CEFood & Congress

11th Central European Congress on Food and Nutrition

"Food, technology and nutrition for healthy people in a healthy environment"

Insights in advanced extraction techniques used for bioactive compounds isolation

Dr **Stela Jokić,** full prof.

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Mail: stela.jokic@ptfos.hr

Slovenia, Čatež ob Savi, 30. September 2022





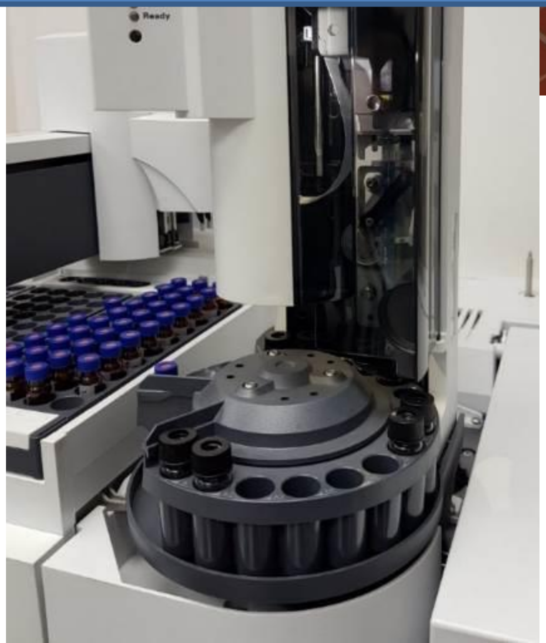

JOSIĆ
CABERNET FRANC
MERLOT

NEW LABORATORIES



NEW EQUIPMENT





INNOVATIVE
EXTRACTION
TECHNIQUES

Why green extraction techniques?

Ultrasound assisted extraction (UAE)

Shorter time

Microwave assisted extraction (MAE)

High voltage electrical discharge extraction

Better quality of extract

Lower solvent consumption

Higher yield

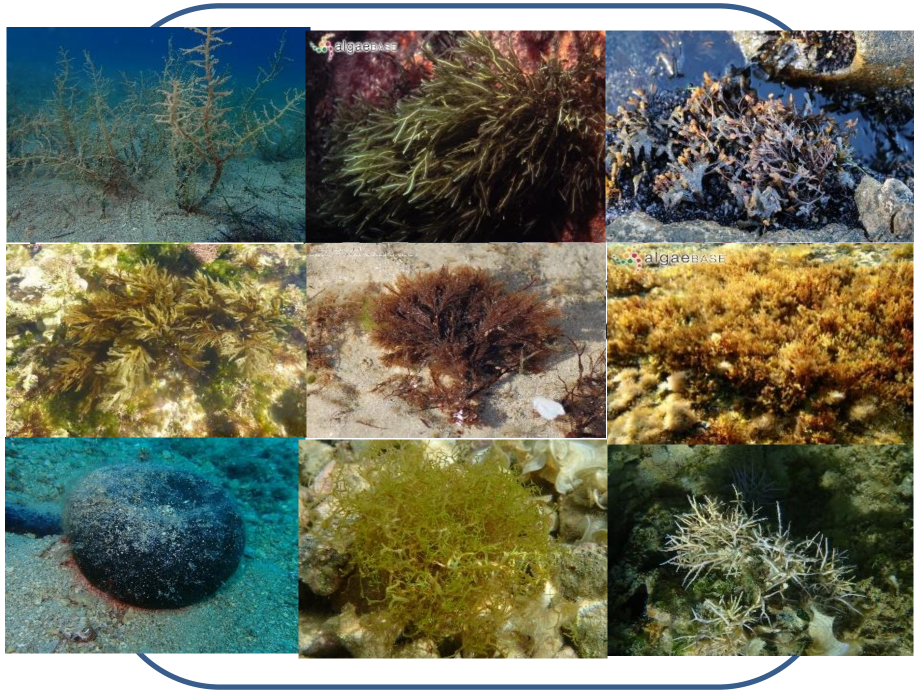
Extraction with deep eutectic solvents

Subcritical water extraction

Efficient energy use

Lower temperatures

Supercritical CO_2 (SCO_2) extraction



SPOJ ZNANSTVENE IZVRSNOSTI PREHRAMBENO-TEHNOLOŠKOGA FAKULTETA OSIJEK I DOBRE INDUSTRIJSKE PRAKSE

U suradnji PTFOS-a i tvrtke Apimel proizvedeni sirupi Bronhimel

Lidija GREGAČEVIĆ, Marija BANOŽIĆ

Pozitivni trendovi povezivanja akademske zajednice s gospodarstvom postali su sve aktualniji posljednjih nekoliko godina. U skladu s tim, Prehrambeno-tehnološki fakultet Osijek nastoji prilagoditi svoje programe tržištu rada, stoga otvara nove studijske programe kako bi obrazovali što kvalitetniju radnu snagu. Osim toga, sve je više projekata koji su nastali samoinicijativno ili kao rezultat potpore različitih programa financiranja, a koji naglasak stavljaju upravo na transfer znanja i tehnologije. Upravo jedan takav projekt rezultirao je suradnjom Prehrambeno-tehnološkog fakulteta Osijek i tvrtke Apimel d.o.o. koja ima dugogodišnju tradiciju (od 1994. godine) proizvodnje i prerade meda i drugih pčelinjih proizvoda. Sjedište je tvrtke u Višnjevcu, a proizvodni je pogon smješten u Bizovcu. Platforma nastala tom suradnjom okupila je tim stručnjaka pod vodstvom prof. dr. sc. Stele Jokić sa suradnicima iz tvrtke Apimel čija je nova ideja bila proizvodnja bronhijalnih sirupa. Razlozi su odabira toga proizvoda višestruki, poput općeg nedostatka visokokvalitetnih dodataka prehrani na bazi meda u Hrvatskoj i u regiji te visoke cijene koju takvi proizvodi postižu na tržištu. Pritom mali proizvođači nemaju odgovarajuću opremu ni znanja pomoću kojih bi implementirali svoje sirovine u takve proizvode. S druge strane PTFOS posjeduje visokosofisticiranu opremu, pilot-postrojenja, analitičku opremu kao i ljudske resurse kojima je moguće razviti nove recepture, riješiti tehnološke probleme te takve gotove projekte dati na raspolaganje malim proizvođačima koji bi na temelju njih proizvodili visokovrijedne i atraktivne dodatke prehrani te ih plasirali na tržište. Suradnja PTFOS-a i tvrtke Apimel urodila je plodom ove godine. Na hrvatskom tržištu našao se Apimel Bronhimel sirup za odrasle i Apimel Bronhimel Junior za djecu, visokokvalitetni proizvodi koji su prvi put predstavljeni u svibnju 2019. na sajmu Vitafoods Europe u Ženevi. Od same ideje do realizacije i puštanja u proizvodnju bilo je potrebno mnogo truda i rada. PTFOS i Apimel nastavljaju suradnju i planiraju razvoj novih proizvoda.

NISKE OTKUPNE CIJENE SIROVINA

Primarni proizvođači (u prvom redu uzgajivači pčela i uzgajivači ljekovitog bilja) često se susreću s vrlo niskim otkupnim cijenama svojih sirovina. Neke procjene navode da se samo 10 % ljekovitoga bilja zadrži na hrvatskom tržištu, a ostatak se izvozi kao sirovina ili poluproizvodi. Nasuprot tomu, cijene gotovih proizvoda, dodataka prehrani i kozmetičkih pripravaka dosežu visoke iznose, i po nekoliko desetaka puta veće od cijene sirovina.

"The science of today is the technology of tomorrow. „

- Edward Teller

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DOI: 10.17559/TV-20150311100920

SUPERCRITICAL CO_2 EXTRACTION PILOT PLANT DESIGN – TOWARDS IoT INTEGRATION

Goran Horvat, Krunoslav Aladić, Stela Jokić

Prelin

The interest in high pressure technology during last decades increased intensively. Supercritical Fluid Extraction (SFE) is a process importance as an alternative to conventional separation processes. SFE uses environmentally friendly CO_2 as the extracting agent in the its relatively low critical pressure (7,38 MPa), its low critical temperature (304 K), its non-dangerous character and low cost. Durir necessary to use high pressures in the procedure. The extractor vessel (pressure vessel) is the most important equipment of the supercritical conditions need to be established and the extraction occurs. Also other devices (separator vessel, heat exchangers, valves to be involved in the process due to used high pressures. Safety is the most important factor while dealing with SFE systems and equipment with full safety of process is very hard task. Therefore, to achieve the high desired safety level, a reliable control system n the control system and data communication segment. Various different process parameters such as CO_2 mass flow rate, extrac temperatures affect the extraction process and the quality of the extract; hence these parameters need to be precisely controlled and m extraction. A design of one supercritical CO_2 extraction laboratory-pilot plant and development of a remote control and its supervision in this paper. The developed SFE system (mechanical and electrical components) was compared with the existing commercial sy advantages over the existing systems are presented. By enabling remote control and supervision the classical process control is joined Internet of Things (IoT), where the information becomes omnipresent in the vast realm of Internet.

Keywords: *embedded system; process control; supercritical fluid extraction; system construction.*

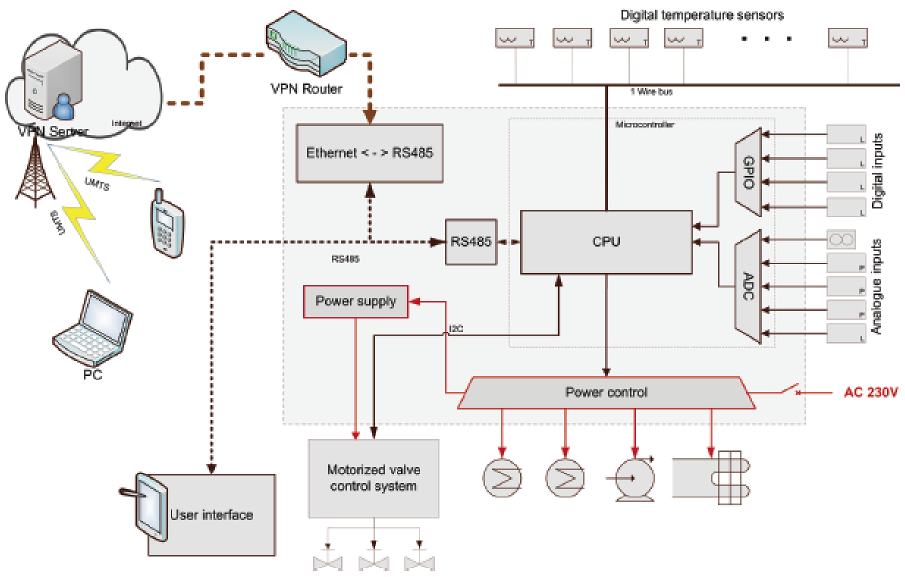


Figure 2 Block diagram of the supporting electronic system

Chapter 5

Design of SFE System Using a Holistic Approach: Problems and Challenges

Stela Jokić[1], Goran Horvat[2] and Krunoslav Aladić[3]*
[1]University of Josip Juraj Strossmayer in Osijek, Faculty of Food Technology Osijek, Osijek, Croatia
[2]University of Josip Juraj Strossmayer in Osijek, Faculty of Electrical Engineering, Osijek, Croatia
[3]Croatian Veterinary Institute, Branch, Veterinary Institute Vinkovci, Vinkovci, Croatia

Abstract

Supercritical fluid extraction (SFE) emerged in the last few decades as a promising green technology and a good alternative in food and natural products processing. SFE has proven to be technically and economically feasible with a lot of advantages over the traditional extraction methods with organic solvents. By using carbon dioxide (CO_2) as solvent the SFE becomes environmentally friendly process resulting in extracts free of toxic solvents. Today over few hundred commercial plants in the world are using the process of SFE. SFE technology continuously increases its application in different fields and operating extraction conditions have the most influence on the performance of such processes.

