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ADSORPTION OF PHENOLIC COMPOUNDS FROM OLIVE MILL WASTEWATERS ON SPENT COFFEE GROUNDS: ISOTHERMS, PURE PHENOLS ADSORPTION

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OLIVE OIL PRODUCTION

- One of the most widely consumed oils
- Economic importance for Mediterranean countries

2.4 million tons of olives/year

- 95% of total world production
- 90% is destined for olive oil production

(Solomakou and Goula, 2021)

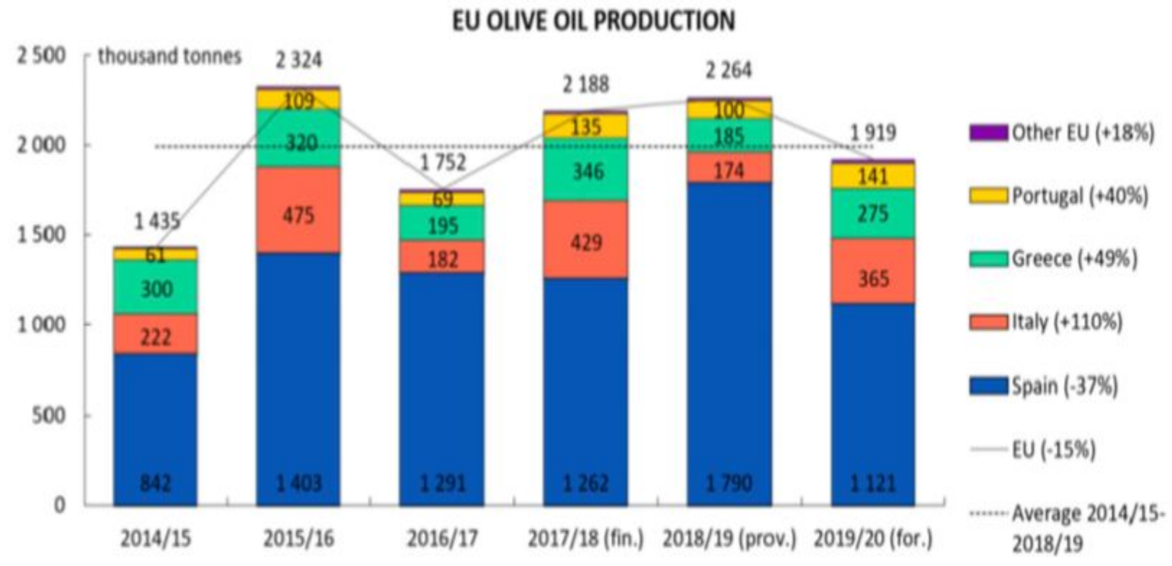
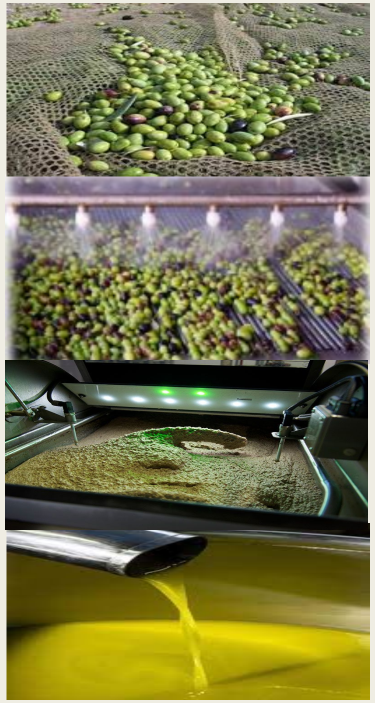
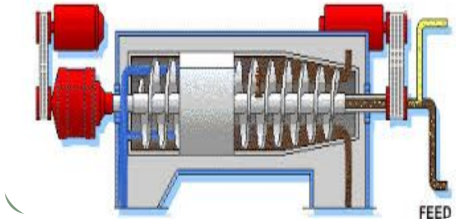


Fig. 1 Olive oil production within the European Union (International Olive Council, 2021)



- **Olive collection**
- **Purification-Washing**
- **Olive crashing**
- **Oil separation**

