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HOLISTIC EXPLOITATION OF SPENT COFFEE GROUNDS: RECOVERY OF PHENOLIC COMPOUNDS AND USE AS BIOSORBENT

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COFFEE

MAIN SPECIES FOR COMMERCIAL PRODUCTION

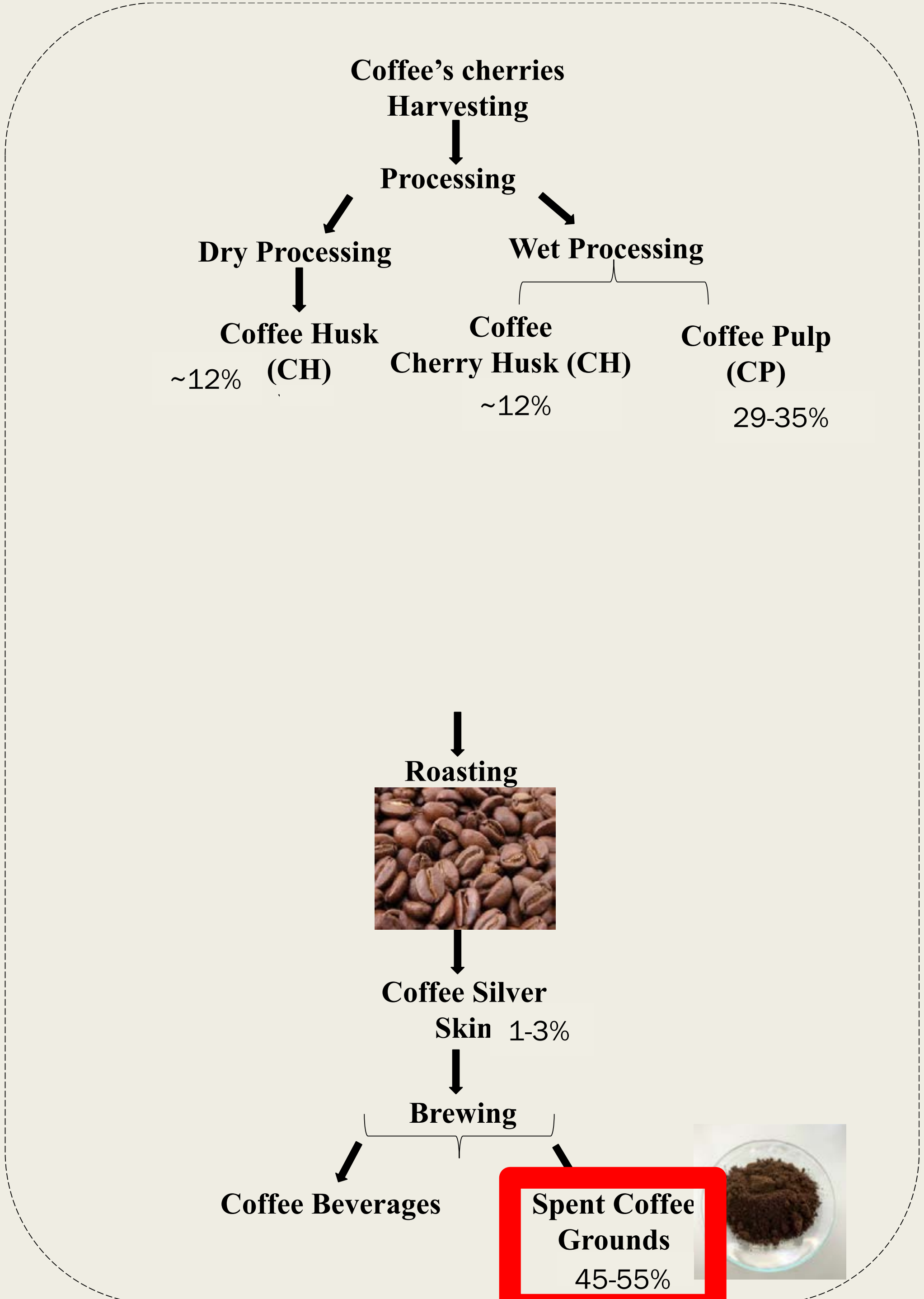
COFFEA ARABICA (ARABICA)

COFFEA CANEPHORA VAR. ROBUSTA (ROBUSTA)

- 75% of the global production
- Superior due to its milder and more flavorful taste (Bertrand *et al*., 2003)

➢ ICO: Coffee consumption ↑ 1.24 million bags of coffee → 169.34 million bags by the year 2019/2020 (ICO, 2019)

COFFEE BY-PRODUCTS



SPENT COFFEE GROUNDS (SCG)

- SCG consists a dark colored solid residue, with high moisture content, coffee aroma and high organic content

- 1 ton of green coffee beans ➡ 650 kg of SCG

- 1 kg of soluble coffee ➡ 2 kg of wet SCG

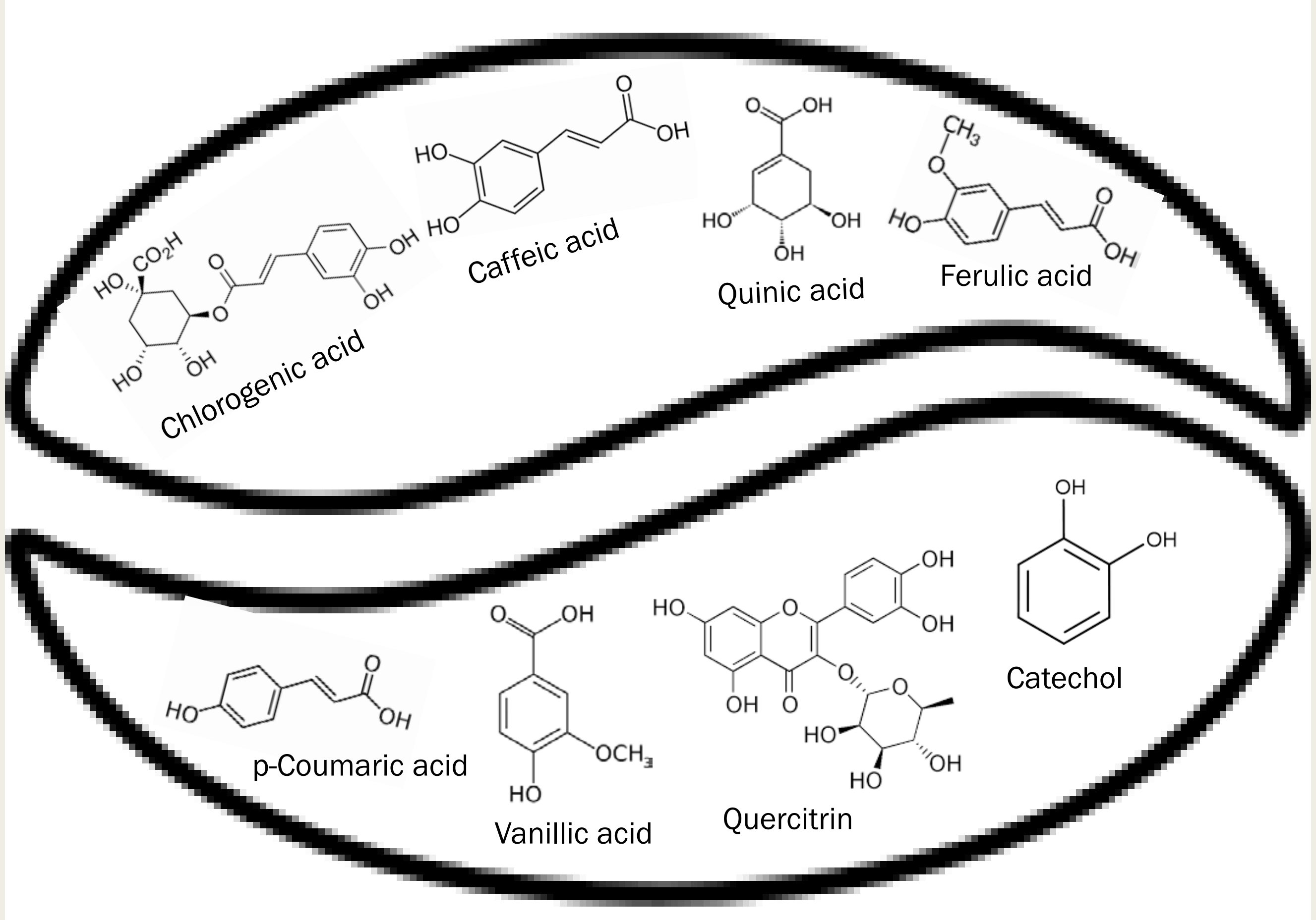
(Murthy and Naidu, 2012 and Mata *et al*., 2018)