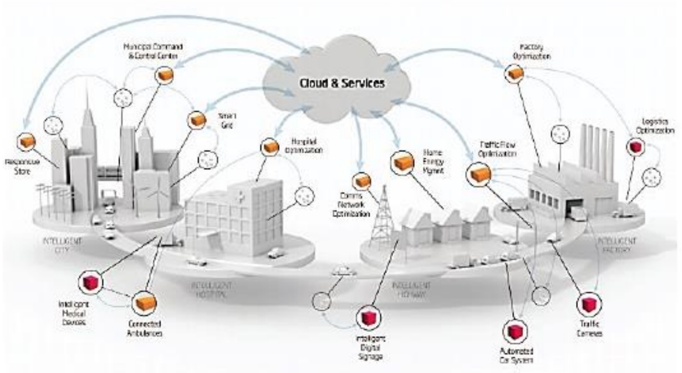
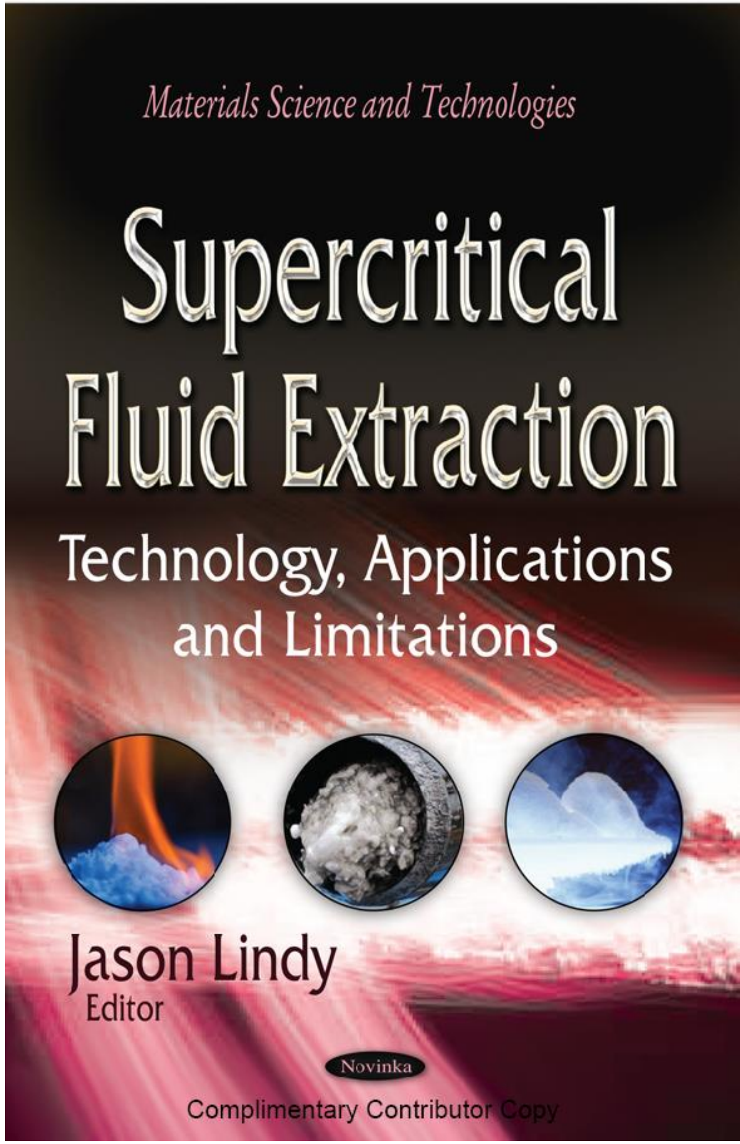
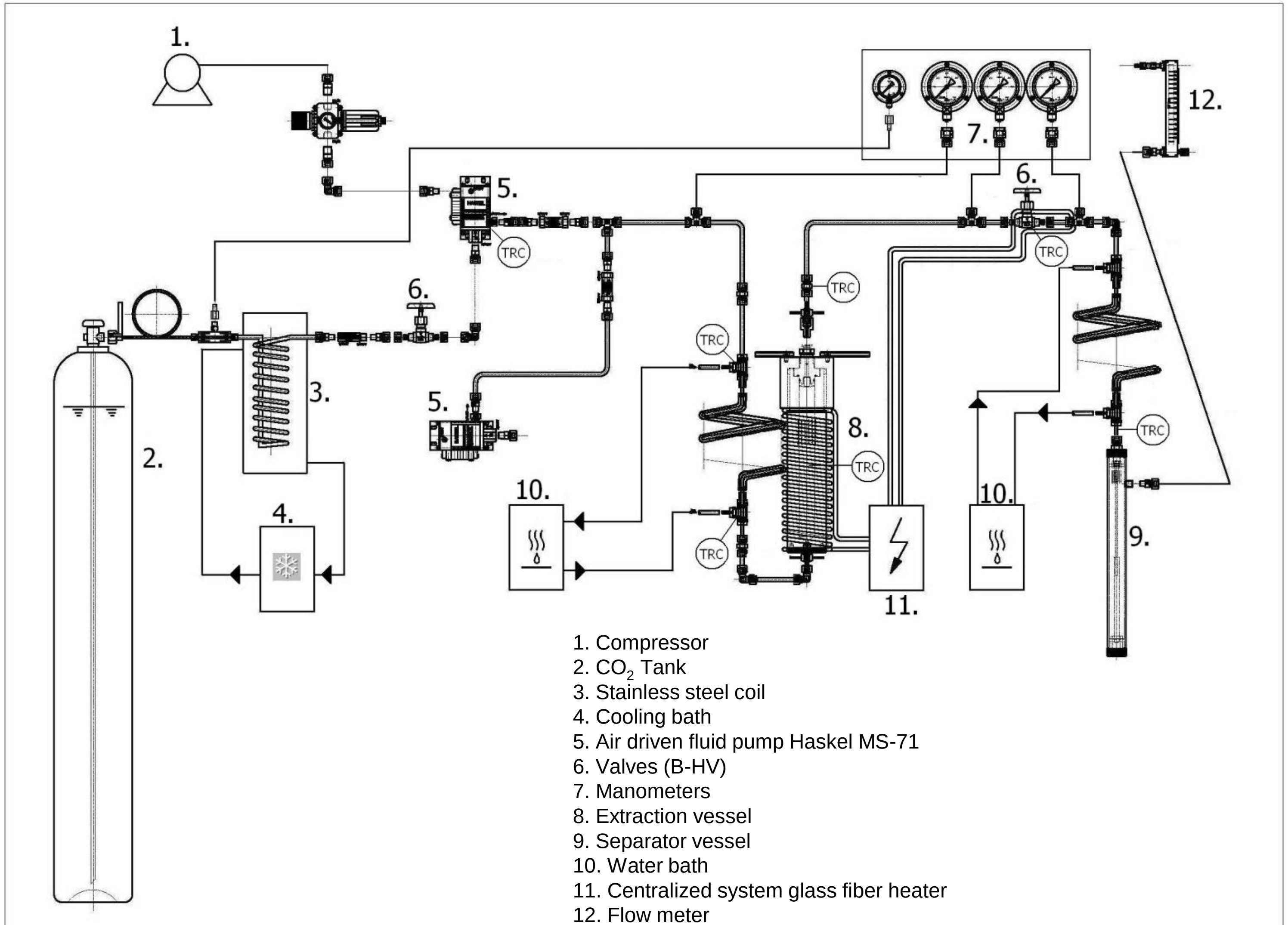


Figure 7 The concept of Internet of Things



CEFood & Congress

SUPERCRITICAL CO_2 EXTRACTION



1. Compressor
2. CO_2 Tank
3. Stainless steel coil
4. Cooling bath
5. Air driven fluid pump Haskel MS-71
6. Valves (B-HV)
7. Manometers
8. Extraction vessel
9. Separator vessel
10. Water bath
11. Centralized system glass fiber heater
12. Flow meter

Table 2 – Advantages and disadvantages of extraction processes.

Extraction technique	Advantages	Drawbacks
SC-CO_2 extraction	• Gentle treatment of heat-sensitive materials (its moderate critical temperature of 31.2 °C is a key issue for the preservation of bioactive compounds in extracts) • Solvent — free products • CO_2 as solvent does not cause environmental problems and is physiologically harmless, germicidal and not flammable. • CO_2 is a Generally recognized as safe (GRAS) solvent • CO_2 is inexpensive solvent • Due to low viscosity and relatively high diffusivity, supercritical CO_2 have enhanced transport properties than liquids, can diffuse easily through solid materials and can therefore give faster extraction rates. • Fragrances and aromas remain unchanged • Selective extraction and fractionated separation • Pure extracts by means of few process steps • Changeable solvating power (possibility of modifying the density of the fluid by changing its pressure and/or temperature) • High solubility for non/low polar substances (for example volatile compounds) • possibility of direct coupling with analytical chromatographic techniques such as gas chromatography (GC) or supercritical fluid chromatography (SFC)	• High pressures • High investment cost (requires a careful business plan contemplating the cost/effective analysis of the desired compounds to be extracted) • Phase equilibrium of the solvent/solute system is complex, making design of extraction conditions difficult • High polar substances (sugars, amino acids, inorganic salts, proteins, . . .) are insoluble • The use of high pressures leads to capital costs for plant, and operating costs may also be high so the number of commercial processes utilizing supercritical fluid extraction is relatively small, due mainly to the existence of more economical processes.

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Food and Bioproducts Processing
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IChemE

New perspective in extraction of plant biologically active compounds by green solvents

Marina Cvjetko Bubalo[a], Senka Vidović[b], Ivana Radojčić Redovniković[a,], Stela Jokić[c]*
[a] University of Zagreb, Faculty of Food Technology and Biotechnology, 10000 Zagreb, Croatia
[b] University of Novi Sad, Faculty of Technology, Bulevar Cara Lazara 1, 21000 Novi Sad, Serbia
[c] University of Josip Juraj Strossmayer in Osijek, Faculty of Food Technology Osijek, Franje Kuhaca 20, 31000 Osijek, Croatia

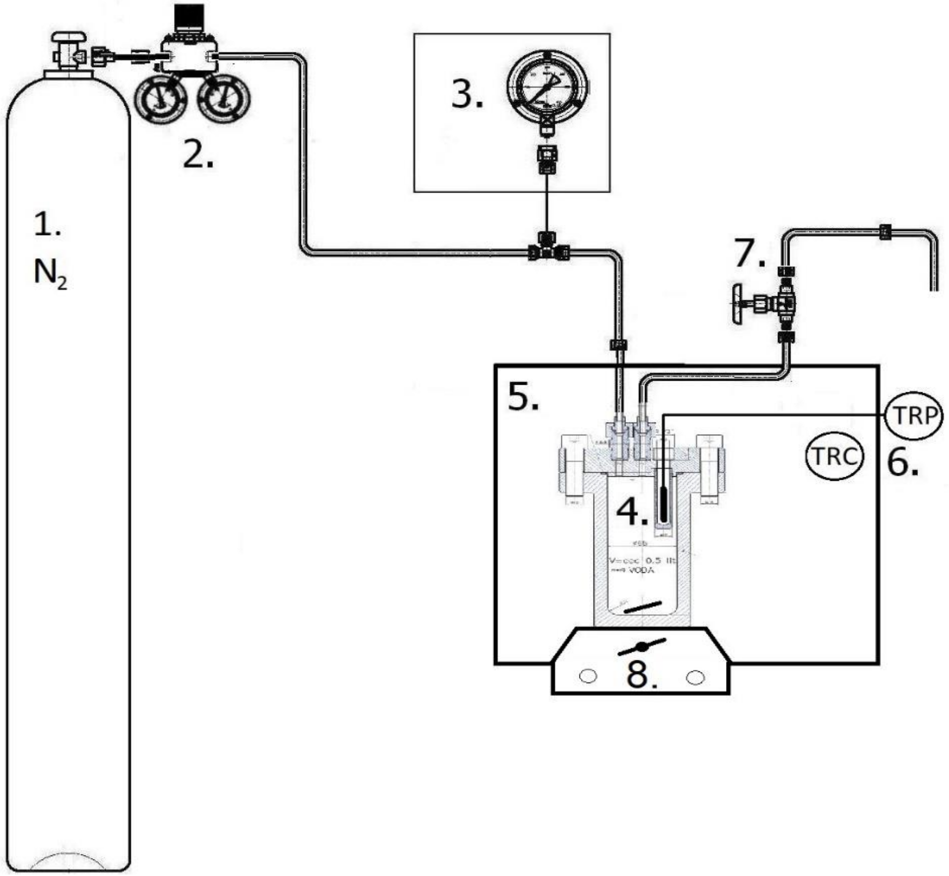
sCO_2 EXTRACTS

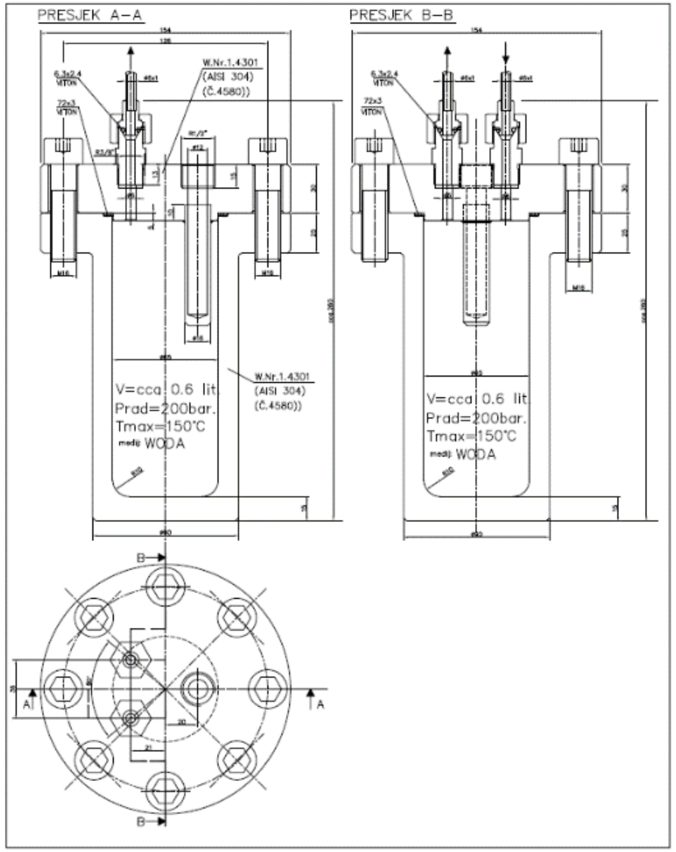

Sustainable Chemistry and Pharmacy
Volume 27, June 2022, 100688

Supercritical CO_2 extracts in cosmetic industry: Current status and future perspectives

Marina Zorić [a], Marija Banožić [b], Krunoslav Aladić [b], Sanda Vladimir-Knežević [c], Stela Jokić [b]

SUBCRITICAL WATER EXTRACTION





(1) N_2 tank (2) Regulator N_2 20/5 MPa (3) Manometer 0-20 MPa (4) Extraction vessel 20 MPa, 200°C (5) Oven 20-300°C (6) TRC - Temperature regulator controller; TRP - Temperature regulated probe (7) High pressure needle valves (8) Magnetic stirrer

Everything starts with a good idea……

but also from raw material….