OLIVE OIL EXTRACTION SYSTEMS



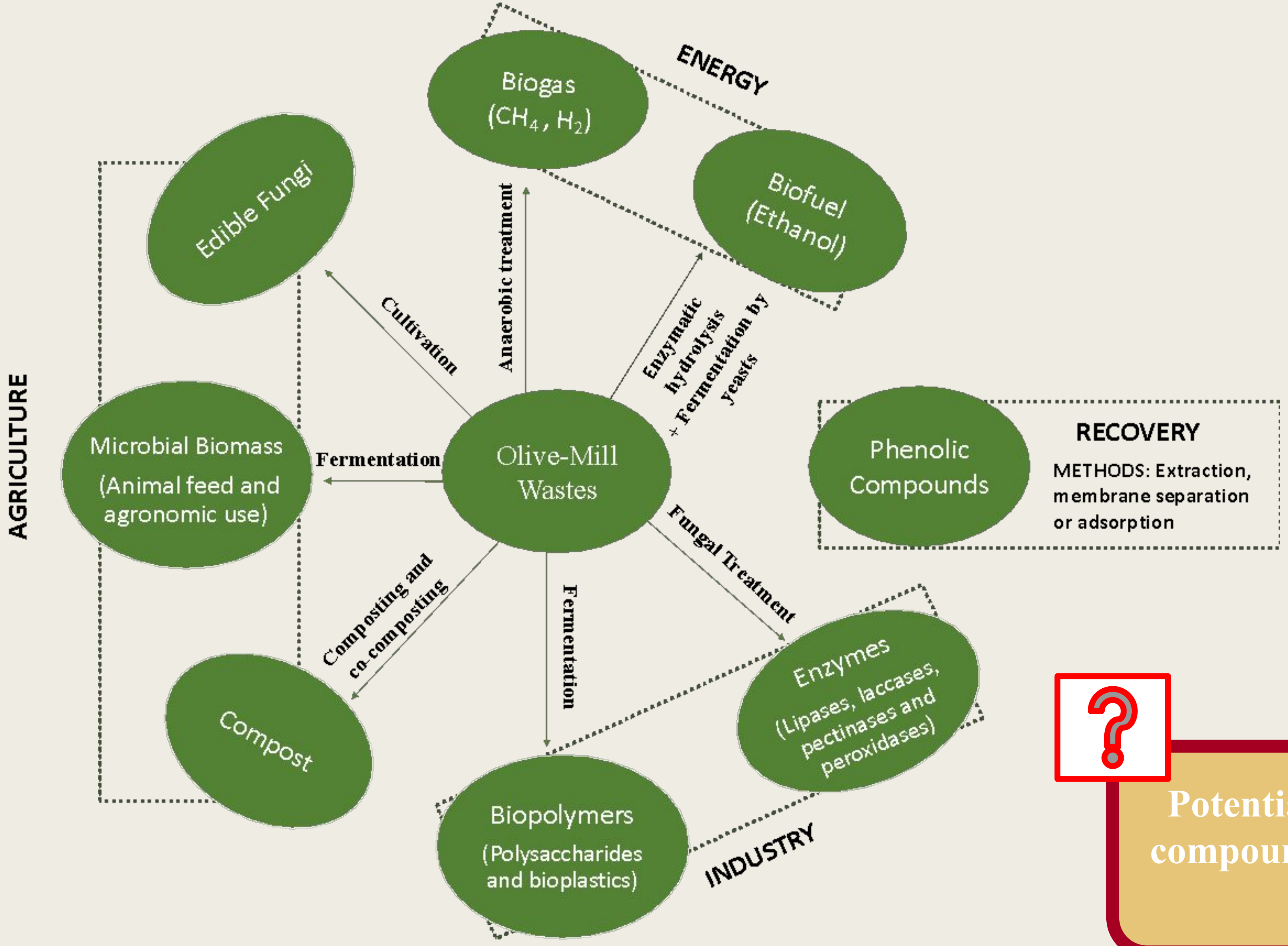
OLIVE MILL WASTEWATER

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)

