperature was kept at 220°C and that of the injector at 260°C. Methyl tricosanoate 99%, from Sigma-Aldrich, was the internal standard.

Solvents

Acetone, ethanol, and isopropanol of analytical grade from F. Maia (São Paulo State, Brazil) were used in the study. These solvents were chosen because they are widely employed in the food industry and because they meet the criteria of green chemistry.

Shaker extraction

Erlenmeyers with rubber taps containing ground passion fruit seeds and one of the three solvents were used in extraction. The solvents were added at seed-to-solvent ratios (weight per volume) of 1:4, 1:6 and 1:8. The erlenmeyers containing the solvent and the ground seeds were placed in a Tecnal (São Paulo State, Brazil) shaker at 40ºC and shaken at 40 rpm. Assays were performed in duplicate.

Ultrasound extraction

An Ultracleaner Unique (São Paulo State, Brazil) ultrasound bath with a frequency of 44 kHz was used. The ground passion fruit seeds were placed in an erlenmeyer and one of the solvents at seed-to-solvent (weight/volume) ratios of 1:4, 1:6, and 1:8 was added. Extraction times were 15, 30, and 60 min. Assays were performed in duplicate.

Soxhlet extraction

The methodology described by the Adolfo Lutz Institute (IAL, 2008) was used, replacing the petroleum ether with one of the above-mentioned solvents, with extraction times of 4, 8, 16, and 24h. Assays were conducted in triplicate and the means are shown in the study.

A Tecnalsoxhlet extractor (São Paulo State, Brazil) with nominal power of 1500 W was used. Soxhlet temperature was kept constant (70ºC) in all assays and above the solvent boiling point. The soxhlet extraction balloon was coupled to a condensation column in a Marconi thermo-bath (São Paulo State, Brazil) at 10°C to ensure the total condensation of the boiling solvent.

Extraction Yield

The extraction yield was calculated by Equation 1:

$$\text{Yield} = 100 \cdot \frac{m_0}{m_s} \quad (1)$$

Where m_0 is the weight of the oil obtained and m_s is the weight of the seed used in the extraction.

Experimental design and statistical analysis

The experimental design was based on a 3 x 3 complete factorial design in duplicate for the shaker and ultrasound extractions, and on a 3 x 4 factorial design in triplicate for the soxhlet extraction. In the extractions by shaker and ultrasound, the variables time of extraction (T), solvent type (S) and ratio of seed weight to solvent volume (R) were investigated, whereas in the extractions with soxhlet, the variables time of extraction (T) and type of solvent (S) were investigated. The experiments were designed according to the methodology by Barros Neto et al. (1995). The mean yield values were calculated and compared by variance analysis (ANOVA) with SAS 8.2 at 5% level of significance.

Results and discussion

Seed characterization

Tables 1 and 2 show the physical and chemical results for the passion fruit seeds and the fatty acids, respectively. The Sauter diameter of ground seed was 0.778 mm. The passion fruit seeds used in current assay had a percentage lipid content close to that found by Correa et al. (1994).

Table 1. Physical and chemical characterization of yellow passion fruit seeds.

Physical and chemical analysis	
Moisture and volatile substances (% m m^{-1})	0.02 ± 0.0001
Fixed mineral residue (% m m^{-1})	10.9 ± 0.0001
Raw fiber (% m m^{-1})	46.5 ± 0.09
Crude protein (% m m^{-1})	13.2 ± 0.01
Total lipids (% m m^{-1})	24.8 ± 0.07

Table 2. Fatty acids of yellow passion fruit seeds.

Fatty acids	Composition (%)
16:0	16.3
18:0	5.20
18:1n9c	20.7
18:2n6	50.8
Total lipids	-
Saturated fats	21.5
Mono-unsaturated fatty acid	20.7
Poly-unsaturated fats	57.8
Trans fats	0.00

Prasad (1980) reported 11% palmitic acid (16:0), 2% stearic acid (18:0), 14% oleic acid (18:1n9c) and 73.5% linoleic acid (18:2n6) in passion fruit oil. Liu et al. (2009) reported 8.57% palmitic acid (16:0), 1.66% stearic acid (18:0), 16.25% oleic acid (18:1n-9), and 72.695% linoleic acid (18:2n-6) in passion fruit oil extracted by supercritical carbon dioxide.

Yields by different techniques

Tables 3, 4, and 5 give the yields of extraction by ultrasound, shaker, and soxhlet techniques, respectively.