Application of innovative techniques of the extraction of bioactive components from by-products of plant origin"

(2018-2023)

Principal Investigator: : prof. dr. Stela Jokić

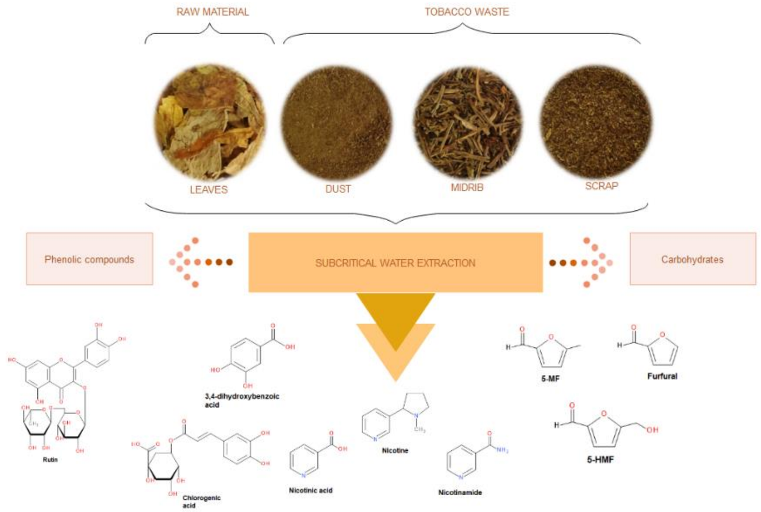
(Budget: ***1.607.708,72 HRK****)*

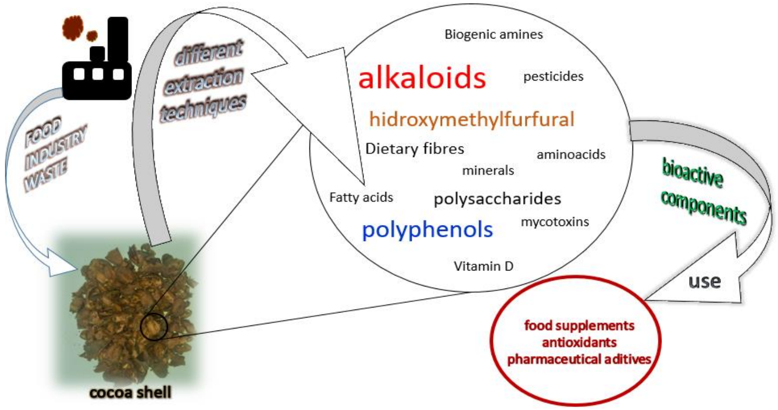
CITRUS PEEL

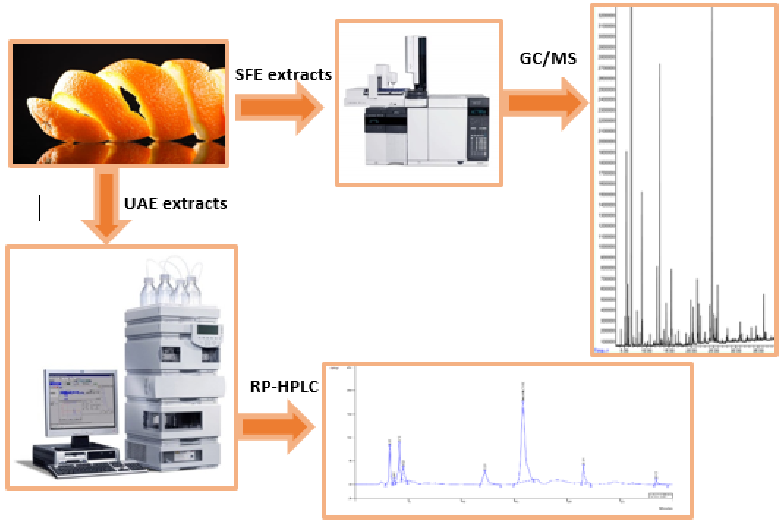
COCOA SHELL

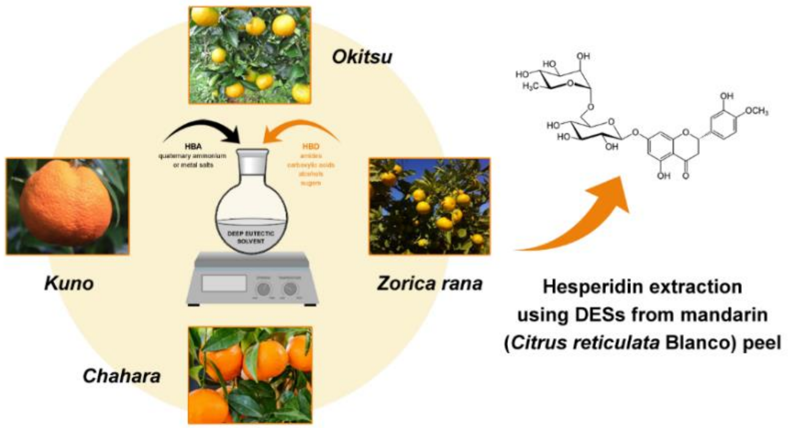
TOBBACO WASTE

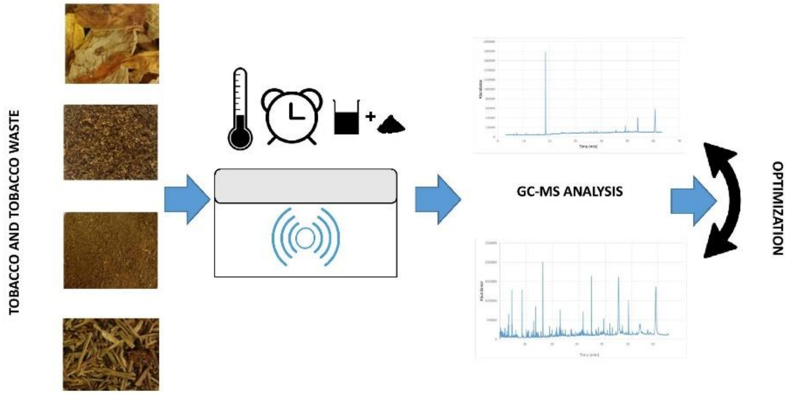
INNOVATIVE EXTRACTION TECHNIQUES

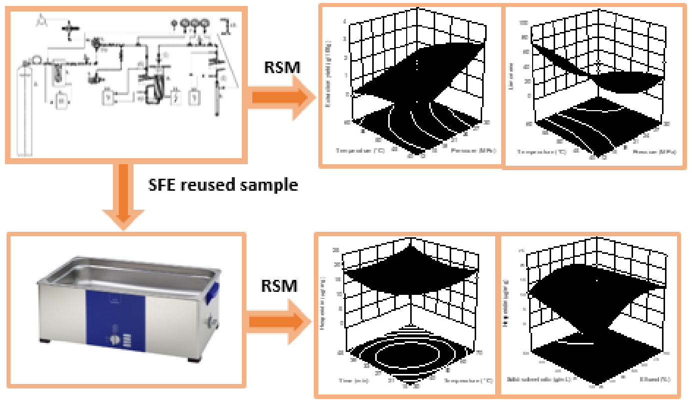




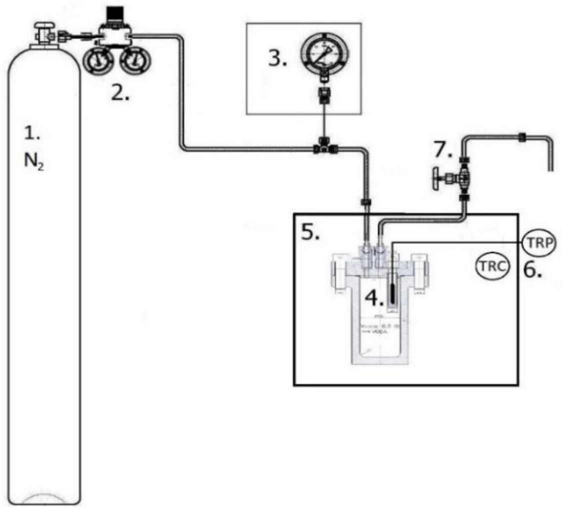






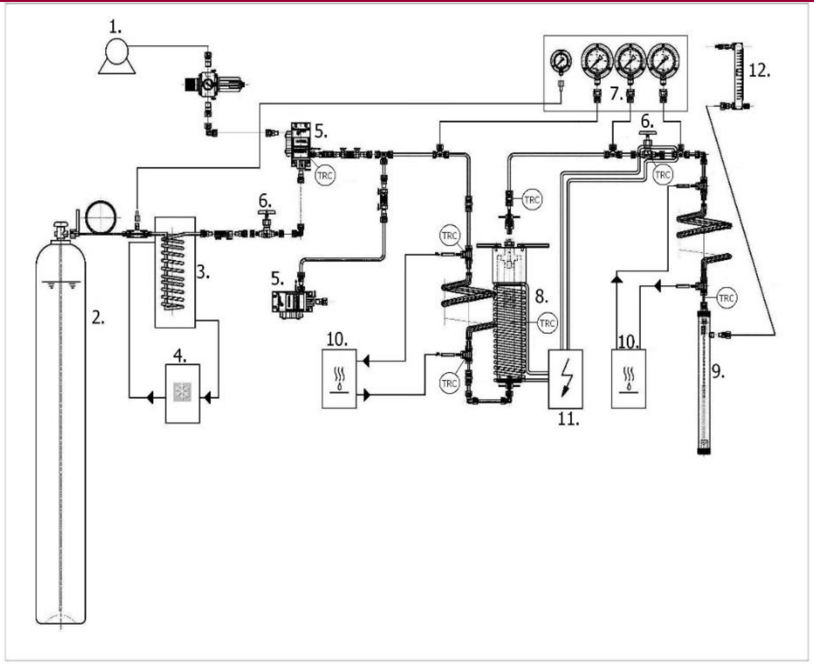


ULTRASOUND-ASSISTED EXTRACTION

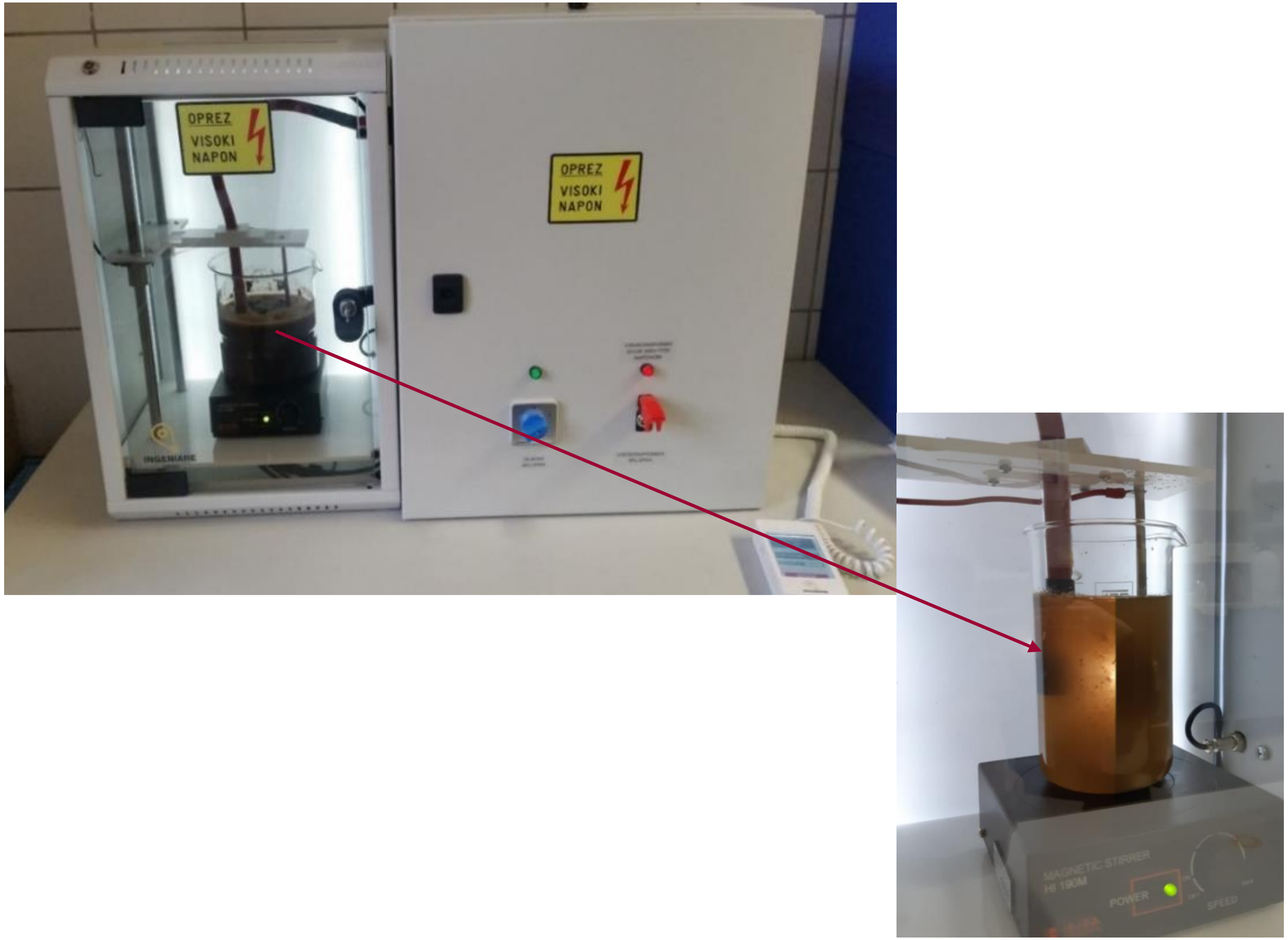


SUBCRITICAL WATER EXTRACTION

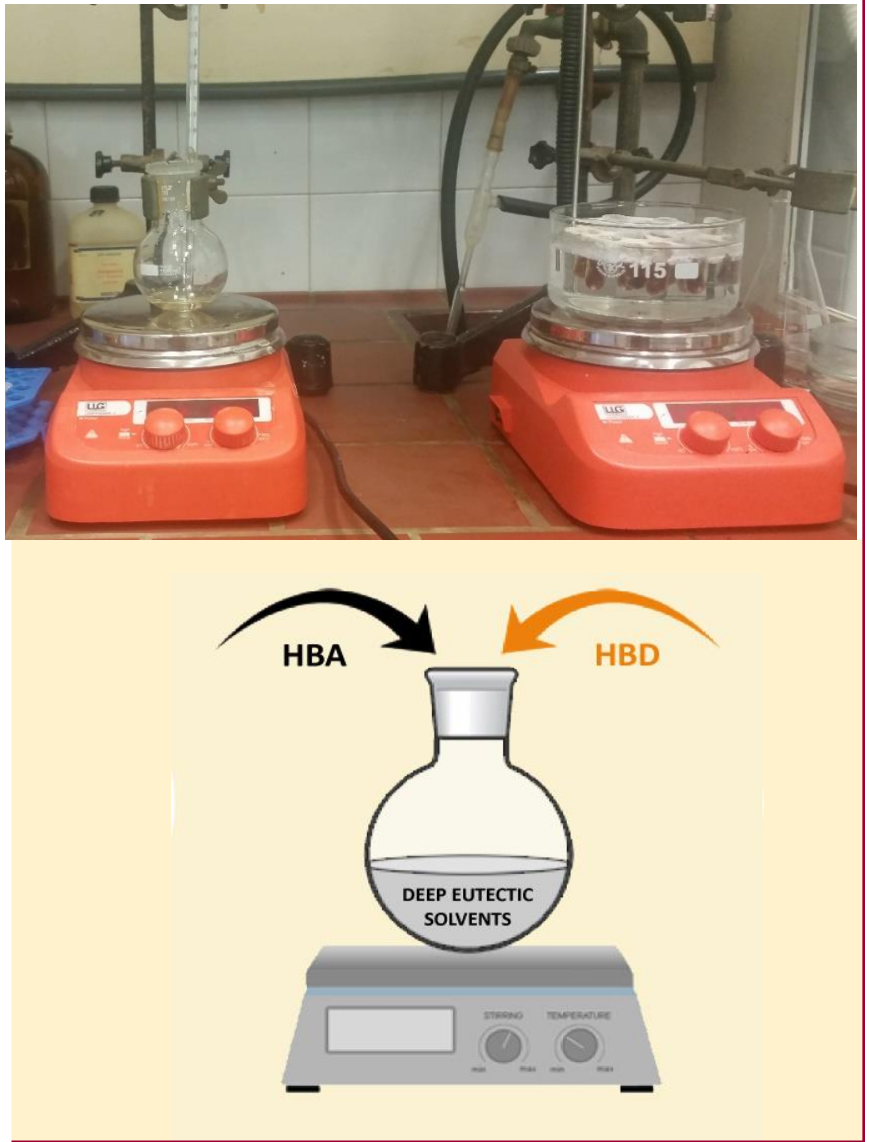
MICROWAVE-ASSISTED EXTRACTION



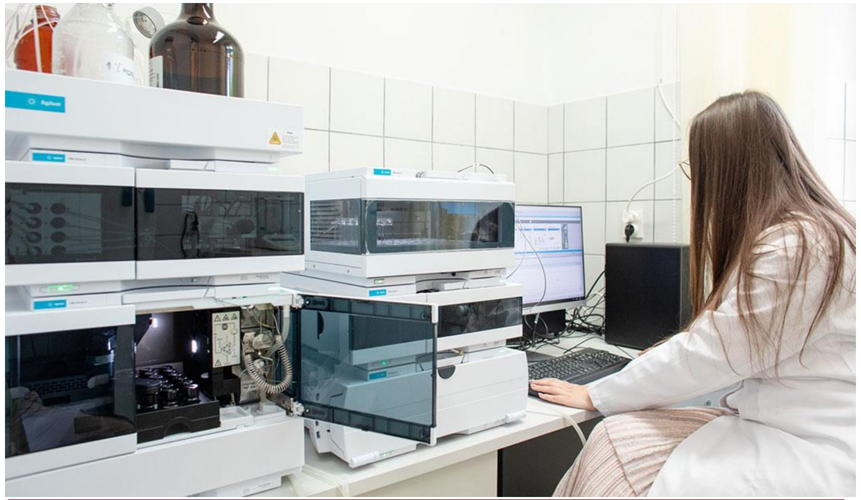
SUPERCRITICAL CO2 EXTRACTION



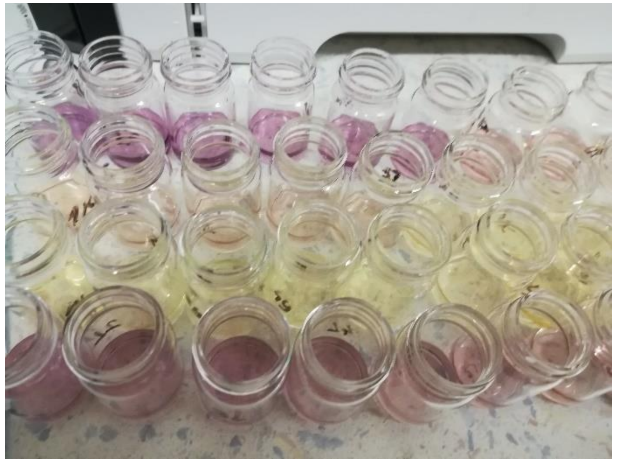
HIGH-VOLTAGE ELECTRIC DISCHARGE EXTRACTION

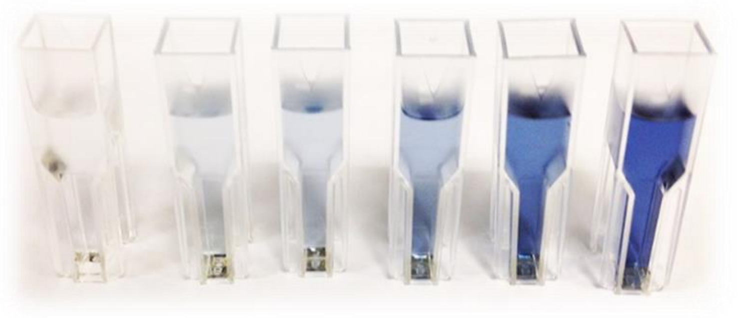


EXTRACTION USING DEEP EUTECTIC SOLVENTS (DES)

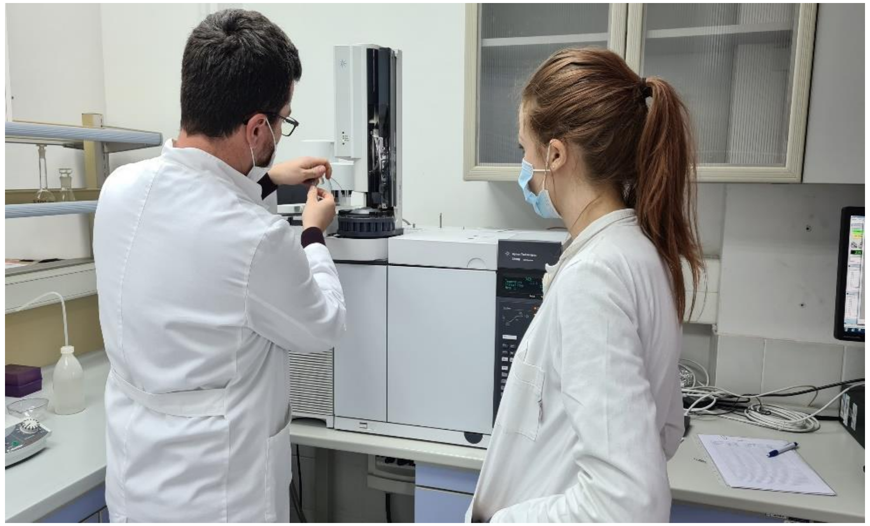


HIGH-PERFORMANCE
LIQUID CHROMATOGRAPHY (HPLC)

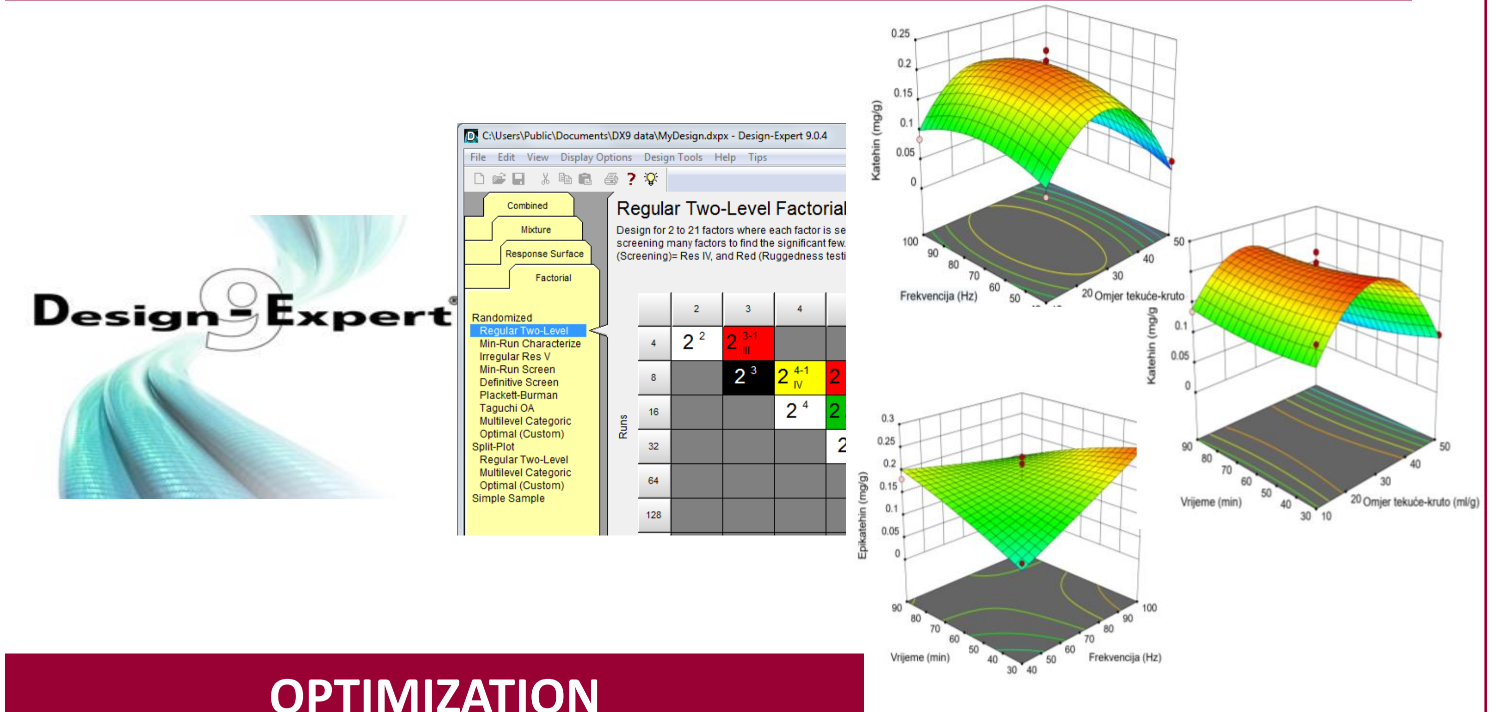




SPECTROPHOTOMETRIC METHODS



GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS)



OPTIMIZATION

SPRAY DRYING

FOOD REVIEWS INTERNATIONAL
https://doi.org/10.1080/87559129.2021.1938601
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Spray Drying as a Method of Choice for Obtaining High Quality Products from Food Wastes– A Review