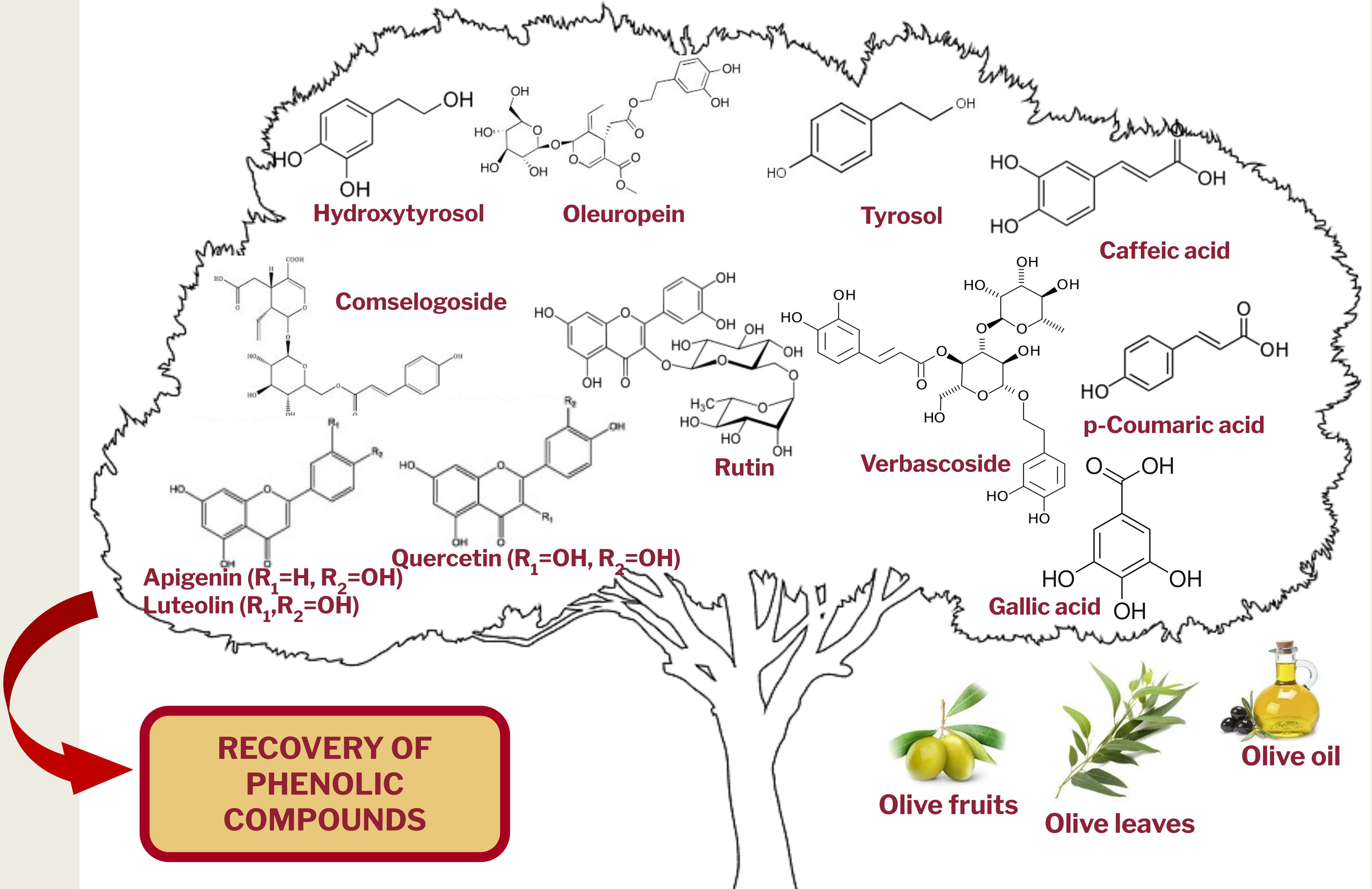
- Liquid waste of three-phase extraction system
- Aqueous, dark, foul smelling
- High **organic content** (57.2-62.1%)
- **Acidic** character (pH 2.2-5.9)
- **Phenolic** compounds (up to 80 g/L)
- **Solid matter** (total solids up to 20 g/L)

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

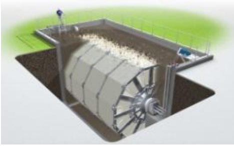
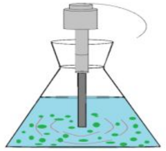
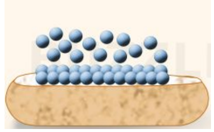
OMW MANAGEMENT