Yields by ultrasound and shaker techniques were lower than 3.5% (Table 4), while those by soxhlet lay between 13 and 16.5% (Table 5). Soxhlet extraction is thus economically viable when compared to ultrasound and shaker techniques. The comparison between oil extraction yield from passion fruit seeds by soxhlet (16.2%) and the oil content percentage in the initial matrix (24.2%), given in Table 2, shows that more than 65% of the oil in the initial matrix was extracted. Soxhlet extraction yield was higher because the solvent was almost pure in each reflux solvent in the equipment. Thus, the concentration gradient between solid matrix and solvent was always high and the equilibrium of extraction was constantly modified to enable oil solubility.

With regard to soxhlet extraction, Rui et al. (2009) reported yield of approximately 6.13% for the oil extraction from white pitaya. These results are close when compared to other techniques such as microwave-assistant extraction, aqueous enzymatic extraction and CO2-supercritical extraction.

Table 3. Oil extraction yield of passion fruit seeds by solvent and ultrasound techniques.

Experiment no.	Independent variables			Mean yield (% m m^{-1})
	Solvent	Seed/ solvent ratio	Time (min.)	
1	Acetone	1/4	15	2.11
2	Acetone	1/4	30	1.92
3	Acetone	¼	60	1.79
4	Acetone	1/6	15	1.52
5	Acetone	1/6	30	1.55
6	Acetone	1/6	60	1.57
7	Acetone	1/8	15	1.28
8	Acetone	1/8	30	1.34
9	Acetone	1/8	60	1.25
10	Ethanol	1/4	15	1.53
11	Ethanol	1/4	30	1.14
12	Ethanol	¼	60	1.18
13	Ethanol	1/6	15	0.813
14	Ethanol	1/6	30	1.14
15	Ethanol	1/6	60	1.18
16	Ethanol	1/8	15	1.07
17	Ethanol	1/8	30	1.00
18	Ethanol	1/8	60	0.930
19	Isopropanol	1/4	15	1.95
20	Isopropanol	1/4	30	1.98
21	Isopropanol	1/4	60	1.04
22	Isopropanol	1/6	15	1.26
23	Isopropanol	1/6	30	1.42
24	Isopropanol	1/6	60	1.18
25	Isopropanol	1/8	15	1.23
26	Isopropanol	1/8	30	1.13
27	Isopropanol	1/8	60	0.950

Table 4. Oil extraction yield of passion fruit seeds by solvent and shaker techniques.

Experiment no.	Independent variables			Mean yield
	Solvent	Seed/solvent ratio	Time	(% m m^{-1})
1	Acetone	1/4	4	3.48
2	Acetone	1/4	8	2.52
3	Acetone	1/4	16	2.59
4	Acetone	1/6	4	2.26
5	Acetone	1/6	8	1.86
6	Acetone	1/6	16	1.74
7	Acetone	1/8	4	1.61
8	Acetone	1/8	8	1.82
9	Acetone	1/8	16	1.66
10	Ethanol	1/4	4	1.01
11	Ethanol	1/4	8	1.24
12	Ethanol	1/4	16	0.65
13	Ethanol	1/6	4	1.07
14	Ethanol	1/6	8	0.99
15	Ethanol	1/6	16	0.88
16	Ethanol	1/8	4	0.76
17	Ethanol	1/8	8	1.11
18	Ethanol	1/8	16	0.94
19	Isopropanol	1/4	4	1.80
20	Isopropanol	1/4	8	2.33
21	Isopropanol	1/4	16	1.94
22	Isopropanol	1/6	4	1.44
23	Isopropanol	1/6	8	1.49
24	Isopropanol	1/6	16	1.43
25	Isopropanol	1/8	4	2.75
26	Isopropanol	1/8	8	1.16
27	Isopropanol	1/8	16	1.28

Döker et al. (2010) registered that sesame seed oil by CO2-supercritical extraction and hexane soxhlet solvent extraction yielded about 0.450% and 50.6%, respectively. Jadhav et al. (2009) made a comparative study on soxhlet and ultrasound assisted extraction of vanillin from vanilla pods.

During soxhlet extraction the authors tested polar and non-polar solvents (methanol, ethanol, acetone, chloroform, hexane and acetonitrile) and they observed that extraction of vanillin was higher in polar solvents such as ethanol and methanol.

Table 5. Oil extraction yield of passion fruit seeds by soxhlet.

Experiment no.	Independent variables		Mean yield
	Solvent	Time (h)	(% m m^{-1})
1	Acetone	4	14.6
2	Acetone	8	16.2
3	Acetone	16	14.5
4	Acetone	24	15.1
5	Ethanol	4	13.5
6	Ethanol	8	14.4
7	Ethanol	16	14.0
8	Ethanol	24	14.0
9	Isopropanol	4	14.2
10	Isopropanol	8	14.7
11	Isopropanol	16	15.5
12	Isopropanol	24	15.9

Effect of the variables

Variables with significant effects at 95% confidence interval on oil extraction yield from passion fruit seeds were R and S for extraction by ultrasound and shaker, and S for soxhlet extraction. First-order and second-order interactions - T*S, R*S, T*R, T*R*S - for ultrasound and shaker extraction were also estimated and none of them had significant effect. The S*T was estimated for shaker extraction but no significant effect was observed.