- It consists mainly of carbohydrates, lipids, proteins and polyphenols

COMPOSITION OF SCG

Component	Content
Moisture	1.18 - 74.72 (%)
Cellulose	12.40 ± 0.79 (g/100g d.b.)
Hemicellulose	39.10 ± 1.94 (g/100g d.b.)
Arabinose	3.60 – 6 (g/100g d.b.)
Mannose	19.07 – 47 (g/100g d.b.)
Galactose	16.43 – 30 (g/100g d.b.)
Lignin	23.90 ± 1.70 (g/100g d.b.) Insoluble 17.59 ± 1.56 Soluble 6.31 ± 0.37
Fat	2.29 – 19 (g/100g d.b.)
Protein	4.3 -17.44 (g/100g d.b.)
Total dietary fibers	36.87 - 60.46 (g/100g d.b.) Insoluble 50.78 ± 1.58 Soluble 9.68 ± 2.70

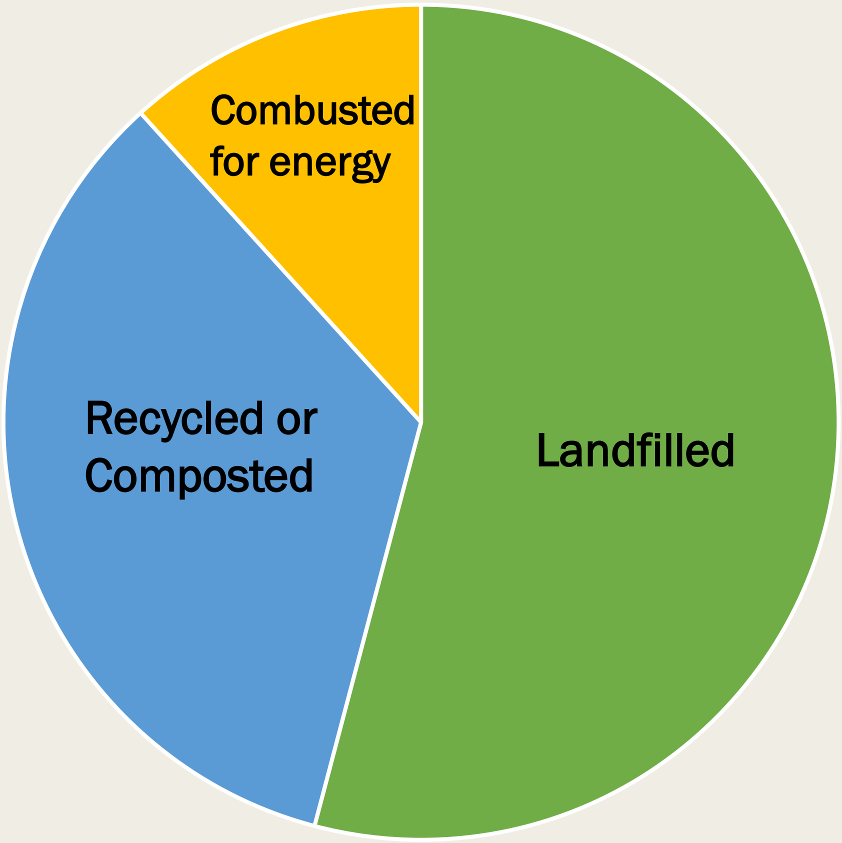
PHENOLIC COMPOUNDS



(Acevedo *et al.*, 2013 ; Ballesteros *et al*., 2014; Cerino-Córdova *et al*., 2020)