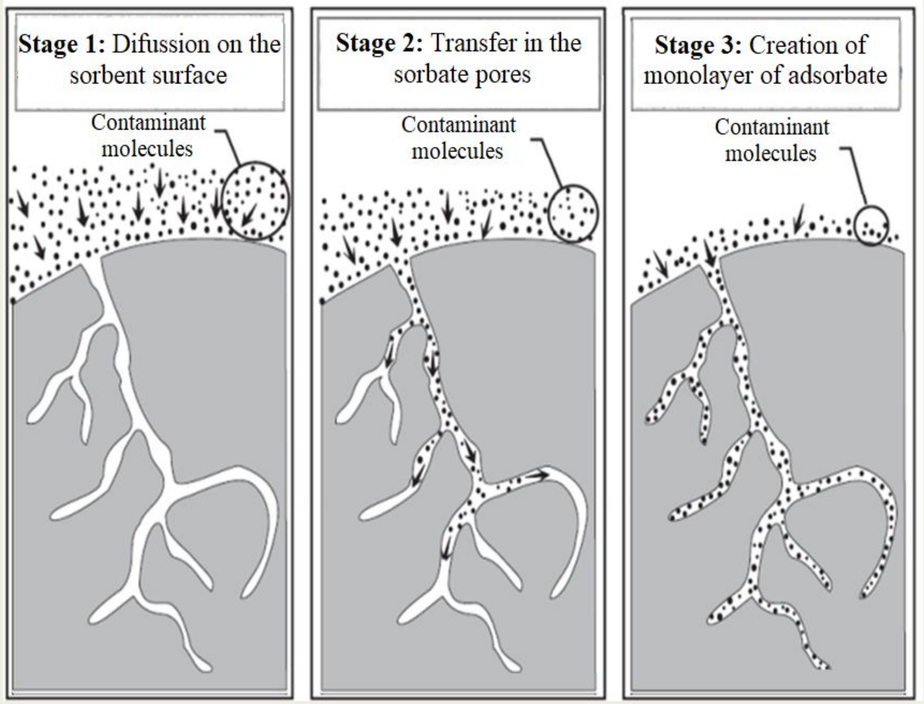
Potential source of phenolic compounds and other natural antioxidants!


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

RECOVERY OF BIOACTIVE COMPOUNDS

- Membrane separation 
- Extraction 
- Chromatographic separation 
- Adsorption 

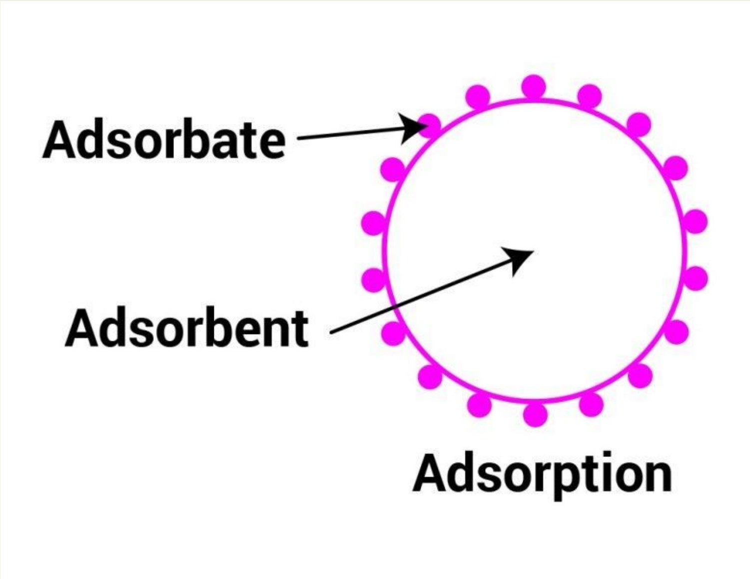
Transfer of a solute from either a gas or liquid/solution to a solid. The solute is held to the surface of the solid as a result of intermolecular attraction with the solid molecules.



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

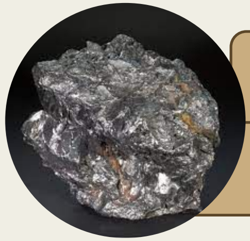
ADSORPTION AFFECTING PARAMETERS

- Temperature
- pH
- Solvent of adsorbate/sorbent ratio
- Initial concentration of adsorbate
- Particle size of biosorbent

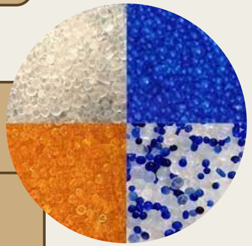


ADSORBENTS

COMMERCIAL ADSORBENTS




- *Activated Carbon*
- *Graphite*

- *Silica Gel*
- *Zeolite*

- *Polymer Resins*

- High initial cost
- Need for regeneration

BIOSORBENTS

- ✔ Natural materials from food industry
- ✔ Low cost & abundant
- ✔ Environmentally friendly

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	Phenolic compounds 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	Phenolic compounds from OMW	≤40%	Stasinakis et al., 2008
Olive stone and pulp	Phenolic compounds 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

SPENT COFFEE GROUNDS (SCG)

