OPTIMIZATION OF THE ULTRASOUND-ASSISTED EXTRACTION OF CITRIC ACID FROM CITRUS PEELS

Filipa A. Fernandes[1,2], Sandrina A. Heleno[1*], Márcio Carocho[1], José Pinela[1], Miguel A. Prieto[2], Isabel C.F.R. Ferreira[1], Lillian Barros[1*]

[1] Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal

[2] Grupo de Nutrición y Bromatología, Departamento de Química Analítica y Alimentaria, Facultad de Ciencias de Ourense, Universidad de Vigo-Ourense Campus, E-32004 Ourense, Spain

ipb INSTITUTO POLITÉCNICO DE BRAGANÇA
Universidade de Vigo
CIMO Centro de Investigação de Montanha
BioChem Core
FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR
NORTE2020
PORTUGAL 2020
UNIÃO EUROPEIA

Introduction

Orange, lemon and lime are citrus fruits widely produced and consumed.

Consumed in fresh

Production of citrus juices

Which generates a large amount of industrial waste (peels, pomace and seeds)

Citrus peels

Molasses
Pectin
Limonene

→ Used mainly for the manufacture of cattle feed

Amino acids
Dietary fibers
Organic acids
Vitamins

→ Valorization of citrus by-products

Introduction

Currently, there is a great interest in foods formulated with natural ingredients, making the development of healthier foods a hot topic of the food research.

Organic acids

- Preservative capacity
- Found in natural matrices
- Recognized as safe in the food industry

Citric acid

Strong potential to be used as a preservative in the food industry

Objectives

Optimize the ultrasound-assisted extraction (UAE) of **citric acid** from citrus peels using the response surface methodology (RSM).

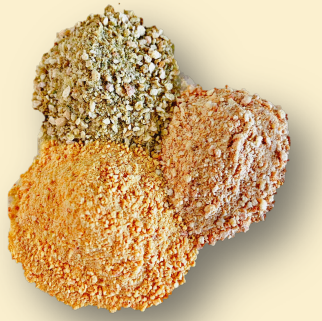
Valorization of citrus biowaste by recycling it into bio-based ingredients.

Methodology

Samples

Citrus peels

Lyophilized and reduced to a fine powder (20 mesh).



Experimental Design for Extraction Process Optimization

A central composite rotatable design (CCRD) combining five-level of the independent variables

X_1 - time, 2–45 min
X_2 - ultrasonic power, 50–500 W
X_3 - ethanol proportion, 0–100%, *v*/*v*

The Design-Expert software (Version 11) was used to generate the **20 experimental points** of the RCCD design.

These designs included
8 factorial points
6 axial or star points
6 replicated centre points

The 20 experimental runs were randomized to minimize the effects of unexpected variability in the observed responses.

Methodology

Ultrasound-Assisted Extraction

Citrus peel samples (~1 g) → 50 mL of solvent (ethanol/water mixtures)

Extractions were performed at 20 g/L at room temperature

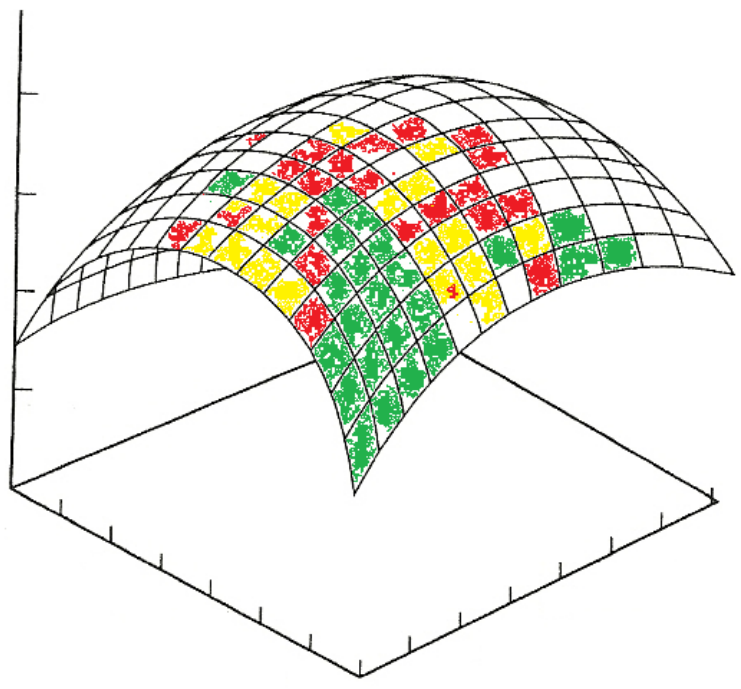
Chromatographic Analysis of Citric Acid

Extract solutions (~1.5 mL) → Analyzed by ultra-fast liquid chromatography, coupled to a photodiode array detector (UFLC-PDA)

Methodology

Extraction Process Optimization by Response Surface Methodology

The **citric acid** content was the **dependent variable** used in the extraction process optimization.