WASTE MANAGEMENT

Waste management of coffee by-products



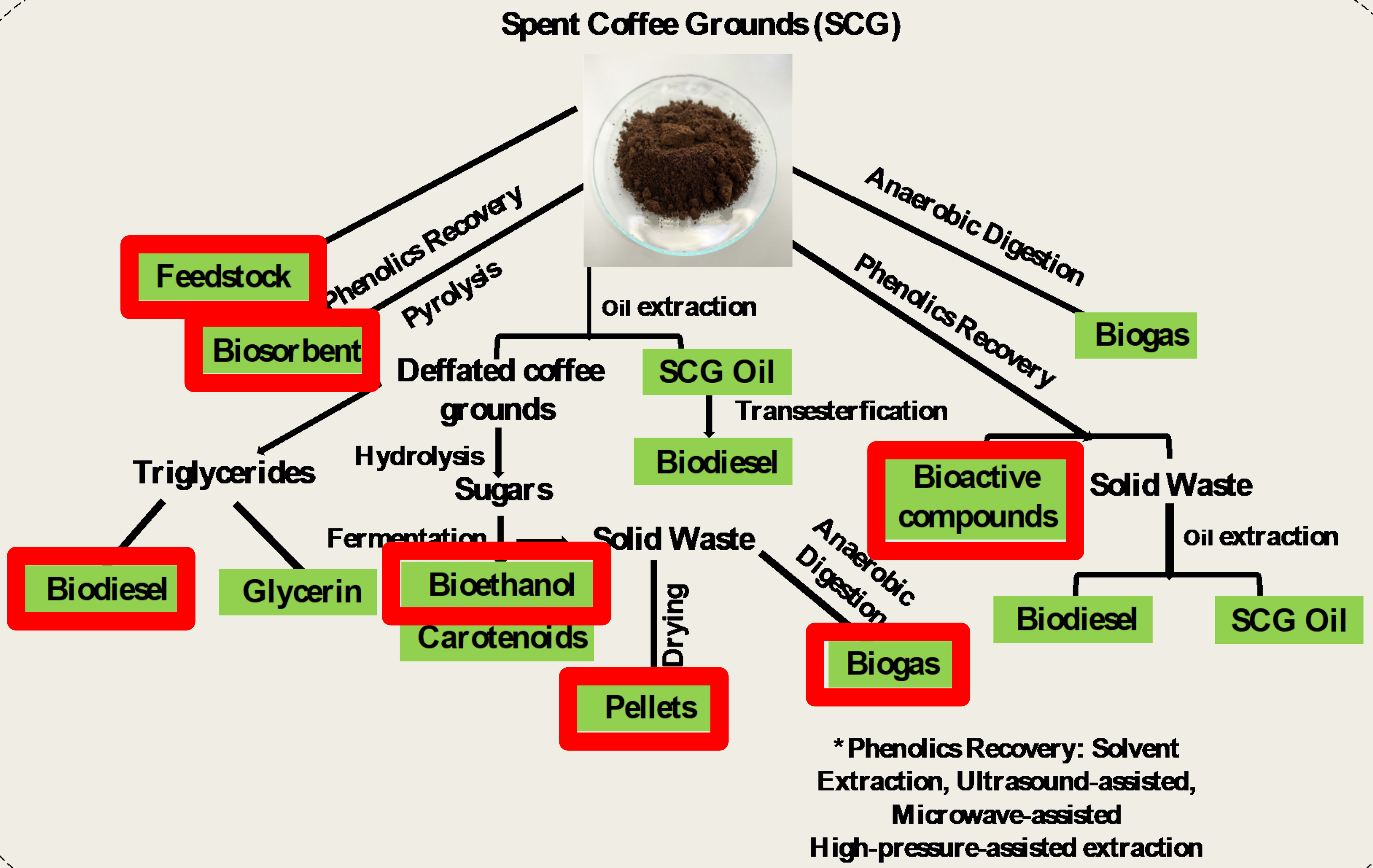
⬆ Organic content

⬆ Toxicity

Pose a severe threat for the environment

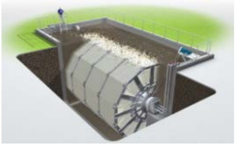
Waste management of coffee by-products (U.S. Environmental Protection Agency (EPA, 2017).

POTENTIAL USES OF SCG

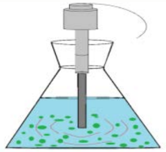


RECOVERY OF PHENOLIC COMPOUNDS FROM SCG

Membrane separation



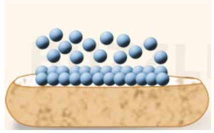
Extraction



- CONVENTIONAL MACERATION EXTRACTION
- ULTRASOUND ASSISTED EXTRACTION

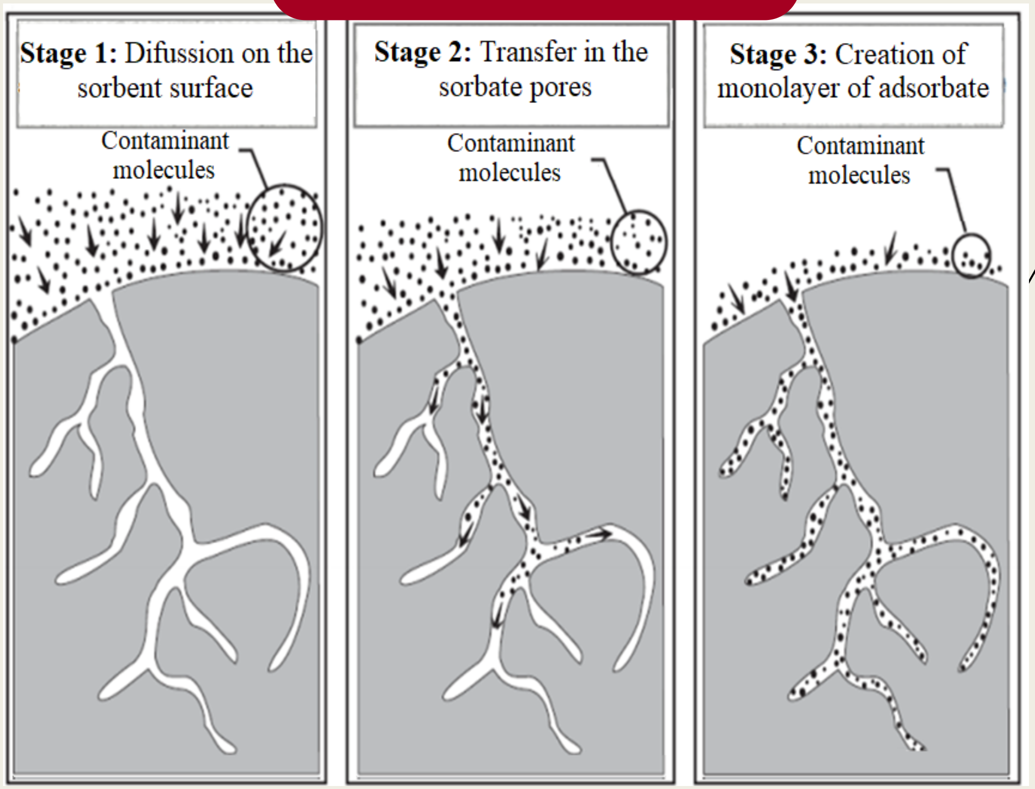
Chromatographic separation

Adsorption



USE OF SCG AS BIOSORBENT

ADSORPTION



✓ The best, effective, low-cost and frequently used method

Transfer of a solute from either a gas or liquid/solution to a solid. The solute is held to the surface of the solid as a result of intermolecular attraction with the solid molecules.

FACTORS AFFECTING THE ADSORPTION PROCESS

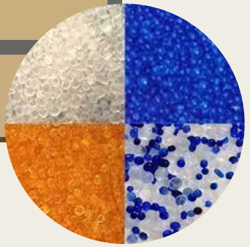
- Adsorption temperature
- pH
- Solvent/sorbent ratio
- Initial concentration of phenolics
- Particle size of biosorbent

COMMERCIAL ADSORBENTS

Oxygen Containing Compounds

Generally Hydrophilic & Polar
Examples: Silica Gel & Zeolites

Silica Gel



Zeolite

Carbon Based Compounds

Generally Hydrophilic & Non Polar
Examples: Activated Carbon
Graphite

Activated Carbon

Graphite

Polymer Based Compounds

Polar or Non Polar functional groups in a polymer matrix
Examples: Polymers & Resins

Polymer Resins

BIOSORBENTS

Biosorbent	Adsorbed compound	Yield (%)	Reference
Pine wood char	Pb, Cd, Ar from water	3-54	Dinesh Mohan *et al*., 2007
Oak bark char		26-98	
Banana peel	Cd from water	77.0- 89.2	Jamil *et al*., 2010
	Pb from water	76.0 -58.3	
	Cr from leather tanning	99.1- 100	Jamil *et al*., 2008
Banana pith	Direct red from water	55-80	Namasivayam, 1998
	Acid brilliant blue from water	65-95	
Apple pomace	Textile dye effluent	91-100	Robinson *et al*., 2001

Biosorbent	Adsorbed compound	Yield (%)	Reference
Azolla	Polyphenols from OMW	-	Ena *et al*., 2012
Banana peel	Phenolic compounds from OMW	60—88	Achak *et al*., 2009
Nutshells	Phenolic compounds from aqueous solutions	-	Goud et al., 2005
Olive pomace	Total phenols from OMW	≤40%	Stasinakis *et al*., 2008
Olive stone and pulp	Total phenols from OMW	13.5-73%	Galiatsou et al., 2002
Pomegranate peel and orange juice by-product	Phenolic compounds from OMW	≤93.13, 89.59% respectively	Ververi and Goula 2019
Pomegranate seeds	Phenolic compounds from OMW	≤92.8	Papaoikonomou *et al*., 2019
Wheat bran	Phenolic compounds from OMW	≤94	Achak *et al*., 2014
Wheat husk	Phenols from aqueous solution	91.7	Devaanshi et al., 2017