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

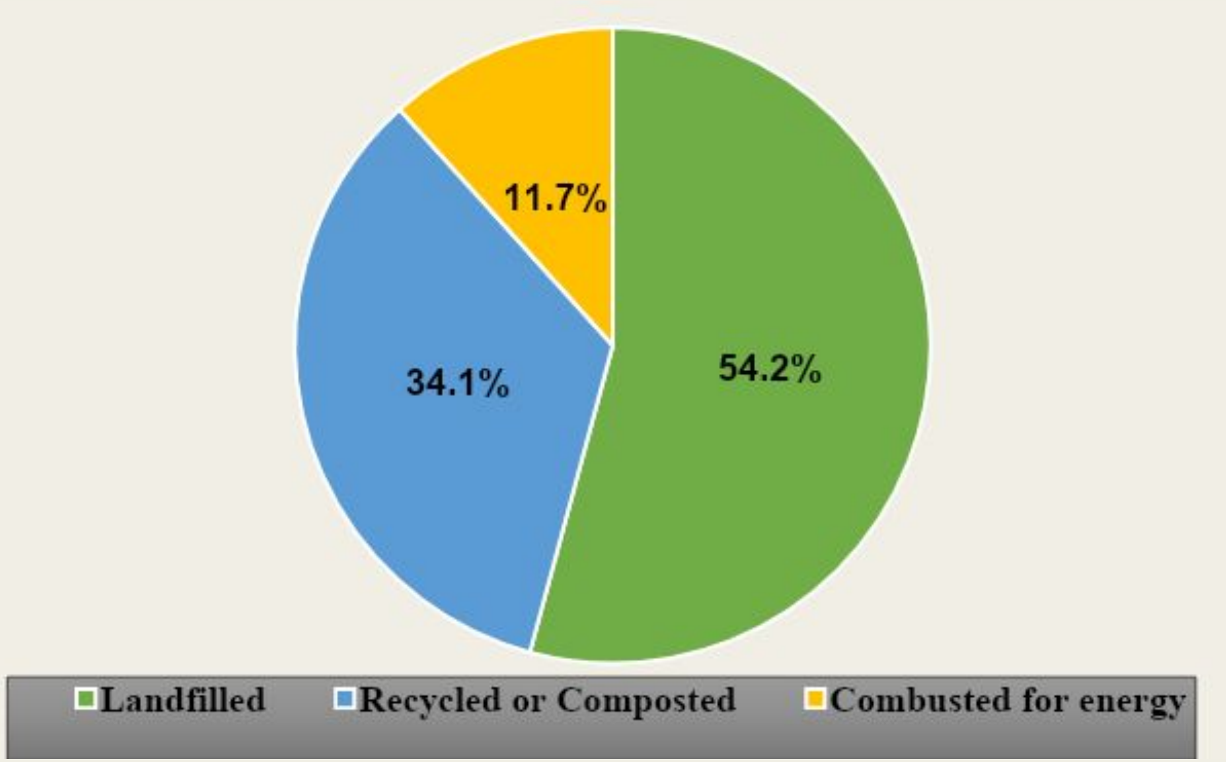
- 1 ton of green coffee beans → 650 kg of SCG

- 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

WASTE MANAGEMENT



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

⬆ Organic content

⬆ Toxicity

 Pose a severe threat for the environment

- ✔ Low cost & abundant biosorbent
- ✔ Environmentally friendly
- ✔ Source of bioactive components
- ✔ Used only as activated carbon

AIM OF THE STUDY

- ✔ **Holistic exploitation** of SCG as a **source of phenolics** and as a **biosorbent** for the recovery of bioactive components from OMW
- ✔ **Optimization** of batch adsorption process
- ✔ Experimental adsorption of **pure compounds** in order to investigate OMW's adsorption mechanism
- ✔ Development of a **novel, low cost** method for the recovery of phenolic compounds from OMW and their exploitation as **food additives** in food industry