Marija Banožić[a], Jelena Vladić[b], Ines Banjari[a], Darko Velić[a], Krunoslav Aladić[a], and Stela Jokić[a]

CEFood Congress

PROJECT RESULTS

hrzz Croatian Science Foundation

33 JOURNAL PUBLICATIONS

FOOD REVIEWS INTERNATIONAL
https://doi.org/10.1080/87559129.2021.1938601

Spray Drying as a Method of Choice for Obtaining High Quality Products from Food Wastes– A Review

Marija Banožić[a], Jelena Vladić[b], Ines Banjari[a], Darko Velić[a], Krunoslav Aladić[a], and Stela Jokić[a]

S. Jokić et al., High-Voltage Electric Discharge Extraction of Bioactive Compounds…, Chem. Biochem. Eng. Q., 33 (2) 271–280 (2019) 271

High-Voltage Electric Discharge Extraction of Bioactive Compounds from the Cocoa Bean Shell+

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S. Jokić,[a,*] N. Pavlović,[b] A. Jozinović,[a] Đ. Ačkar,[a] J. Babić,[a] and D. Šubarić[a]

COCOA ... Kernel Cake

by Jelena Čakarević [1], Senka Vidović [1], Jelena Vladić [1], Aleksandra Gavarić ... Stela Jokić [2,*], Nika Pavlović [3], Marijana Blažić [4] and Ljiljana Popović

Plum oil cake protein isolate: a potential source of bioactive peptides

Jelena C. Čakarević[1], Senka S. Vidović[1], Jelena Z. Vladić[1], Stela D. Jokić[2], Nika S. Pavlović[3], Ljiljana M. Popović*[1]

50 CONFERENCES

Subcritical Water Extraction Laboratory Plant Design and Application

...Jokić[1], S., Aladić[2], K., Šubarić[1*], D.