OLIVE MILL WASTEWATER

OMW →

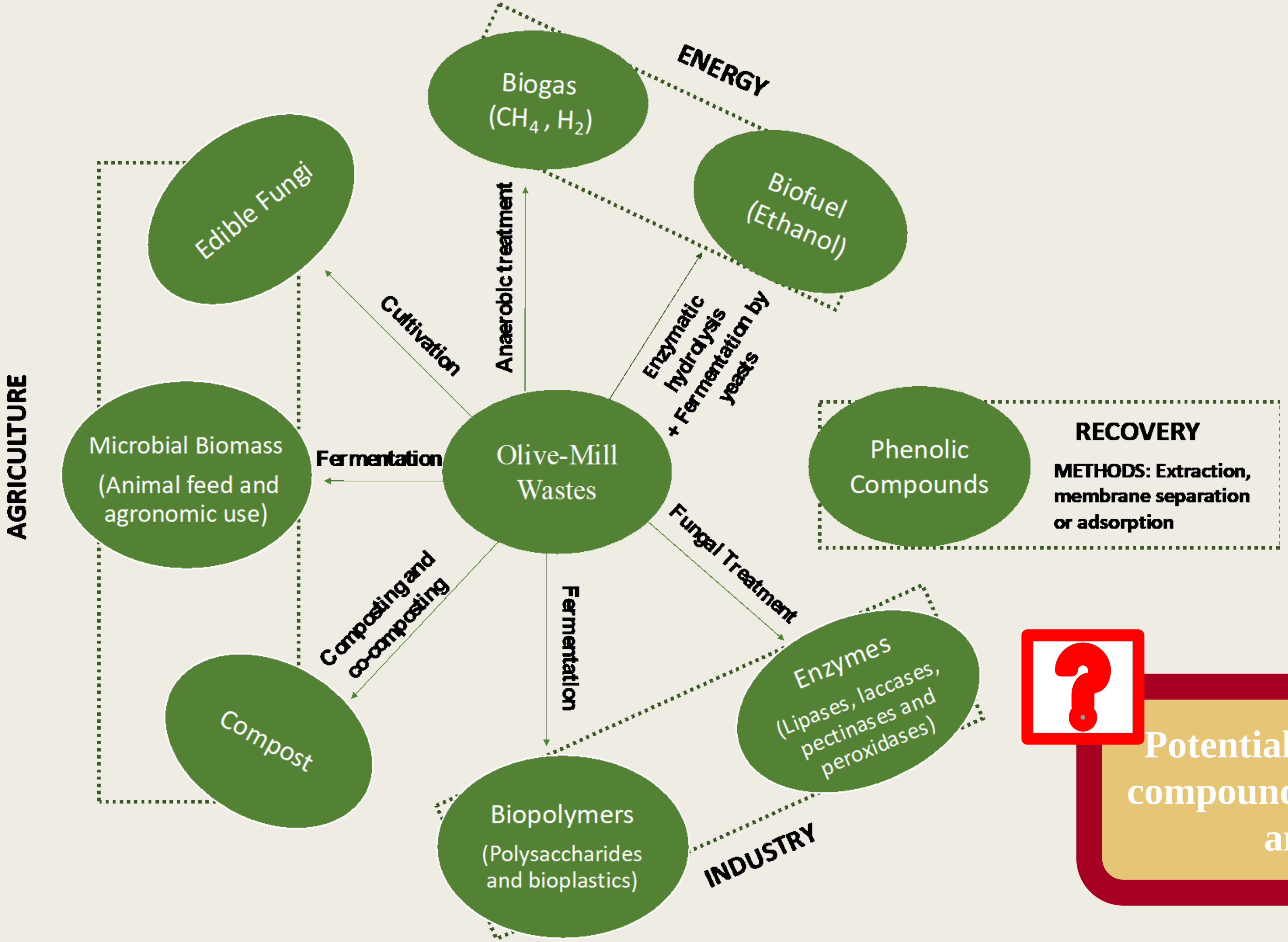
- Liquid waste of three-phase extraction system
- Aqueous, dark, foul smelling
- High **organic content** (57.2-62.1%)
- **Acidic** character (pH 2.2-5.9)
- **Phenolic** compounds (up to 80 g/L)
- **Solid matter** (total solids up to 20 g/L)

- High **phytotoxicity**
- Threatening aquatic life
- Mediterranean countries: 2.4 million tons of olives per year (95% of world production)

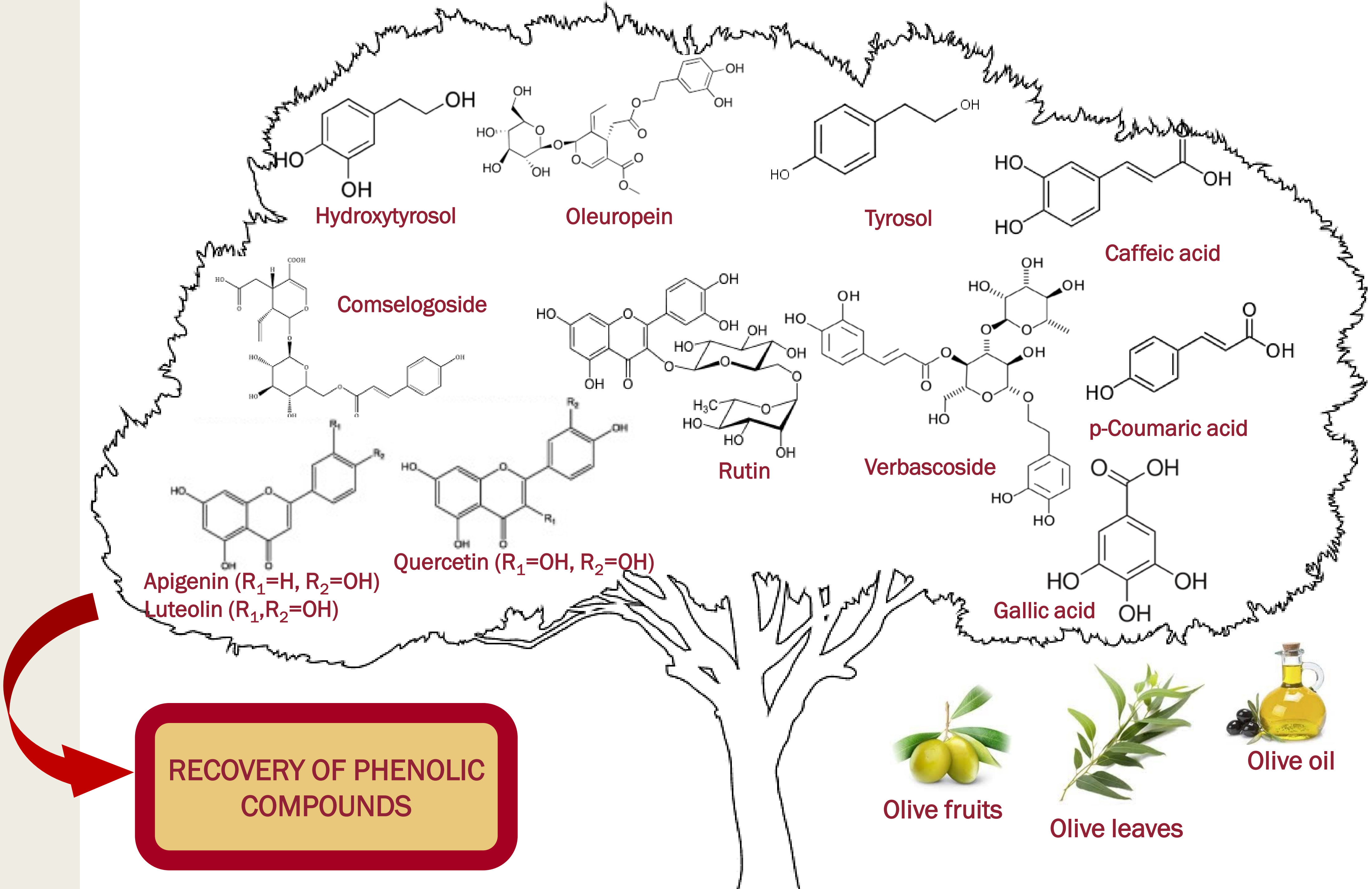
(Ochando-Pulido *et al.*, 2013)