The response surface models were fitted using the following second-order polynomial equation:

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{\substack{i=1 \\ j>1}}^{n=1} \sum_{j=2}^{n} b_{ij} X_i X_j + \sum_{i=1}^{n} b_{ii} X_i^2$$

Eq. (1)

Results

The response data were fitted to the Eq. (1) polynomial model

Run	Experimental Design Matrix			Experimental Responses		
	Time	Power	Solvent	Citric acid content (g/100 g dry peel)		
	min	W	% (v/v)	Orange peel	Lime peel	Lemon peel
1	11(-1)	142(-1)	20(-1)	4.39	1.98	4.74
2	36(+1)	142(-1)	20(-1)	5.71	2.36	5.05
3	11(-1)	409(+1)	20(-1)	5.52	2.71	5.90
4	36(+1)	409(+1)	20(-1)	4.63	2.22	5.96
5	11(-1)	142(-1)	80(+1)	1.51	0	0
6	36(+1)	142(-1)	80(+1)	2.80	0	0
7	11(-1)	409(+1)	80(+1)	2.52	0	0
8	36(+1)	409(+1)	80(+1)	2.52	0	0
9	2(-1.68)	275(0)	50(0)	2.68	2.21	0
10	45(+1.68)	275(0)	50(0)	3.29	2.26	0
11	24(0)	51(-1.68)	50(0)	2.86	0.60	0
12	24(0)	500(+1.68)	50(0)	3.93	0	0
13	24(0)	275(0)	0(-1.68)	6.06	2.46	0
14	24(0)	275(0)	100(+1.68)	1.00	0	0
15	24(0)	275(0)	50(0)	3.20	0.82	0
16	24(0)	275(0)	50(0)	3.60	0.61	0
17	24(0)	275(0)	50(0)	3.86	0.36	0
18	24(0)	275(0)	50(0)	3.58	0.34	0
19	24(0)	275(0)	50(0)	3.69	0.32	0
20	24(0)	275(0)	50(0)	3.72	0.21	0

For lemon peels, citric acid was not detected in most of the runs, so it was not possible to construct a predictive model.

Results

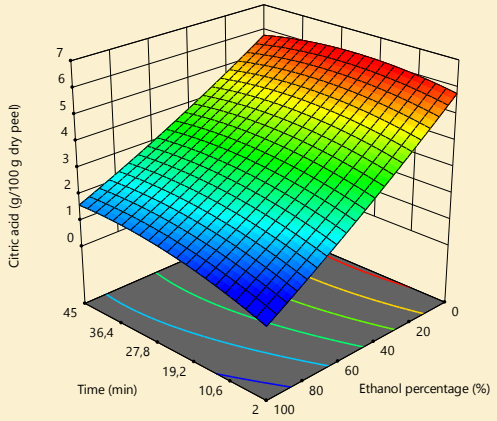
Results of ANOVA and regression analyses

Effect		Orange Peel	Lime Peel
Intercept	b_0	3.55±0.07	0.4±0.1
Linear effects	b_1	0.20±0.08	*ns*
	b_2	0.19±0.08	*ns*
	b_3	-1.42±0.08	-0.98±0.08
Quadratic effects	b_{11}	*ns*	0.61±0.08
	b_{22}	*ns*	*ns*
	b_{33}	*ns*	0.26±0.08
Interactive effects	b_{12}	-0.4±0.1	*ns*
	b_{13}	*ns*	*ns*
	b_{23}	*ns*	*ns*
Statistics			
Model F-value		69.48	48.68
Lack of Fit		*ns*	*ns*
R^2		0.9488	0.9285
R^2_{adj}		0.9351	0.9094
Ad. Precision		29.02	21.04

R^2: coefficient of determination; R^2_{ajd}: adjusted coefficient of determination; Ad. Precision: adequate precision.