MATERIALS AND METHODS

WASTE PREPARATION & EXTRACTION PROCESS

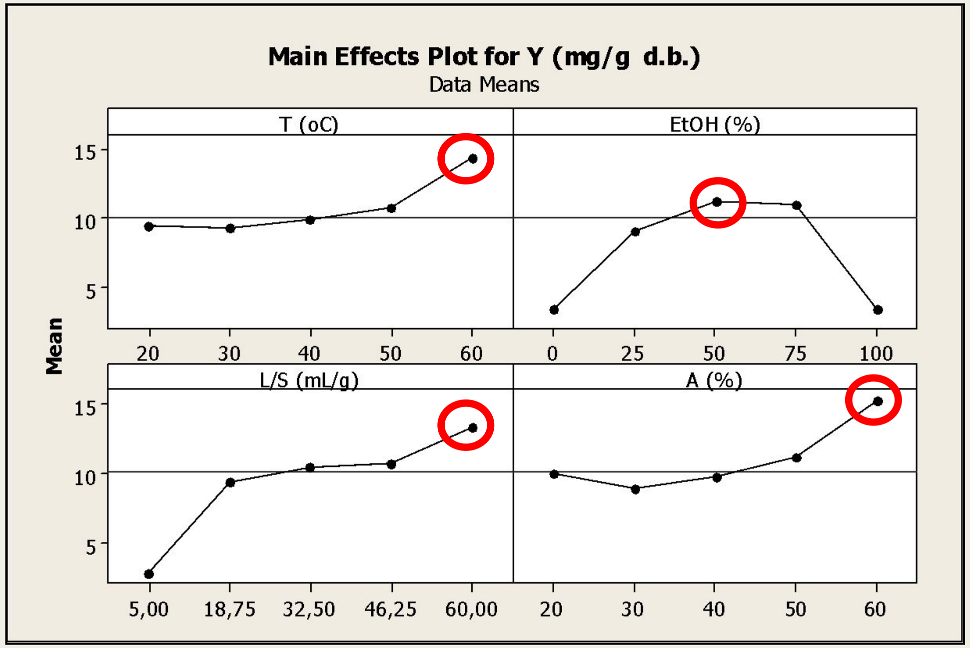
Waste after beverage production

Drying (40ºC, 24 h) → ULTRASOUND: Extraction and removal of phenolics → Filtration

Determination of phenolic compounds → WAST E: Drying (105ºC, 24 h) → Phenolic compounds / OMW: Batch Adsorption (0, 10, 20, 30, 40, 60 min) → Determination of phenolic compounds

SCG PHENOLICS EXTRACTION

- Conventional extraction
- Ultrasound-assisted extraction
- Microwave-assisted extraction



Optimum Yield: 18.54 mg/g d.b

Optimum Conditions			
L/S	Solvent (aqueous EtOH)	T	Amplitude
53 mL/g	50.5% EtOH v/v	60ºC	60%

EXPERIMENTAL DESIGN- ADSORPTION

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

INVESTIGATED PARAMETERS

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

Parameters Levels (RSM Methodology)

T (°C)	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

ADSORPTION ISOTHERMS

- **Langmuir Isotherm**

$$\frac{Ce}{qe} = \frac{1}{bQm} + \frac{Ce}{Qm}$$

- **Freundlich Isotherm**

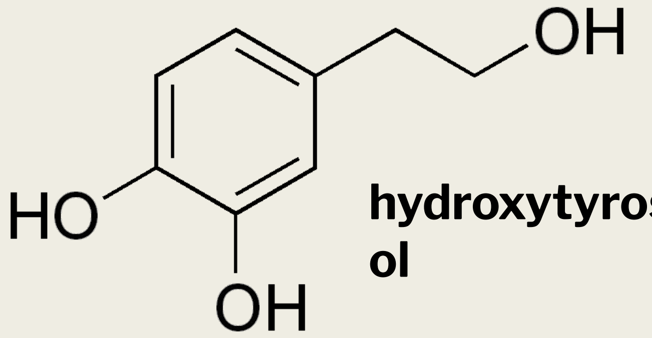
$$\ln q_e = \ln K_F + \frac{1}{n \ln Ce}$$

- **Temkin Isotherm**

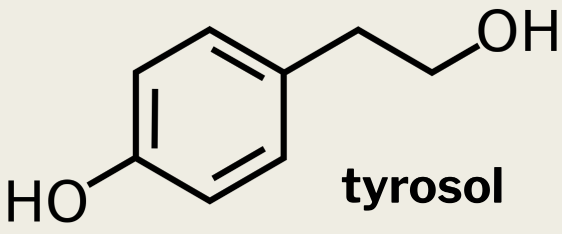
$$q_e = \frac{RT}{B_T}\ln K_T + \frac{RT}{B_T}\ln c_e$$

- **c_e** (g/L): unadsorbed phenolic compounds concentration in solution at equilibrium
- **q_e** (mg/g): amount of phenolic compounds adsorbed at equilibrium
- **b** (L/g): equilibrium constant or Langmuir constant related to the affinity of binding sites
- **Q_m** (mg/g): a particle limiting adsorption capacity when the surface is fully covered with phenolic compounds and assists in the comparison of adsorption performance
- **K_F** : Freundlich constant (indicates adsorption capacity of adsorbent)
- **n** : constant thatshows greatness of relationship between adsorbate and adsorbent
- **B_T (kJ/mol)**: Freundlich constant that shows adsorption capacity of adsorbent
- **K_T** : Temkin isotherm parameter