Production system	Inputs	Outputs
Traditional pressing	Olives (1000 kg) Washing water (100-120 kg)	Oil (200 kg) Solid waste (400 kg) Wastewater (600 kg)
Two-phase system	Olives (1000 kg) Washing water (100-120 kg)	Oil (200 kg) Solid waste (800-950 kg)
Three-phase system	Olives (1000 kg) Washing water (100-120 kg) Mixing water (500-1000 kg)	Oil (200 kg) Solid waste (500-600 kg) Wastewater (1000-1200 L)

OMW MANAGEMENT



Potential source of phenolic compounds and other natural antioxidants!

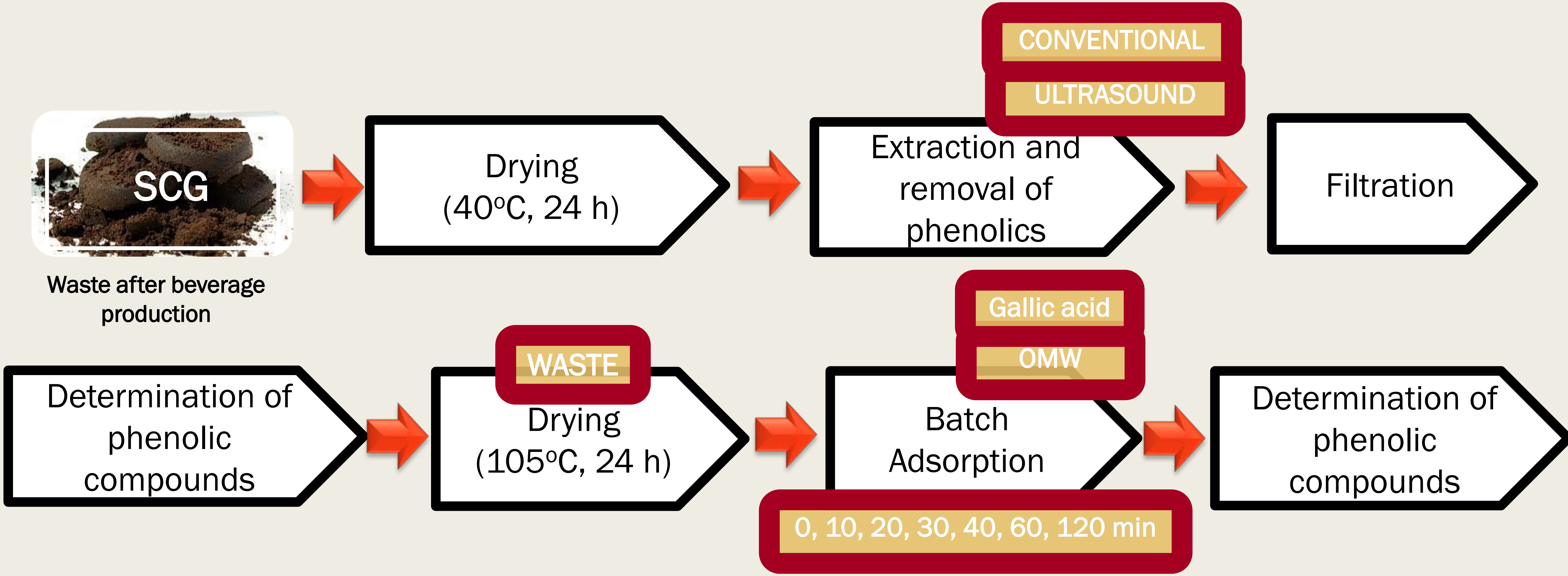

Hydroxytyrosol
Oleuropein
Tyrosol
Caffeic acid
Comselogoside
Rutin
Verbascoside
p-Coumaric acid
Quercetin (R1=OH, R2=OH)
Apigenin (R1=H, R2=OH)
Luteolin (R1,R2=OH)
Gallic acid
RECOVERY OF PHENOLIC COMPOUNDS
Olive fruits
Olive leaves
Olive oil

AIM OF THE STUDY

- ✓ **Recovery** of valuable compounds from SCG
- ✓ **Optimization** of extraction using novel techniques
- ✓ Holistic exploitation of SCG (after extraction of phenolic compounds) as **biosorbent**
- ✓ **Optimization** of batch adsorption process
- ✓ Development and proposal of a novel, low-cost method for the recovery of bioactive compounds from other food industries' wastes using SCG as biosorbent and their **exploitation** as **food additives** in food industry

MATERIALS AND METHODS

WASTE PREPARATION & EXTRACTION PROCESS



EXPERIMENTAL DESIGN- CONVENTIONAL EXTRACTION

Statistical program *Minitab* *(Release 13)* → Input of factors to be tested → Experimental design → **20 experiments**

Parameters	Levels				
Extraction temperature (T, ºC)	20	30	40	50	60
Solvent type (% aqueous ethanol)	0	20	50	80	100
Liquid /Solid ratio (mL/g)	5	16	33	49	60