...Shell: A By-Product with Great Potential for ...e Application

by Jelena Panak Balentić [1], Đurđica Ačkar [1,*], Stela Jokić [1], Antun Jozinović [1], Jurislav Babić [1], Borislav Miličević [1], Drago Šubarić [1] and Nika Pavlović [2]

An Approach to Value Cocoa Bean By-Product Based on Subcritical Water Extraction and Spray Drying Using Different Carriers

by Stela Jokić [1,*], Nataša Nastić [2], Senka Vidović [2], Ivana Flanjak [1], Krunoslav Aladić [1] and Jelena Vladić [2,*]

Sustainable Green Procedure for ...traction of Hesperidin from Selected Croatian Mandarin Peels

by Stela Jokić [1], Silvija Šafranko [1,*], Martina Jakovljević [1], Filip Kolarević [1], Jurislav Babić [1] and Maja Molnar [1]

molecules

Carbohydrates—Key Players in Tobacco Aroma Formation and Quality Determination

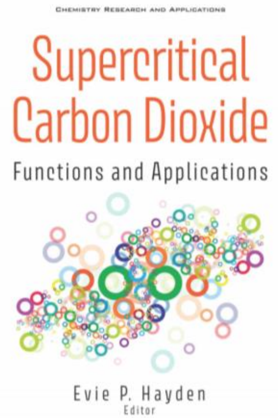
by Marija Banožić [1], Stela Jokić [1,*], Đurđica Ačkar [1], Marijana Blažić [2] and Drago Šubarić [1]

Original scientific paper

Green extraction techniques of bioactive ...

NIKA PAVLOVIĆ*[1], MARTINA JAKOVLJEVIĆ[2], MAJA MIŠKULIN[1], MAJA MOLNAR[2], ĐURĐICA AČKAR[2], STELA JOKIĆ[2]

7 BOOK CHAPTERS



Recent advances in extraction of bioactive compounds from tobacco industrial waste-a review

Marija Banožić, Jurislav Babić, Stela Jokić

Optimization of Ultrasound-Assisted Extraction of Some Bioactive Compounds from Tobacco Waste

by Marija Banožić, ... Jurislav Babić and ...

European Journal of Lipid Science and Technology

Research Article

Recovery of To...

Green Extraction Methods for Active Compounds from Food Waste—Cocoa Bean Shell

by Nika Pavlović [1], Stela Jokić [2], Martina Jakovljević [2], Marijana Blažić [3] and Maja Molnar [2,*]

Journal of the Science of Food and Agriculture

Research Article | Full Access

Volatile organic compounds of tobacco leaves *versus* waste (scrap, dust, and midrib): extraction and optimization

Marija Banožić, Krunoslav Aladić, Igor Jerković, Stela Jokić

3 DOCTORAL THESIS

RESULTS


foods

Article

Green Extraction Techniques for Obtaining Bioactive Compounds from Mandarin Peel (*Citrus unshiu* var. *Kuno*): Phytochemical Analysis and Process Optimization

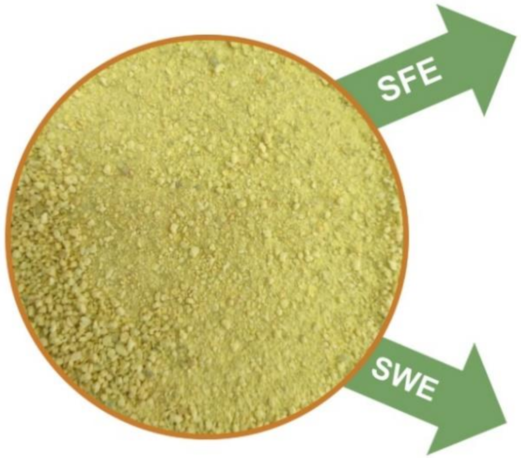
Silvija Šafranko [1], Ina Ćorković [1], Igor Jerković [2], Martina Jakovljević [1], Krunoslav Aladić [1], Drago Šubarić [1] and Stela Jokić [1,*]

Okitsu

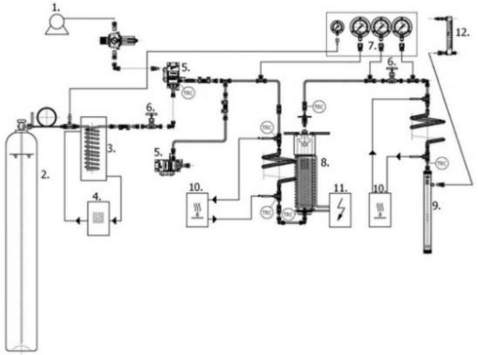
Kuno

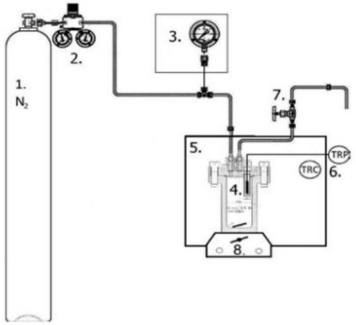
Chahara

Zorica rana

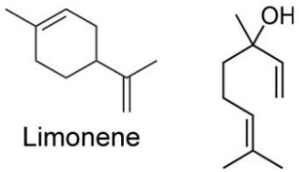


Mandarin peel
(*Citrus unshiu* var. *Kuno*)





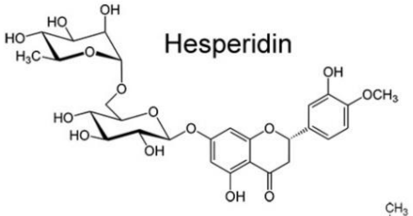
Volatile compounds



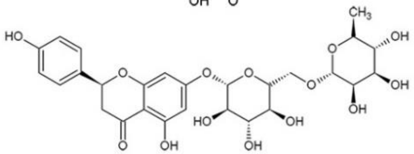
Limonene

Linalool

Bioflavonoids



Hesperidin



Narirutin

Aromatic profile

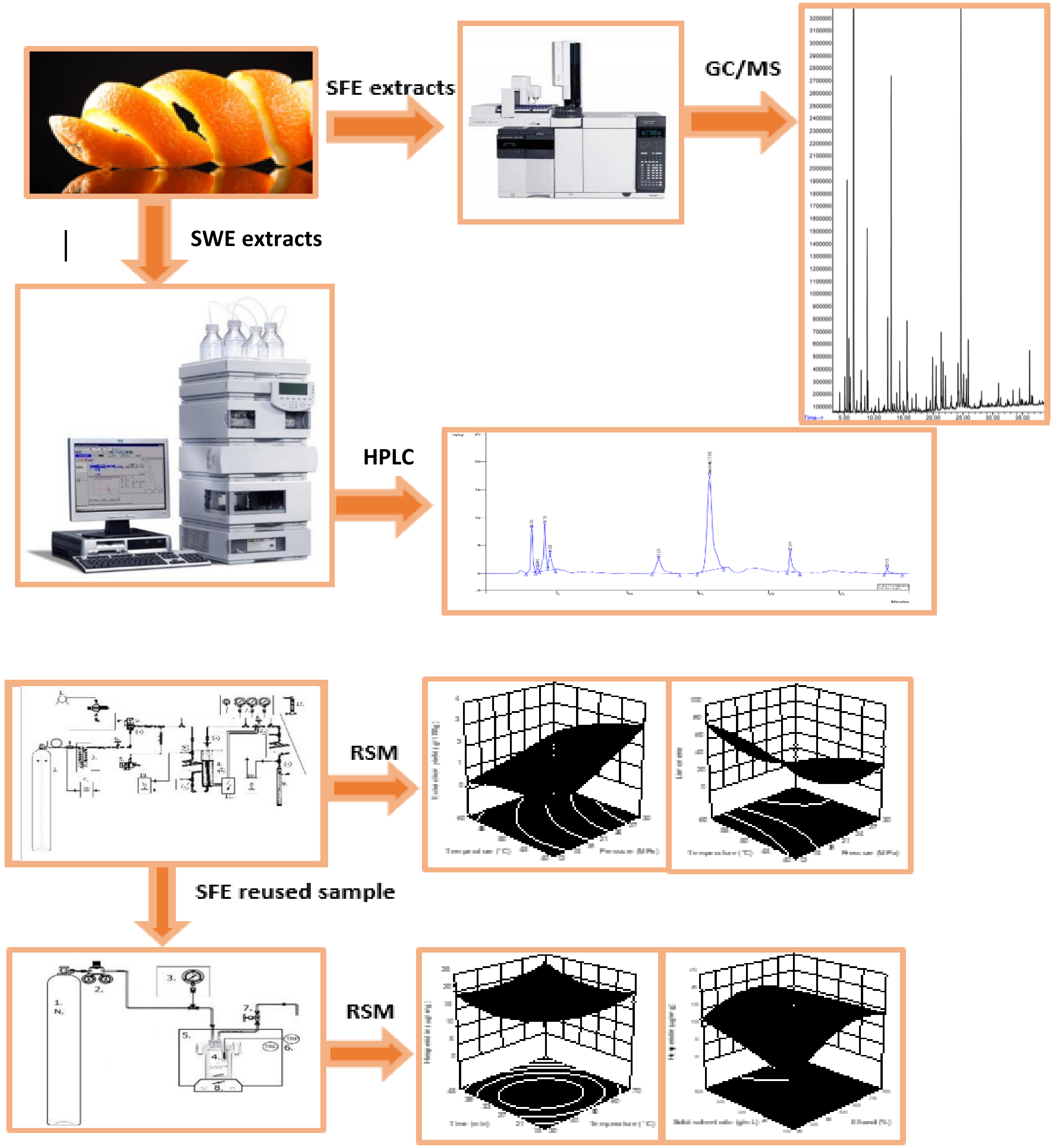
Bioflavonoids

Process optimization

Antioxidant activity

Total phenolic content

RESULTS



Compound	Rt	RI	Zorana		Kuno		Okica		Chanara	
			100 bar	300 bar	100 bar	300 bar	100 bar	300 bar	100 bar	300 bar
α-Thujene	4,082	932	-	-	0.1	0.1	-	-	-	-
α-Pinene	4,237	940	-	-	0.6	0.3	-	0.1	-	-
Sabinene	5,091	978	-	-	0.2	0.1	-	0.1	-	-
β-Pinene	5,191	982	0.1	-	0.4	0.3	0.1	0.1	-	-
β-Myrcene	5,478	992	0.6	0.4	2.3	1.9	0.5	1.0	0.1	0.1
Octanal	5,783	1003	-	-	0.1	0.1	0.1	0.1	-	-
Phellandrene	5,876	1007	-	-	0.1	0.1	-	-	-	-
p-Cymene	6,440	1028	1.2	1.1	0.1	0.1	0.5	0.9	0.3	0.1
Limonene	6,602	1034	37.2	35.1	66.8	66.6	35.4	52.8	11.7	3.5
trans-β-Ocymene	7,110	1051	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
γ-Terpinene	7,467	1062	3.9	4.4	8.4	8.5	5.0	6.6	1.3	1.0
cis-Sabinene hydrate	7,755	1071	0.1	0.1	0.1	0.1	0.1	0.1	-	-
α-Terpinolene	8,437	1089	0.4	0.4	0.6	0.6	0.4	0.6	0.2	0.1
Linalool	8,855	1100	3.4	4.3	1.6	1.7	3.0	2.6	4.3	2.2
Nonanal	8,891	1101	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Citronellal	10,793	1155	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Terpinen-4-ol	11,744	1179	0.2	0.3	0.1	0.1	0.2	0.2	0.3	0.2
α-Terpineol	12,286	1191	1.4	1.6	0.6	0.6	1.2	0.9	2.0	2.2
Decanal	12,864	1204	0.6	0.7	0.4	0.4	0.6	0.4	0.8	0.6
trans-Carveol	13,405	1219	-	-	-	-	0.1	-	-	-
Citronellol	13,809	1230	0.3	0.3	0.1	0.1	0.2	0.1	0.2	0.1
(Z)-Citral	14,283	1242	-	-	0.1	0.1	-	-	-	-
(E)-Citral	15,511	1271	-	-	0.1	0.1	-	-	-	-
Thymol	16,609	1295	0.2	0.4	-	-	-	0.3	-	-
Carvacrol	16,992	1304	0.7	0.9	0.1	0.1	0.1	0.1	0.4	0.6
Undecanal	17,023	1305	-	-	0.1	-	0.1	-	-	-
δ-Elemene	18,253	1337	0.5	0.5	0.2	0.2	0.5	0.3	0.8	0.6
Citronellyl acetate	18,982	1354	-	-	-	-	0.2	0.2	0.3	0.1
Neryl acetate	19,452	1365	0.4	0.4	0.1	0.1	0.2	0.2	0.4	0.4
α-Copaene	19,881	1375	1.3	1.4	0.5	0.6	1.2	0.9	1.7	1.1
Geranyl acetate	20,255	1384	0.6	0.6	0.2	0.2	0.9	0.6	1.1	1.1
β-Cubebene	20,419	1387	1.1	1.1	0.5	0.5	1.1	0.8	1.3	0.9
β-Elemene	20,518	1389	2.9	2.9	0.5	0.5	2.9	1.9	3.8	3.2
Dodecanal	21,254	1407	0.2	0.2	0.1	0.1	0.1	0.1	0.3	0.2
Limonen-10-yl acetate	21,349	1409	0.3	0.3	0.1	0.1	0.5	0.3	0.7	0.3
trans-Caryophyllene	21,572	1415	1.2	1.2	0.3	0.3	1.1	0.8	1.6	1.5
α-Guaiene	22,373	1436	0.2	-	0.1	-	0.2	0.1	0.3	0.1
α-Humulene	22,953	1450	2.1	2.0	0.5	0.5	2.4	1.4	2.8	2.6
Germacrene D	24,085	1477	5.0	4.9	1.9	1.9	5.5	3.2	7.2	7.6
Valencene	24,564	1489	0.3	0.3	0.1	0.1	0.6	0.3	0.4	0.9
Bicyclogermacrene	24,698	1492	1.1	1.1	0.3	0.3	1.6	0.9	1.9	2.8
α-Muurolene	24,873	1496	-	-	0.1	0.2	-	-	0.7	0.9
Eremophilene	25,064	1500	10.4	10.4	2.6	2.8	11.1	7.2	15.2	18.6
(E,E)-α-Farnesene	25,294	1506	7.6	7.5	3.5	3.5	8.8	5.3	12.8	15.8
δ-Cadinene	25,808	1520	1.9	1.9	0.7	0.7	1.7	1.1	2.6	3.2
Elemol	26,833	1547	0.2	0.2	-	-	0.1	0.1	0.2	0.1
Germacrene B	27,026	1552	0.9	0.9	0.3	0.3	0.9	0.5	1.4	1.7
Dodecanoic acid	27,640	1568	0.2	0.2	-	-	0.1	-	0.3	0.9
Spathulenol	27,873	1574	0.1	-	-	-	-	-	-	-
Tetradecanoic acid	34,903	1764	0.6	0.7	0.2	0.3	0.4	0.3	0.8	2.6
Hexadecanoic acid	41,697	1966	1.8	2.4	0.6	1.1	2.0	1.4	5.4	4.8
Linoleic acid	47,065	2132	0.5	0.5	0.6	1.0	2.1	0.9	4.2	11.3