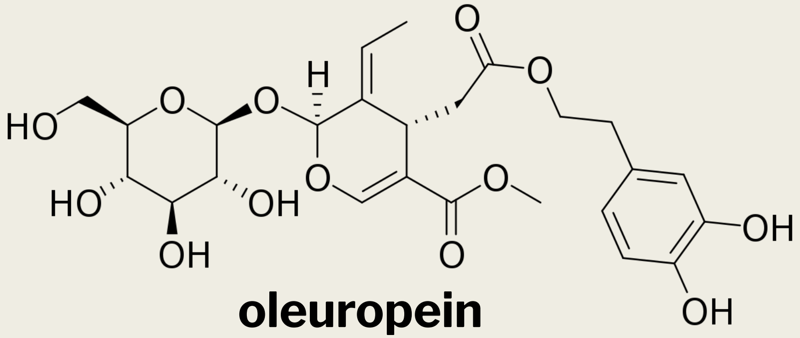
ADSORPTION OF MAIN PHENOLIC COMPOUNDS



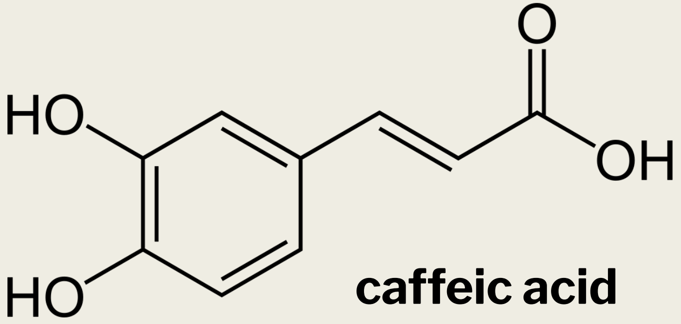
hydroxytyros
ol



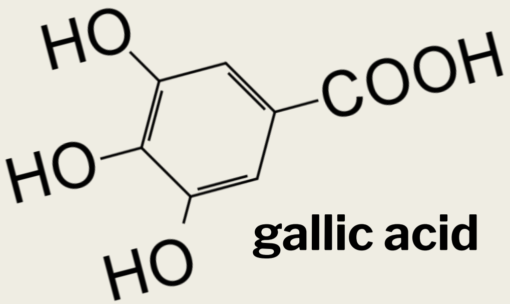
tyrosol



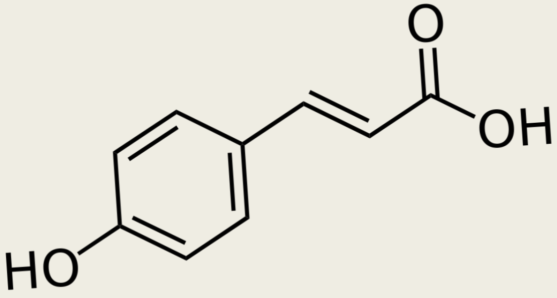