Duration: 180 min

INVESTIGATED PARAMETERS

- Temperature: 20-60ºC
- Solvent: 0-100% EtOH
- Liquid/Solid ratio: 5-60mL/g

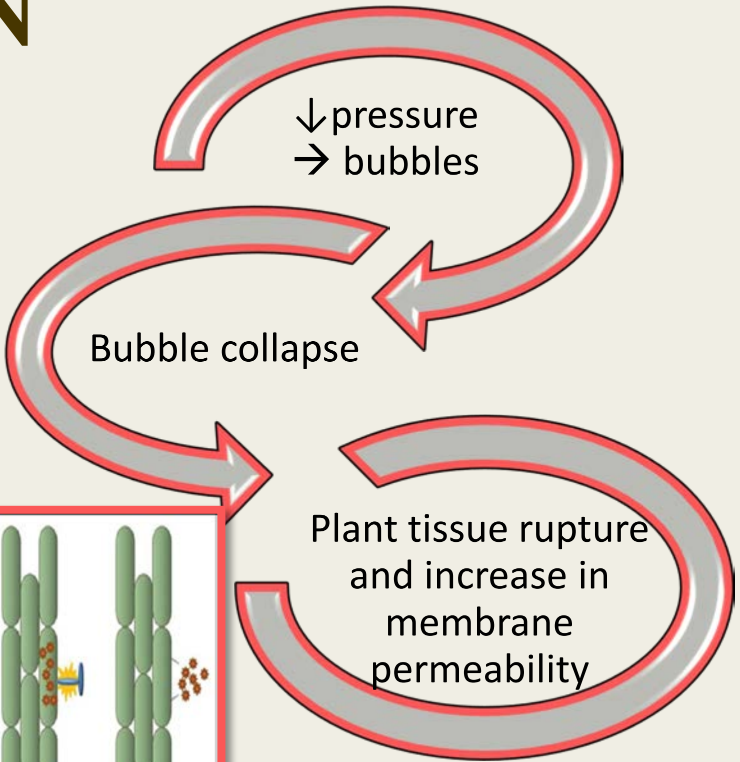
- Time, Solvent and Energy Consuming

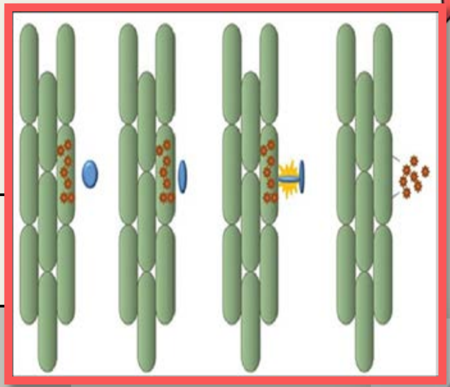
EXPERIMENTAL DESIGN-ULTRASOUND ASSISTED EXTRACTION

INVESTIGATED PARAMETERS

- Temperature: 20-60ºC
- Solvent: 0-100% EtOH
- Liquid/Solid ratio: 5-60mL/g
- Amplitude : 20-60%

+ Lower solvent volume
  Lower extraction time
  Lower temperature
  Preservation of sensitive compounds





Parameters	Levels				
Extraction temperature (T, ºC)	20	30	40	50	60
Solvent type (% aqueous ethanol)	0	25	50	75	100
Liquid /Solid ratio (mL/g)	5	19	33	46	60
Amplitude level (A%)	20	30	40	50	60

Duration: 20 min

130 W, 20 kHz, VCX-130 Sonics & Materials, with Ti–Al–V probe (13 mm)

EXPERIMENTAL DESIGN- ADSORPTION

Statistical program *Minitab* *(Release 13)* → Input of factors to be tested → Experimental design → **31 adsorption experiments**

INVESTIGATED PARAMETERS

- Temperature: 20-60ºC
- pH: 2-10
- L/S ratio: 0.01-0.05 mL/g
- Co : 50-500 mg/L

Parameters Levels (RSM Methodology)			
T (ºC)	pH	Liquid/Solid (r, mL/g)	Initial concentration of phenolics (C_0, mg/L)
20	2.00	0.01	50.0
30	4.00	0.02	162.5
40	6.00	0.03	275.0
50	8.00	0.04	387.5
60	10.00	0.05	500.0

Every experiment in 6 intervals: 0, 10, 20, 40, 60, 120 min

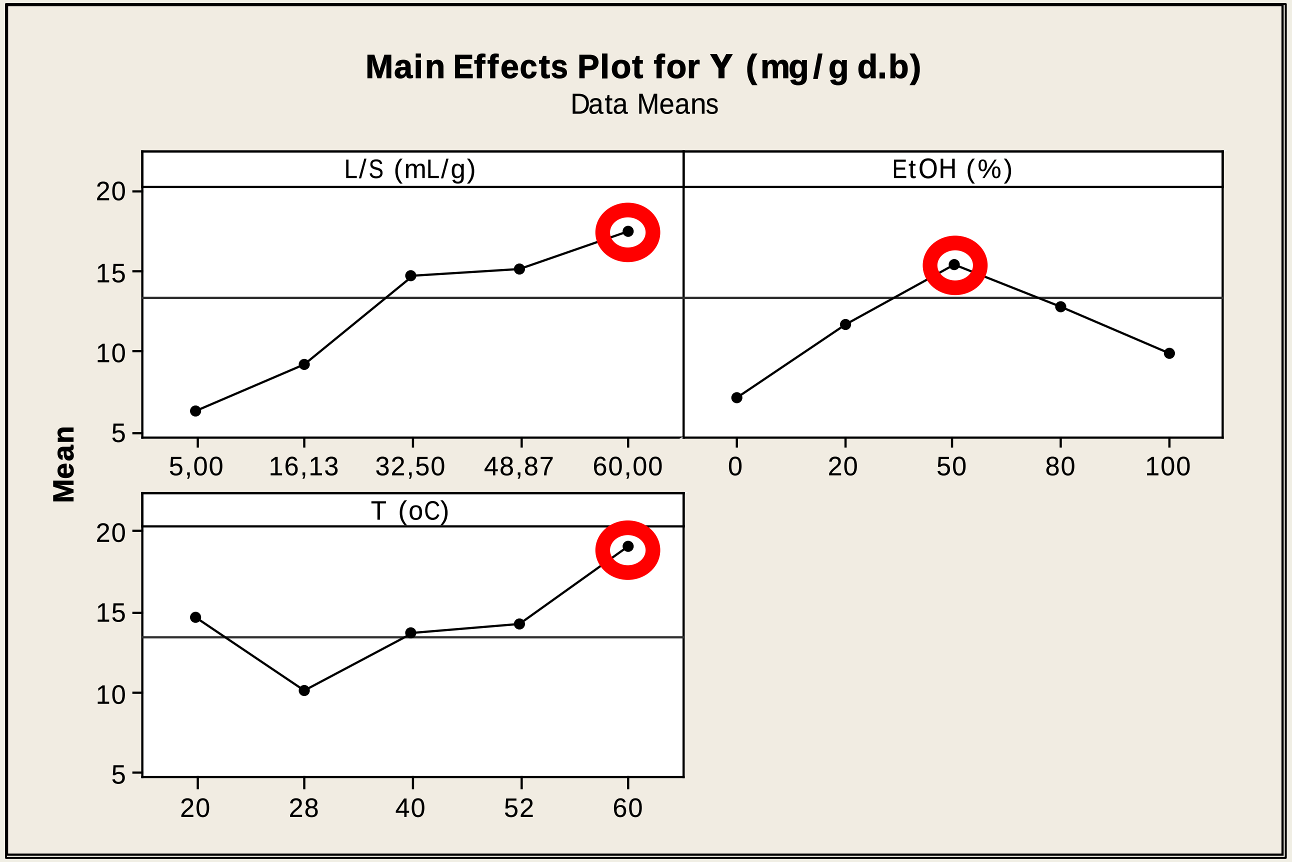
$$\text{Yield (\%)} = \frac{C_0 - C}{C_0} \times 100$$