Since the difference between the treatments was significant, their magnitude was evaluated by multiple comparison tests. Tukey's test was used in current assay to evaluate differences between any two or more than two treatment means. However, comparison among the groups was impossible. Tables, 6, 7, and 8 provide means of the groups (time, seed/solvent ratio and solvent type) evaluated by Tukey's test at 5% probability. Means with equal letters were not significantly different ($p < 5\%$).

Table 6. Global means of the factors studied in the oil extraction from passion fruit seeds with ultrasound.

Solvent		Extraction time		Solute/solvent ratio	
Acetone	1.54a	15 min.	1.44a	1/4	1.58a
Ethanol	1.35b	30 min.	1.39a	1/6	1.31b
Isopropanol	1.13c	60 min.	1.18b	1/8	1.13c

Analysis of the global means for the type of solvent showed that the three types of solvents studied were significantly different from each other when analyzed by the ultrasound and shaker techniques. Acetone was the best solvent, as it presented a higher global mean. In the case of the soxhlet extraction, acetone and isopropanol did not differ. This was because the atoms with lower electro-negativity in molecules made up of atoms with different electro-negativities were partially positively charged, and the atoms with greater electro-negativity were partially negatively charged.

Table 7. Global means of the factors studied in the oil extraction from passion fruit seeds by the shaker technique.

Solvent		Extraction time		Solute/solvent ratio	
Acetone	2.17a	4 hrs	1.79a	1/4	1.95a
Ethanol	1.73b	8hrs	1.60a,b	1/6	1.46b
Isopropanol	0.958c	16 hrs	1.45b	1/8	1.45b

Table 8. Global means of the factors studied in the extraction of oil from passion fruit seeds by the soxhlet technique.

Solvent		Extraction time	
Acetone	15.12a	4h	14.07a
Ethanol	15.03b	8h	15.12a
Isopropanol	13.95a	16h	14.64a
		24h	14.97a

As a result, the bonds were polarized and the dipole moment increased, which in turn affected the way the molecule interacted with the other molecules. Since acetone has a greater dipole moment, it also has a carbon chain around itself with a greater positive charge that is more apolar when compared to ethanol and isopropanol.

The evaluation of the global means of extraction time shows that the highest values were obtained for the shortest extraction times by the shaker and ultrasound techniques. In the case of the soxhlet extraction, the times were equal at 5% probability. The short extraction times contradicted the theories on the extraction processes (COULSON; RICHARDSON, 1976 SCHWARTZBERG, 1987) which stated that a longer contact time allowed the extraction of more solute. As the extraction proceeded, the extraction velocity decreased because the concentration gradient of the solute in the solvent decreased and the viscosity of the solvent increased due to the large quantity of solute. In their studies of cholesterol extraction from dehydrated yoke with acetone, Gomes and Borges (2001) found that the contact time did not significantly influence the extraction yield, a fact attributed mainly to the large contact surface area.

When the global means of the seed/solvent ratio for the ultrasound technique were examined, 5% level differences were found for the three fractions studied. The shaker extraction did not present any significant differences between ratios 1:6 and 1:8. These two extraction techniques provided the greatest global yield means for a 1:4 ratio. The opposite behavior is reported in the literature, which states that reduction of the seed/solvent ratio (that is, a greater availability of solvent) provides a greater extraction of the solute owing to a higher concentration gradient between the phases.

The comparison of the three techniques shows that the soxhlet extraction provided the greatest yield. This fact may be explained because extractions were conducted above the boiling point of the solvents. A rise in the temperature increases the diffusion coefficient of the solute and consequently its solubility. It may also occur because this technique uses practically pure solvent in each looping which makes the mass transfer easier.

Conclusion

The variables that exert greater influence on oil extraction yield from passion fruit oil were extraction time and the seed/solvent ratio for the three techniques studied, coupled to the type of solvent for the ultrasound and shaker techniques.

Higher global means of oil extraction from passion fruit seeds were obtained in the following conditions: (i) ultrasound extraction with acetone as a solvent; assay duration 15 min; seed/solvent ratio of 1:4; (ii) shaker extraction with acetone as a solvent; extraction time 4 hour; seed/solvent ratio of 1:4; (iii) soxhlet extraction with acetone as a solvent; extraction time 4 hour. In this last case, the shorter extraction time chosen is justified by the energy savings and operation ease.

The comparison of the three techniques showed that the soxhlet technique had the highest yields and extracted 65% of the total oil present in the initial matrix.

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