Orange peel

- ✓ The extraction of organic acid was affected mostly through the negative linear effects of the ethanol proportion,



which means that by increasing the ethanol proportion, decreases the amount of citric acid extracted.

Results

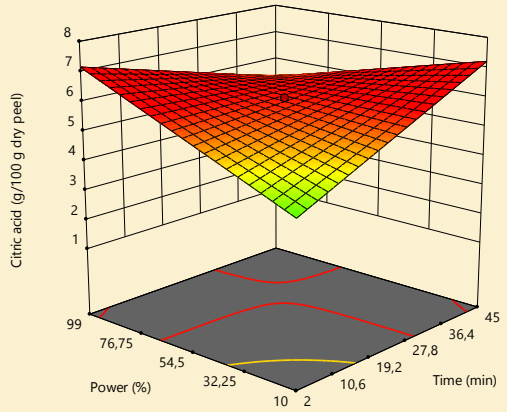
Results of ANOVA and regression analyses

Effect		Orange Peel	Lime Peel
Intercept	b_0	3.55±0.07	0.4±0.1
Linear effects	b_1	0.20±0.08	*ns*
	b_2	0.19±0.08	*ns*
	b_3	-1.42±0.08	-0.98±0.08
Quadratic effects	b_{11}	*ns*	0.61±0.08
	b_{22}	*ns*	*ns*
	b_{33}	*ns*	0.26±0.08
Interactive effects	b_{12}	-0.4±0.1	*ns*
	b_{13}	*ns*	*ns*
	b_{23}	*ns*	*ns*
Statistics			
Model F-value		69.48	48.68
Lack of Fit		*ns*	*ns*
R^2		0.9488	0.9285
R^2_{adj}		0.9351	0.9094
Ad. Precision		29.02	21.04

R^2: coefficient of determination; R^2_{ajd}: adjusted coefficient of determination; Ad. Precision: adequate precision.

Orange peel

- ✓ Negative interactive effects between processing time and ultrasonic power were also noticed,



the extraction yield is higher when processing at high ultrasonic powers for reduced times or at low powers for longer times.

Results

Results of ANOVA and regression analyses

Effect		Orange Peel	Lime Peel
Intercept	b_0	3.55±0.07	0.4±0.1
Linear effects	b_1	0.20±0.08	*ns*
	b_2	0.19±0.08	*ns*
	b_3	-1.42±0.08	-0.98±0.08
Quadratic effects	b_{11}	*ns*	0.61±0.08
	b_{22}	*ns*	*ns*
	b_{33}	*ns*	0.26±0.08
Interactive effects	b_{12}	-0.4±0.1	*ns*
	b_{13}	*ns*	*ns*
	b_{23}	*ns*	*ns*
Statistics			
Model F-value		69.48	48.68
Lack of Fit		*ns*	*ns*
R^2		0.9488	0.9285
R^2_{adj}		0.9351	0.9094
Ad. Precision		29.02	21.04

R^2: coefficient of determination; R^2_{ajd}: adjusted coefficient of determination; Ad. Precision: adequate precision.

Lime peel

- ✓ The ethanol proportion also affected the extraction through negative linear effects.
- ✓ Quadratic effects were observed for this citrus by-product, induced by the extraction time followed by the ethanol proportion.
- ✓ No significant interaction effects occurred in this extraction process.

Results

Optimal processing conditions that maximize the extraction of citric acid from citrus peels and predicted responses.

	Optimal HAE Conditions			Optimum
	Time (min)	Power (W)	Solvent (%)	(g/100 g)
Orange peel	35.5	236.2 (46.8%)	0.0	6.2±0.2
Lime peel	5.8	225.9 (44.7%)	9.0	3.4±0.2

Conclusions

✓ The orange and lime peels proved to be a good source of citric acid.

Optimal processing conditions

medium ultrasonic power
medium-low time
low ethanol proportion

6.2 g of citric acid per 100 g of dry orange peel

3.4 g of citric acid per 100 g of dry lime peel

✓ For lemon peels, citric acid was not detected in most of the runs of the experimental design, so it was not possible to construct a predictive model.

The present work contributes to the valorization of citrus by-products through their recycling into a natural ingredient.

Acknowledgements

ipb INSTITUTO POLITÉCNICO DE BRAGANÇA

Universidade de Vigo

CIMO Centro de Investigação de Montanha

BioChemCore

FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

NORTE2020 PORTUGAL 2020 UNIÃO EUROPEIA

Dra Lillian Barros

Dr Miguel Angel Prieto Lage