C_0 : Initial phenolic concentration in solution

C : Remaining phenolic concentration in solution after adsorption

RESULTS AND DISCUSSION

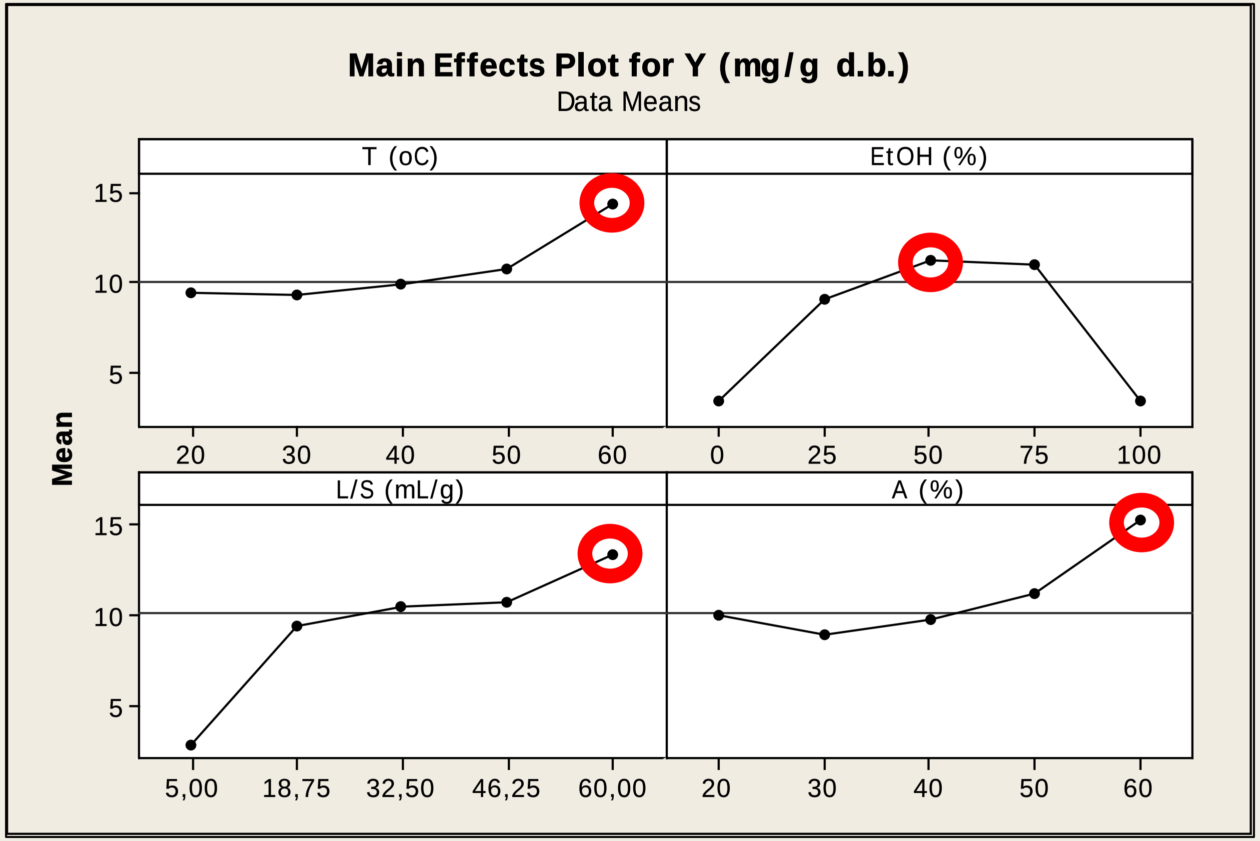
CONVENTIONAL EXTRACTION



Optimum Yield:
22.01 mg/g d.b

Optimum Conditions		
L/S	T°C	Solvent (%EtOH)
49.4 mL/g	60°C	66%

ULTRASOUND ASSISTED EXTRACTION

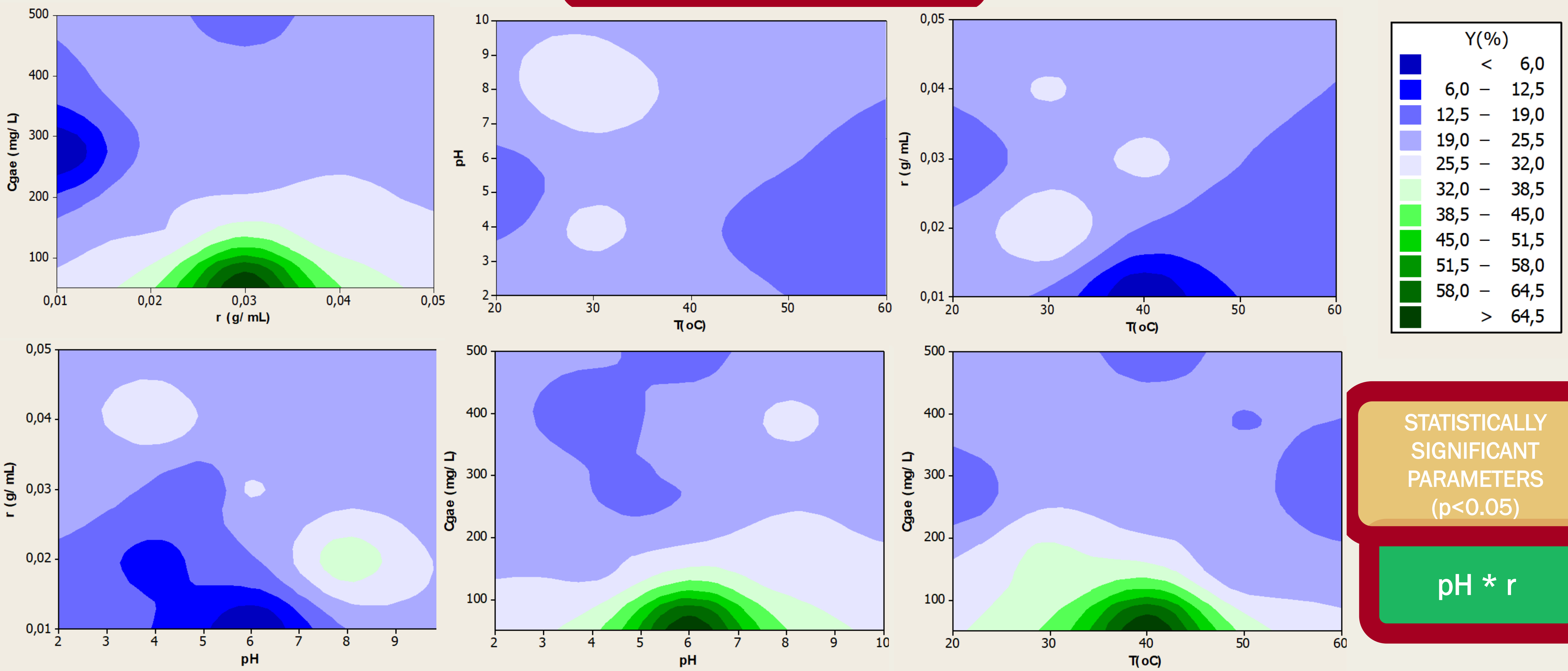


Optimum Yield:
18.54 mg/g d.b

Optimum Conditions			
L/S	Solvent (% EtOH)	T°C	Amplitude
53 mL/g	50.5%	60°C	60%

GALLIC ACID ADSORPTION YIELD-EFFECT OF VARIOUS PARAMETERS

Adsorption Yield: 0-70.69%



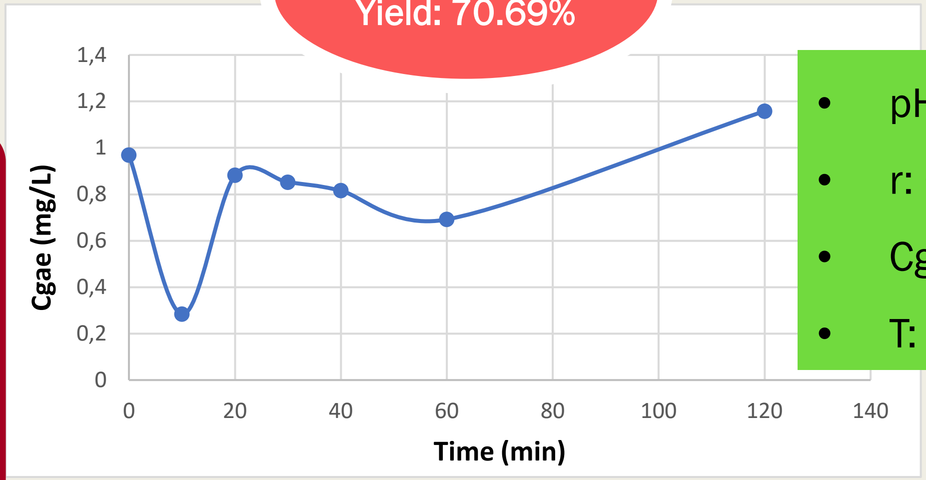
STATISTICALLY SIGNIFICANT PARAMETERS ($p<0.05$)

pH * r

GALLIC ACID/OMW ADSORPTION

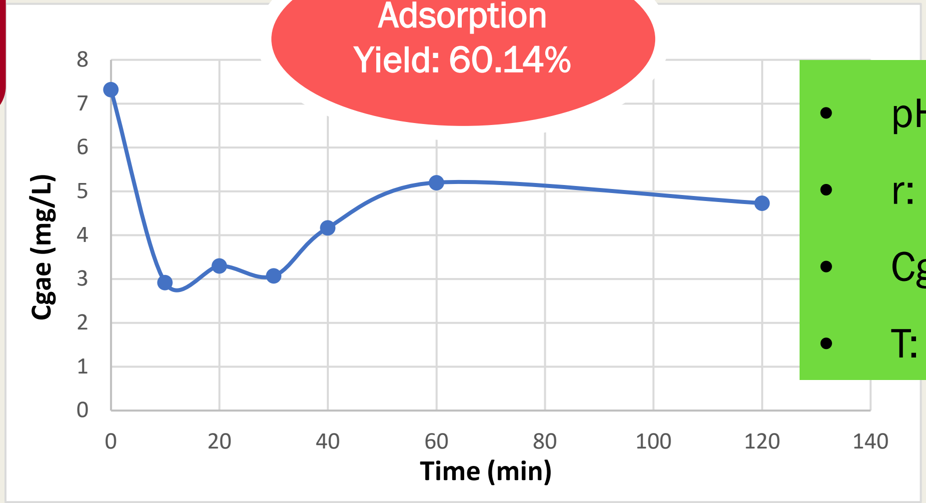
GALLIC ACID

Adsorption Yield: 70.69%



- pH: 6.0