RESULTS

pharmaceuticals

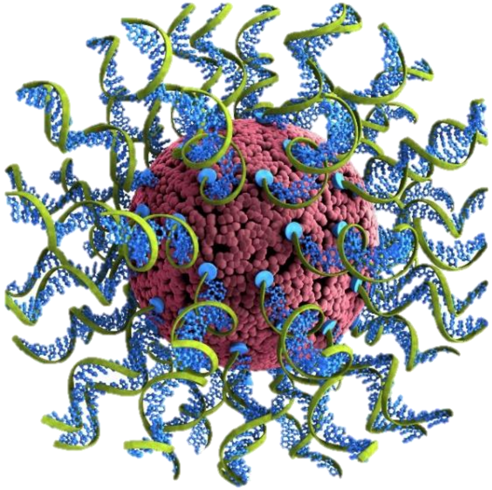
Article

Preparation of Multifunctional N-Doped Carbon Quantum Dots from *Citrus clementina* Peel: Investigating Targeted Pharmacological Activities and the Potential Application for Fe^{3+} Sensing

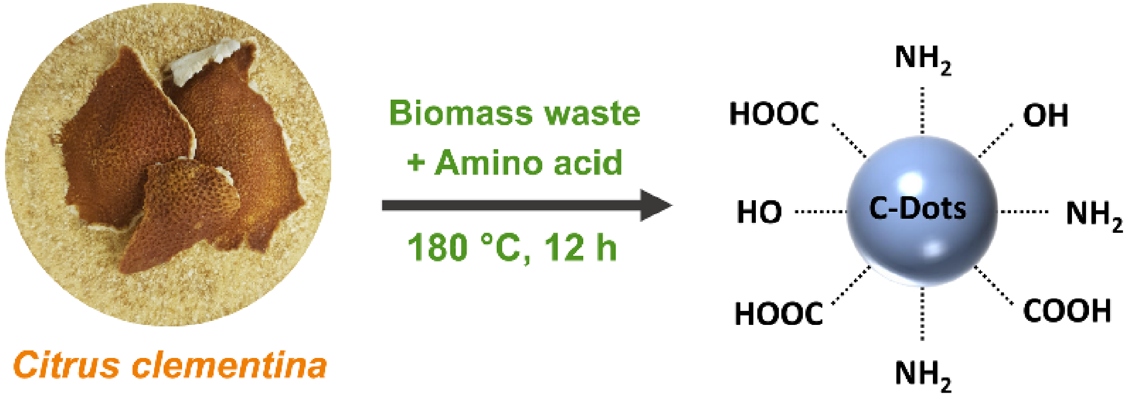
Silvija Šafranko [1], Anamarija Stanković [2], Sugato Hajra [3], Hoe-Joon Kim [3], Ivica Strelec [1], Maja Dutour-Sikirić [4], Igor Weber [5], Maja Herak Bosnar [6], Petra Grbčić [7], Sandra Kraljević Pavelić [8], Aleksandar Széchenyi [9], Yogendra Kumar Mishra [10], Igor Jerković [11,*] and Stela Jokić [1,*]

CITRUS PEEL AS A CARBON SOURCE IN CARBON QUANTUM DOTS TECHNOLOGY

Investigating the potential biological activity and applications in biomedicine



POTENTIAL APPLICATIONS

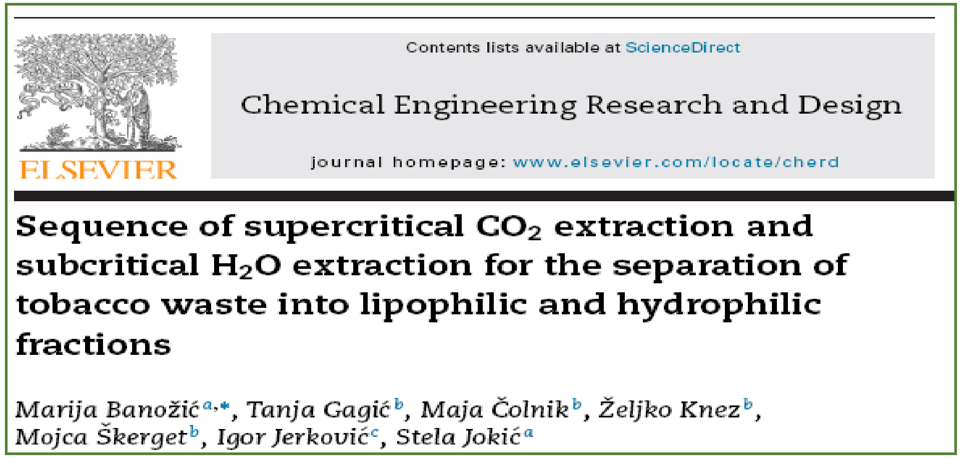


Citrus clementina waste

1. Antioxidant activity
2. Antitumor effect
3. Fe^{3+} sensing
4. Cellular imaging
5. Fluorescent ink

BIOMASS CAN BE USED AS A CARBON SOURCE FOR CQDs PREPARATION

RESULTS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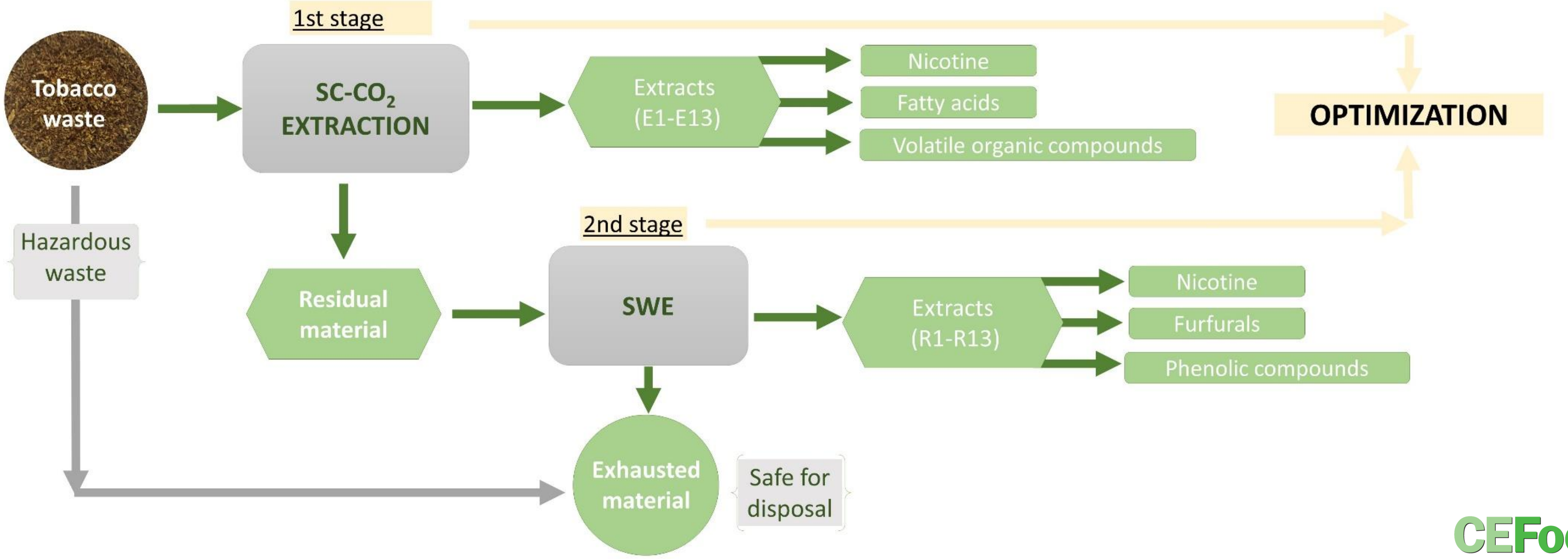
Sequence of supercritical CO_2 extraction and subcritical H_2O extraction for the separation of tobacco waste into lipophilic and hydrophilic fractions

Marija Banožić[a,], Tanja Gagić[b], Maja Čolnik[b], Željko Knez[b], Mojca Škerget[b], Igor Jerković[c], Stela Jokić[a]*

Tobbaco waste (dust, midrib, scrap)



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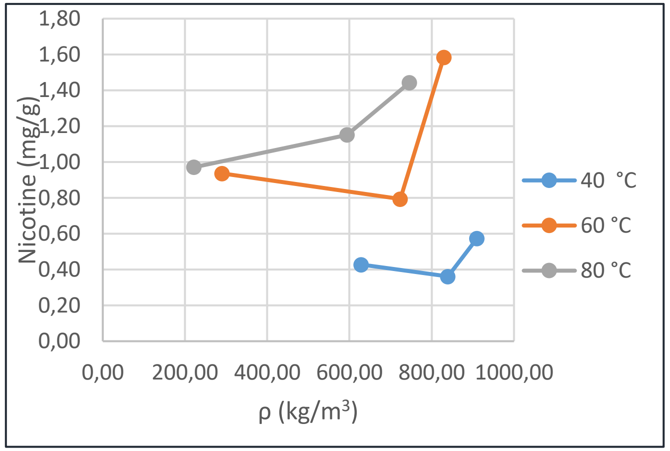
Sequence of supercritical CO_2 extraction and subcritical H_2O extraction for the separation of tobacco waste into lipophilic and hydrophilic fractions

Marija Banožić[a,*], Tanja Gagić[b], Maja Čolnik[b], Željko Knez[b], Mojca Škerget[b], Igor Jerković[c], Stela Jokić[a]

SUPERCRITICAL CO_2 EXTRACTION

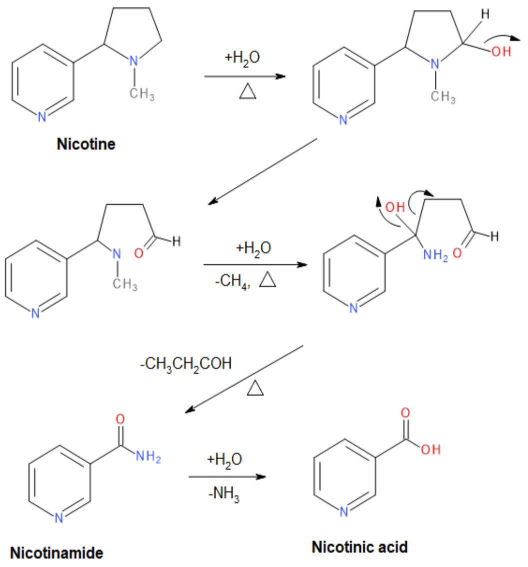
Tested variables	Pressure (bar)	Temperature (°C)	Time (min)
Experimental range	100-300	40-80	5-120
Detected compounds	Fatty acids, nicotine, volatile organic compounds		
Optimal conditions	Type: scrap, 120 min, 300 bar and 61.22 °C		

RUN	Pressure (bar)	Temperature (°C)	Nicotine (mg/g)	Other detected compounds
E1	100	40	4.28	*Duva-4.8.13-triene-1.3-diol*
E2	300	40	5.74	*2.3'-Dipyridyl*
E3	100	80	9.71	*3-Oxo-α-ionol*
E4	300	80	14.43	*Cotinine*
E5	100	60	9.37	*Solavetivone*
E6	300	60	15.85	*Neophytadiene*
E7	200	40	3.62	*Hexahydrofarnesyl acetone*
E8	200	80	11.52	*(E.E)-Farnesyl acetone*
E9	200	60	9.03	*Hexadecanoic acid*
E10	200	60	7.96	*Thunbergol*
E11	200	60	7.62	*Phytol*
E12	200	60	8.31	Fatty acids (palmitic acid, stearic acid, linoleic acid, linolenic acid, oleic acid
E13	200	60	6.76	
Soxhlet			8.34	