- r: 0.03 g/mL
- Cgae: 50 mg/L
- T: 40ºC

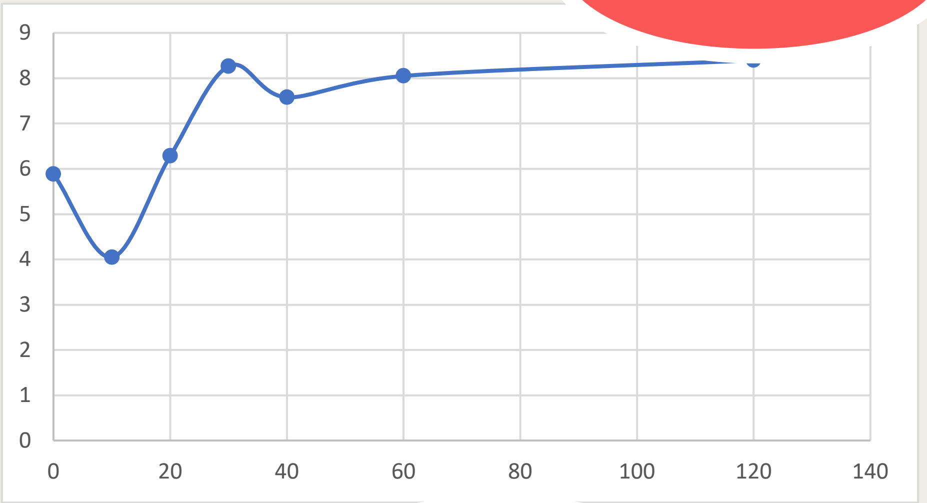
Adsorption Yield: 60.14%



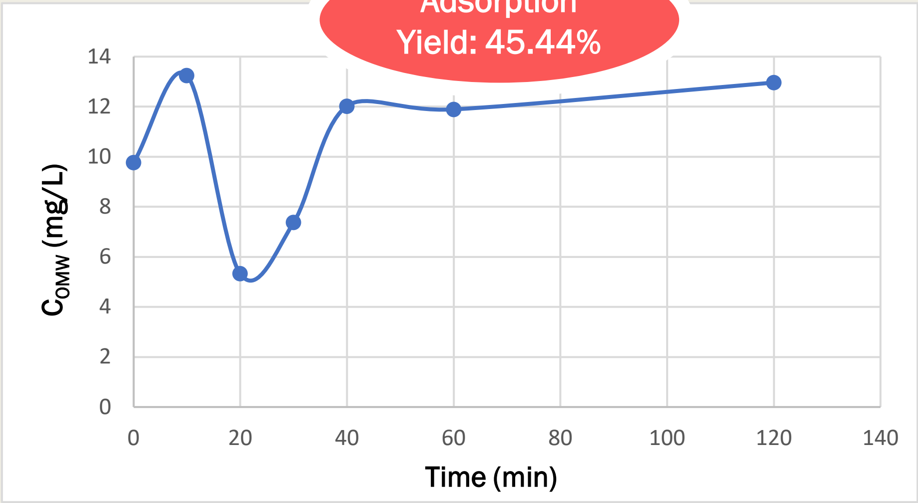
- pH: 8.0
- r: 0.02 g/mL
- Cgae: 162.5 mg/L
- T: 30ºC

OMW

Adsorption Yield: 31.19%



Adsorption Yield: 45.44%



CONCLUSIONS

- Conventional and UAE presented similar yield rates
- UAE: ↓ Extraction time
  ↓ Amount of solvent required → Most suitable option
- SCG can be used as a biosorbent, with adsorption efficiency up to 70%
- Further studies are required in order to:
  - Optimize batch adsorption yield of OMW bioactive compounds
  - Evaluate the adsorption yield of other main phenolic compounds of OMW, besides gallic acid
  - Investigate the adsorption mechanism and the possible adsorption sites of SCG

THANK YOU FOR YOUR ATTENTION…