Nicotine content of tobacco waste *vs.* solvent density (ρ) at different temperatures during SC-CO_2 extraction

Proposed degradation mechanism:



SUBCRITICAL-WATER EXTRACTION

Tested variables	Time (min)	Temperature (°C)	Solvent/solid ratio (mL/g)
Experimental range	5-25	150-250	10-30
Detected compounds	Phenolic compounds, carbohydrates, chlorogenic acid, rutin, nicotine, 3.4 DHBA, nicotinic acid, nicotinamide, 5-HMF, furfural and 5-MF		
Optimal conditions	Scrap: 150 °C. 23 min. 28 mL/g	Dust: 160 °C. 20 min. 10 mL/g	Midrib: 150 °C. 25 min. 30 mL/g

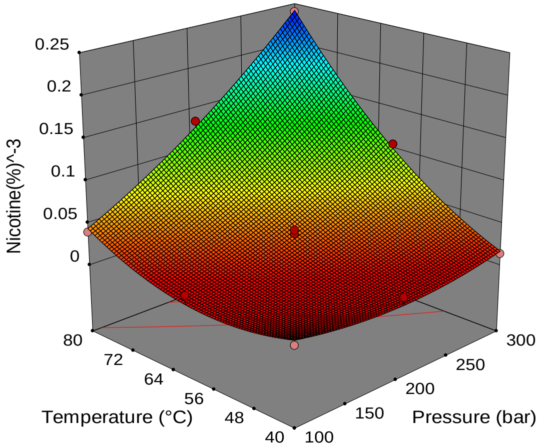
Nicotine mg/g			
	SCRAP	DUST	MIDRIB
1	26.6	15.0	9.07
2	44.3	22.8	19.7
3	46.1	23.1	12.3
4	29.9	18.0	10.2
5	33.5	27.2	13.0
6	51.4	27.5	17.7
7	32.5	21.5	11.0
8	42.4	32.2	17.1
9	40.5	24.3	14.8
10	42.5	29.5	15.7
11	30.6	21.7	12.5
12	39.4	23.6	14.7
13	32.01	26.9	13.0
14	37.1	28.0	15.2
15	32.4	26.4	13.3
16	32.4	24.5	14.1
17	32.1	27.8	14.0

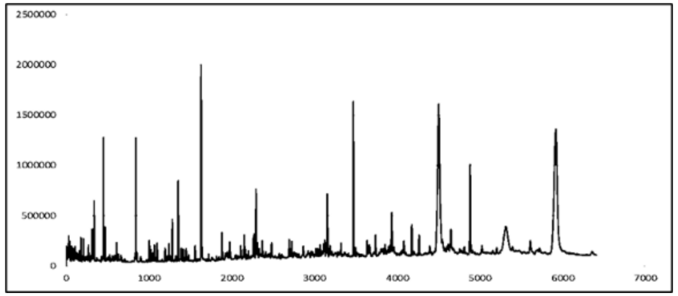
SEQUENCE OF SUPERCRITICAL CO_2 EXTRACTION AND SUBCRITICAL WATER EXTRACTION

Tested SFE variables	Pressure (bar)	Temperature (°C)	Time (min)
Experimental range	100-300	40-80	5-120
Tested SWE variables	Temperature (°C)	Time (min)	Solvent: solid ratio (mL/g)
Experimental conditions	150	23	28
Detected compounds	Nicotine, Phenolic compounds, nicotinic acid, nicotinamide,5-HMF, furfural and 5-MF		
Optimal conditions	Type: scrap, SFE 120 min. 300 bar and 61.22 °C		

RUN	Extraction yield (%)	Nicotine (mg/g)	Nicotinamide (mg/g)	Nicotine acid (mg/g)
R1	54.08	46.70	4.02	2.39
R2	59.15	42.10	3.71	1.87
R3	58.34	29.30	3.04	1.43
R4	74.05	16.10	1.98	1.18
R5	52.47	42.90	4.28	2.22
R6	65.83	21.10	2.58	1.33
R7	51.39	45.60	4.25	2.19
R8	54.50	19.50	3.03	1.47
R9	53.62	31.40	3.46	2.05
R10	56.50	36.40	3.65	1.72
R11	60.42	30.00	3.07	1.62
R12	52.68	30.20	3.29	1.59
R13	54.77	28.70	3.03	1.54
Raw material	54.57	38.10	3.15	22.58

Two-stage extraction process (SC-CO_2 extraction followed by SWE) can enhance the extraction efficiency due to the elimination of fats during SC-CO_2 extraction which enables better dissolution of the other compounds in subcritical H_2O.

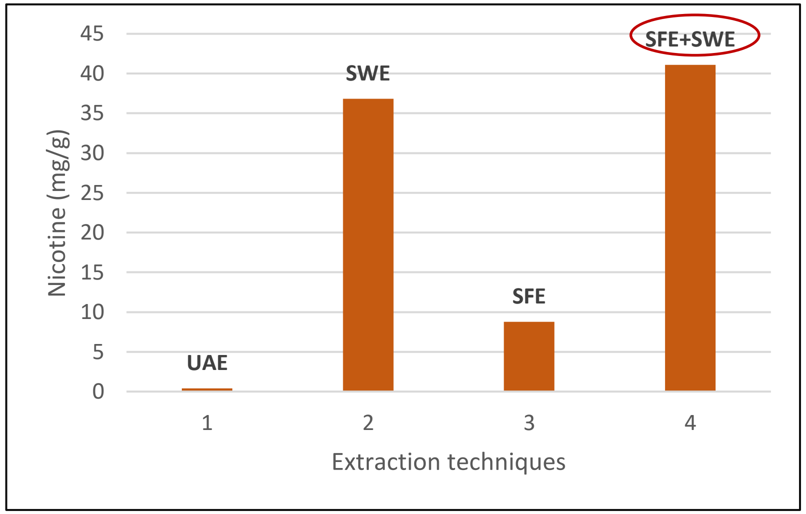




GC-MS midrib chromatogram obtained after SFE

Proposed model:

$$Y_1^{-3} = 0.0369 + 0.0495X_1 + 0.0634X_2 + 0.0491X_1X_2 + 0.0148X_1^2 + 0.0279X_2^2$$



Comparison of different methods in extraction of nicotine form tobacco waste

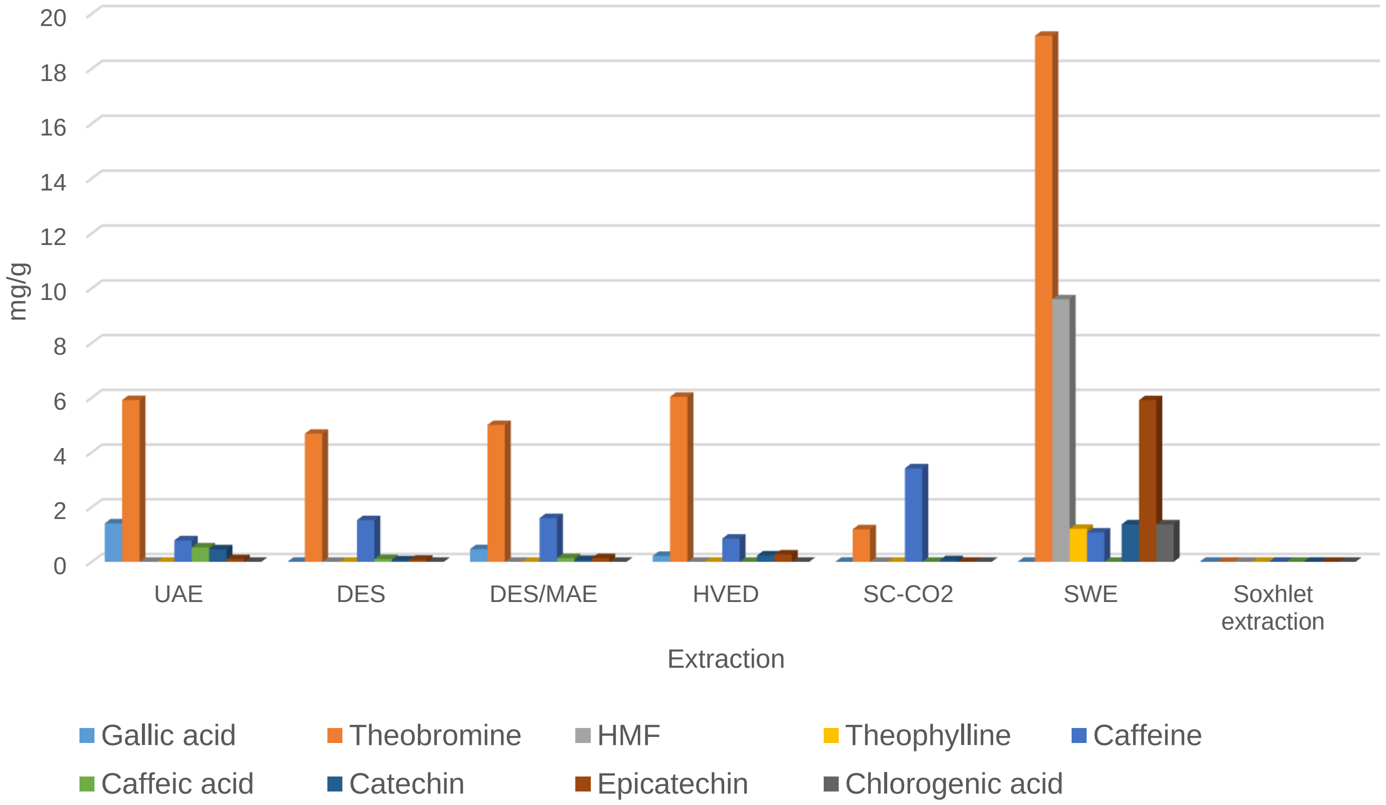
RESULTS

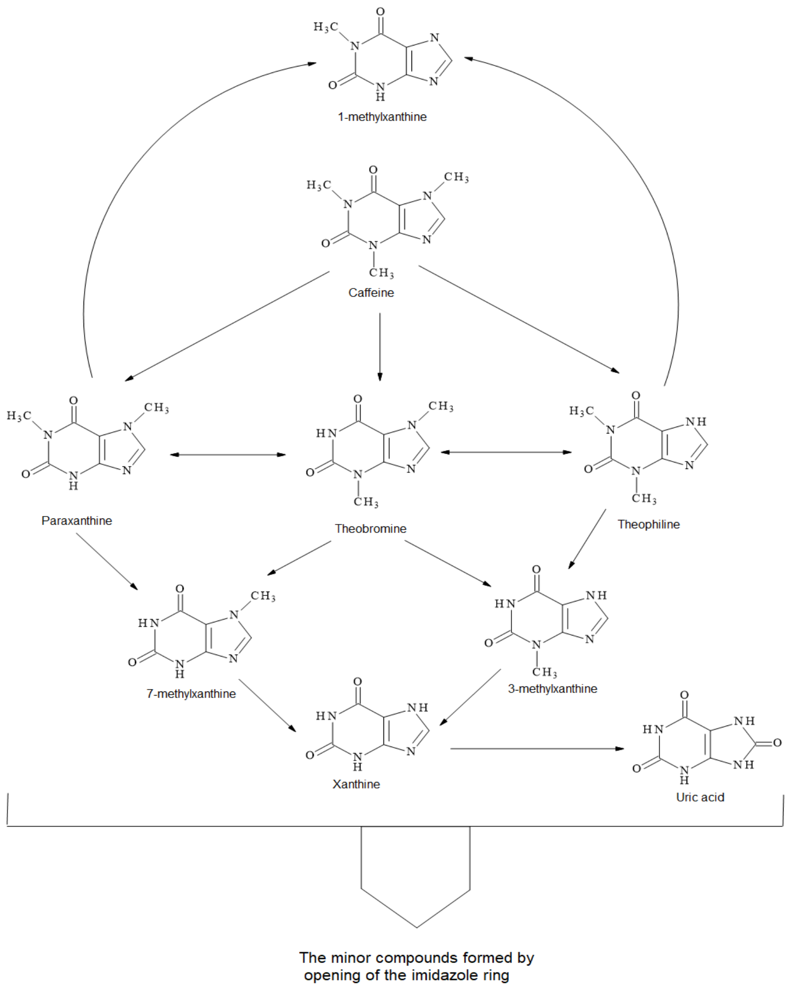
molecules MDPI

Article

Separation of Active Compounds from Food by-Product (Cocoa Shell) Using Subcritical Water Extraction

Stela Jokić [1,*], Tanja Gagić [2], Željko Knez [2,3], Drago Šubarić [1] and Mojca Škerget [2]





Scheme 1. Proposed degradation mechanism of methylxanthines within hydrothermal degradation of cocoa shell.

3rd International conference Food industry by-products
29th August 2022, Osijek, Croatia

APPLICATIONS OF SPRAY-DRYING IN MICROENCAPSULATION OF HESPERIDIN DELIVERED FROM CITRUS PEEL

Marija Banožić[1*], Krunoslav Aladić[1], Małgorzata Krzywonos[2], Hanna Pińkowska[3], Igor Mucha[4], Adrianna Złocińska[4], Stela Jokić[1]

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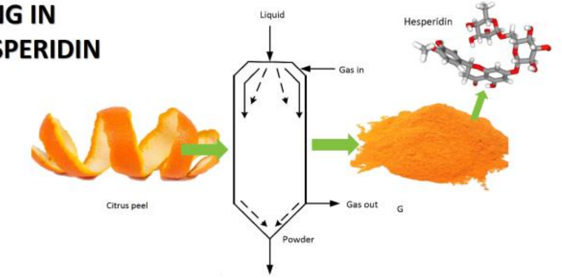

INTRODUCTION

Citrus fruits are one of the most important crops with worldwide production, while citrus by-products represent a problem regarding their disposal due to the environmental risk. The citrus peel contains hesperidin, a flavonoid with a wide range of biological activities. Recent scientific literature discusses the extraordinary versatility of hesperidin, which is reflected in its antioxidant, anti-inflammatory, cardio-protective and antidiabetic properties. However, hesperidin is quite unstable and therefore should be encapsulated to protect its bioactivity from the effects of environmental conditions. Among the other popular microencapsulation techniques, spray drying allows rapid evaporation of water and maintains a relatively low temperature within the particles. The aim of this study was to investigate the possibility of applying spray drying technique for the encapsulation of hesperidin from mandarin peel (*Kuno* variety), formed as by-products during the growth and fresh fruit processing.

METHODS

Samples (whole citrus fruits, satsuma mandarin, Citrus unishu, medium late variety Kuno) were obtained from family farm OPG Pačić. Citrus fruits were grown and harvested in the Metković, Neretva Valley, Croatia in the season 2021/2022. After harvesting, the peel was removed and stored at -80 °C. Before extraction peel was dried, grounded at a laboratory mill and sieved. Citrus peel extracts were produced by ultrasonic-assisted extraction with 70% ethanol as a solvent. Carriers (maltodextrin and Arabic gum) were added to feed in the amount of 100% compared to the dry matter of the extract. The feed flow rate was adjusted to 4 ml/min, the airflow rate was 283 L/h and the temperature of drying was 120 °C. Microcapsules were separated using a high-performance cyclone and collected in the collecting chamber, weighted and stored until further analysis. Determination of hesperidin was performed using high-performance liquid chromatography, and microcapsules were characterized using Powder X-Ray diffraction analysis, Fourier-transform infrared spectroscopy and thermogravimetric analysis.
Encapsulation efficiency was calculated using equation:

$$EE=(THC-SHC)/THC$$

where THC is total hesperidin content and SHC is surface hesperidin content.

RESULTS

Table 1 Encapsulation efficiency of hesperidin microcapsules produced using spray drying

No	Samples	Total hesperidin content [µg ml-1]	Surface hesperidin content [µg ml-1]	Encapsulation efficiency (EE) [%]
1	CPE+MD+SD	461.025	261.332	43.32
2	CPE+GA+SD	433.760	400.940	7.56

CPE – citrus peel extract
MD - maltodextrin, GA - gum Arabic, SD - spray drying

Figure 1 presents PXRD diffractograms of hesperidin microparticles. Few patterns were observed in hesperidin microparticles which showed few peaks with different peak intensities. These findings provide evidence that hesperidin microparticles were lost its crystalline structure during encapsulation processes.

The FTIR spectra of hesperidin as pure compound, hesperidin microparticles were recorded in the range from 400 to 4000 cm^{-1} and compared in **Figure 2.** In hesperidin microcapsules, the peaks existent in frequencies between 2900 cm^{-1} to 3500 cm^{-1} were predominantly found pertaining to hydrogen bonds (O-H stretch), carboxylic acids and residual water. The band around 1604 was assigned to the carbonyl (C=O) stretching in microcapsules with maltodextrin.

TGA data suggest that the thermal degradation of the hesperidin microparticles is a complex process, which occurs in several stages as evidenced by the presence of several peaks in the TGA curve in **Figures 3.** This is likely a consequence of citrus peel complex chemical composition, which is characterized by the presence of several macrocomponents (i.e., pectin, cellulose, hemicelluloses, and lignin) and minor constituents (e.g., proteins, fats, phenolic compounds, etc.) in varying proportions. Hesperidin microcapsules with maltodextrin were thermally stable up to the temperature of about 125 °C while and decomposed in three-stage, while microcapsules with gum Arabic were thermally stable up to the temperature of approximately 115 °C and decomposing in two stages.

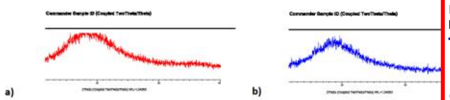

Figure 1 . PXRD patterns for Hesperidin microparticles a)maltodextrin b)Arabic gum

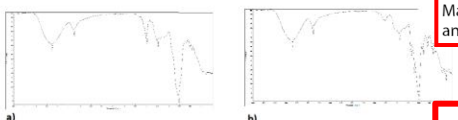

Figure 2. FTIR spectra of Hesperidin microparticles a)maltodextrin b) Arabic gum

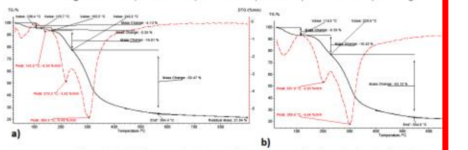

Figure 3. TGA diagrams for Hesperidin microparticles a)maltodextrin b) Arabic gu

CONCLUSION

While dealing with pure flavonoid-hesperidin is more convenient from an analytical standpoint, non-purified phenolic extracts are more commercially viable, saving time, cutting costs, and delivering the largest yield of polyphenols without waste. Citrus peel showed as a possible alternative to commercial hesperidin sources, while spray drying showed as a reliable and effective tool for its encapsulation. The amorphous form of bioactive compounds, such as hesperidin represents the most energetic solid state, which provides the greatest advantage in terms of solubility and bioavailability. The hesperidin retention in the microcapsules was 461.03 and 433.76 mg/g for microcapsules encapsulated with maltodextrin and gum Arabic, respectively. However, higher encapsulation efficiency (difference between surface and total hesperidin content) and highest thermal stability was achieved when maltodextrin was used as an encapsulating agent.

Acknowledgments:
This work has been supported by Croatian Science Foundation under the project "Application of innovative techniques of the extraction of bioactive components from by-products of plant origin" (UIP-2017-05-9909)

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Spray Drying as a Method of Choice for Obtaining High Quality Products from Food Wastes– A Review

Marija Banožić[a], Jelena Vladić[b], Ines Banjari[a], Darko Velić[a], Krunoslav Aladić[a], and Stela Jokić[a]

sustainability
MDPI

Article

An Approach to Value Cocoa Bean By-Product Based on Subcritical Water Extraction and Spray Drying Using Different Carriers

Stela Jokić [1,*], Nataša Nastić [2], Senka Vidović [2], Ivana Flanjak [1], Krunoslav Aladić [1] and Jelena Vladić [2,*]

CEFood Congress

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RECYCLING OF FOOD INDUSTRY BY-PRODUCTS: PRODUCTION OF COCOA BEAN SHELL POWDER USING SPRAY DRYING TECHNIQUE

Jelena Vladić[1], Senka Vidović[1], Ivana Flanjak[2], Mojca Škerget[3], Stela Jokić[2*]

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Introduction

Cocoa bean shell, which represents waste generated in the production of cocoa and its products, is proven to contain numerous bioactive components that can be applied in food, cosmetic, and pharmaceutical industry. To valorize this material, it is necessary to develop an adequate method that can provide quality and stabile products of cocoa bean shell that contains bioactive components. With that goal in mind, the spray drying technique with two carriers – maltodextrin and whey protein was applied.

Methods

The obtained dry extracts were characterized in terms of physico-chemical properties: moisture content, hygroscopicity, bulk density, rehydration, water absorption index and water solubility index, content of total phenols and total flavonoids. Furthermore, the content of bioactive components (theobromine, caffeine, gallic acid, caffeic acid, p-coumaric acid, (+)-catechin, (-)-epicatechin and (-)-epicatechin gallate) was performed by HPLC method.

Results and discussion

By using maltodextrin, an approximately 74% efficacy of the process was achieved, while with whey protein it was 59%. The powders obtained with both carriers had a moisture content below 6%, which secures the extended stability of the extract if it is stored in an adequate manner. Similar results were achieved in the case of hygroscopicity which is the capacity of the material to absorb moisture. This capacity was monitored after 2, 5, 7, 10, and 14 days and it ranged from 12.40 to 16.68% for both powders.
The value of the bulk density of the obtained powders were higher in the case where maltodextrin was used, while whey protein was more efficient and adequate carrier for the preservation of polyphenols. As a result, a higher content of total phenols and flavonoids in dry powders dried with whey protein was determined. Higher content of methylxanthines and phenolic acids, except caffeic acid, was obtained when whey protein was used as a carrier while the content of other analyzed active components was the same regardless of carrier type.

Table 1. Powder characterization

Carrier	Efficiency (%)	Moisture content (%)	Rehidratation (s)	Bulk density (mg/mL)	WSI (%)	WAI (%)
Maltodextrin	73.52	5.54	5.3	421.58	62.4	29.6
Whey protein	58.61	5.83	4.3	302.43	72.8	12.8

e 1. HPLC analyses of phenols

Carrier	Maltodextrin	Whey protein
Gallic acid	0.37	0.48
Catechin	1.48	1.47
catechin	0.15	0.11
feic acid	0.04	0.03
chin gallate	0.07	0.06
maric acid	0.02	0.03

Table 2. HPLC analyses of methylxanthines

Carrier	Maltodextrin	Whey protein
Teobromine	5.95	7.34
Caffeine	1.10	1.34

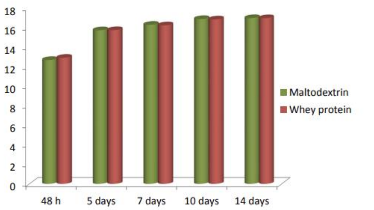

Figure 1. Hygroscopicity (%)

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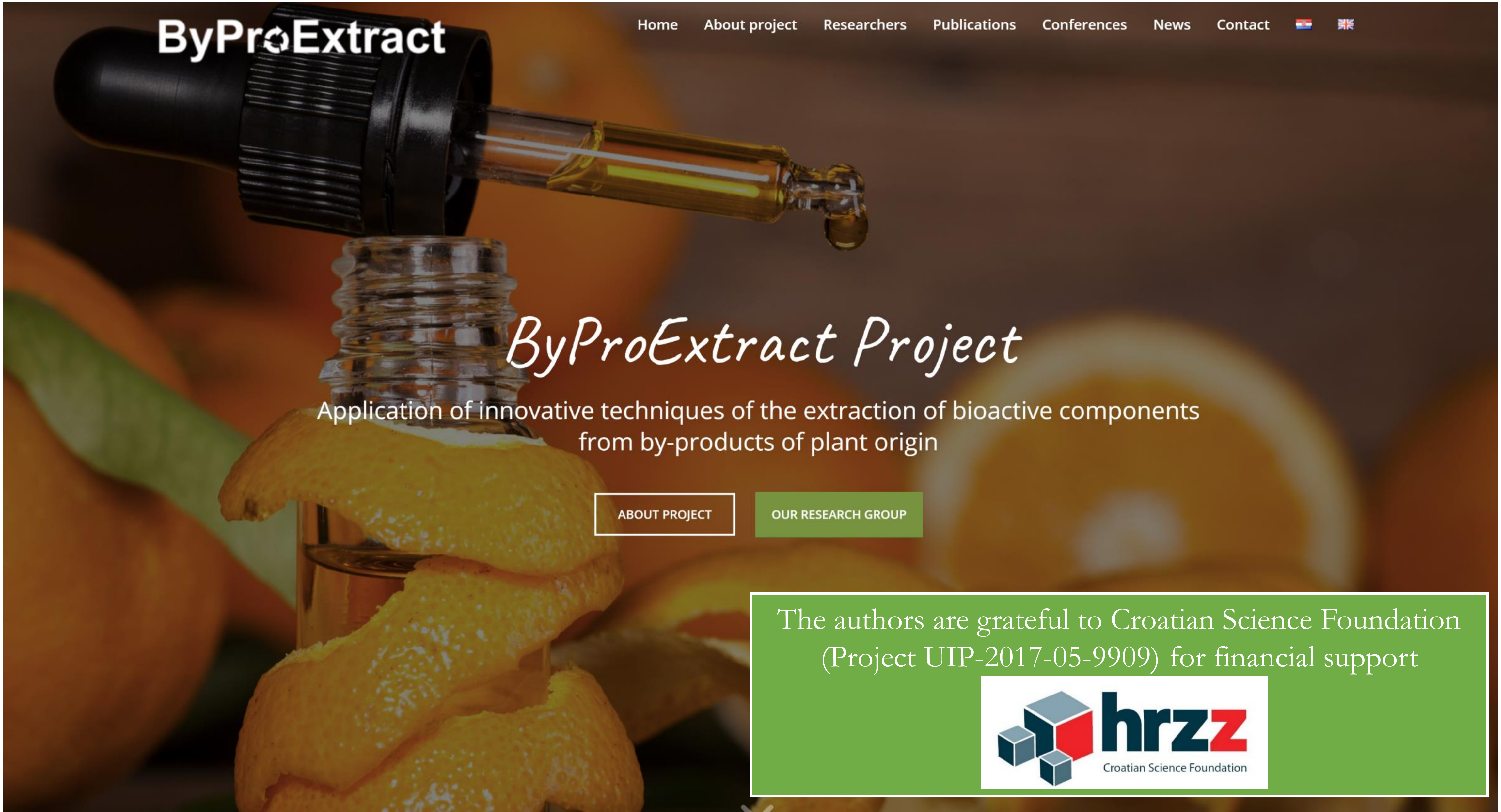
„Alone we can do so little;
Together, we can do so much."
- Helen Keller

Thank you for your attention!



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