oleuropein



caffeic acid



gallic acid

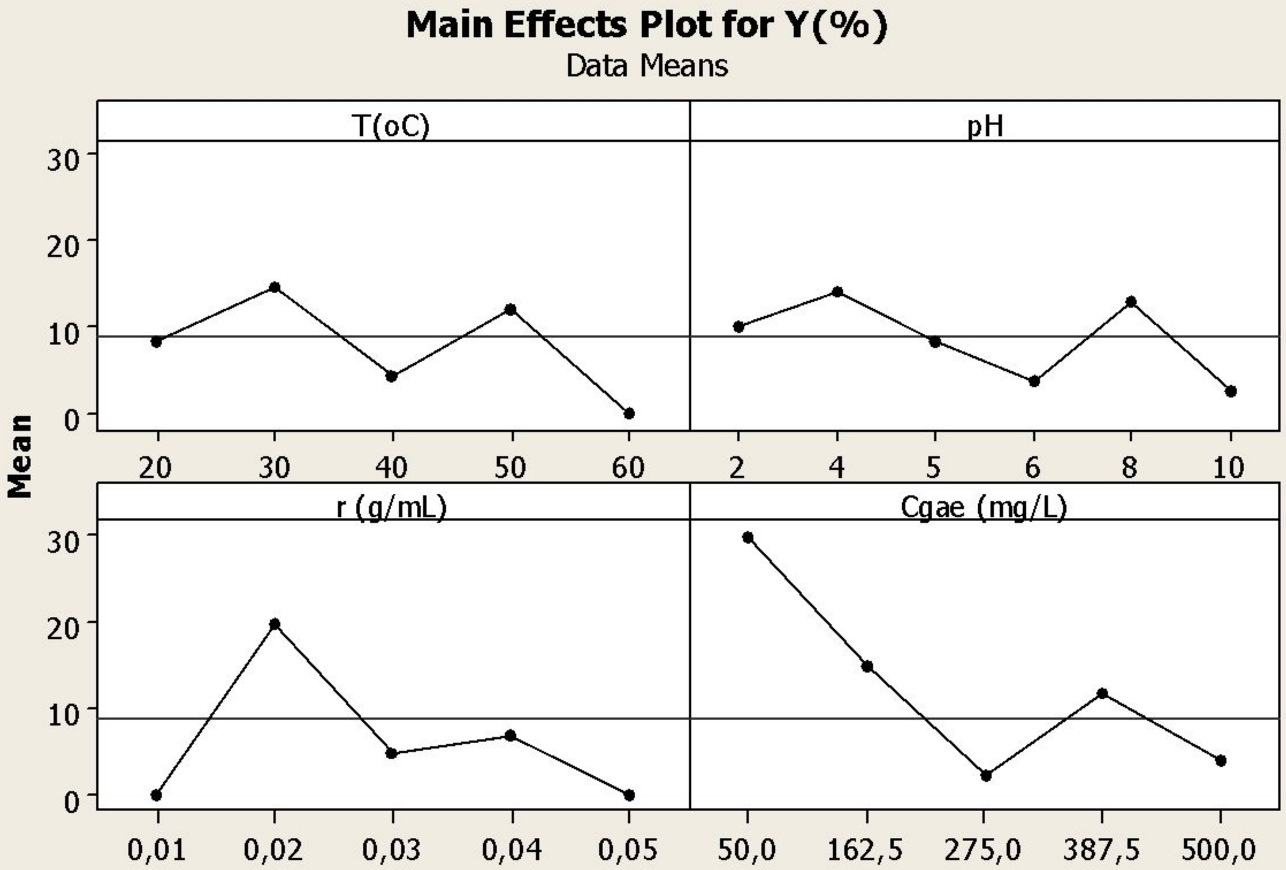


p-coumaric
acid

Adsorption at optimum
condition

RESULTS AND DISCUSSION

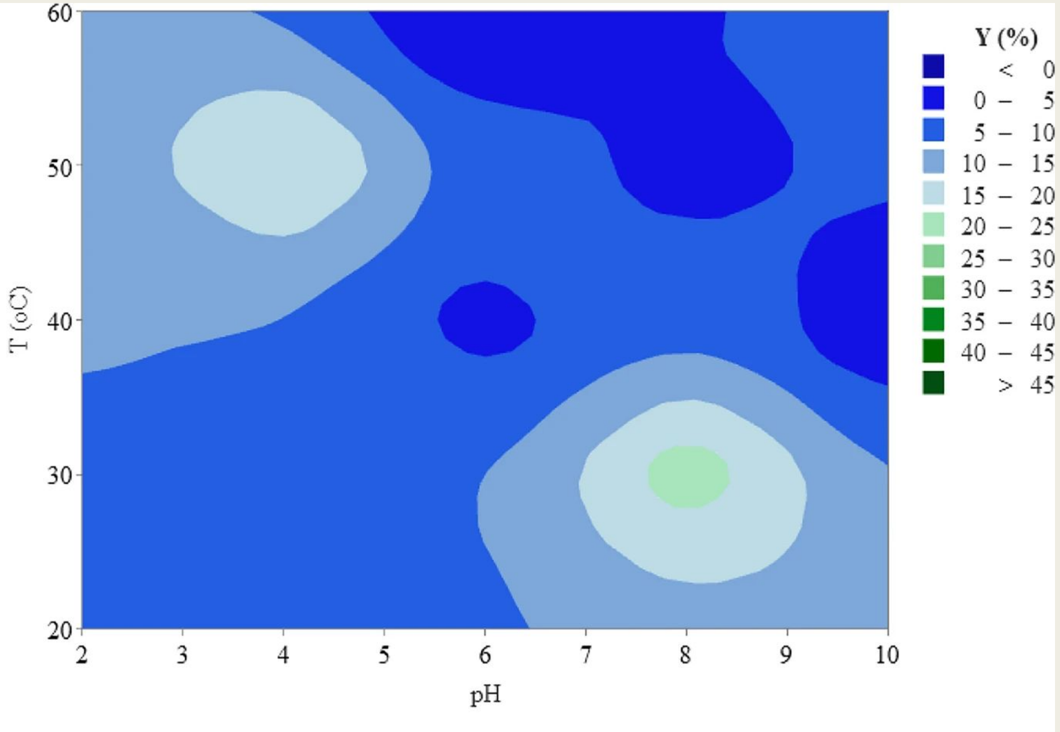
ADSORPTION OF OMW PHENOLIC COMPONENTS

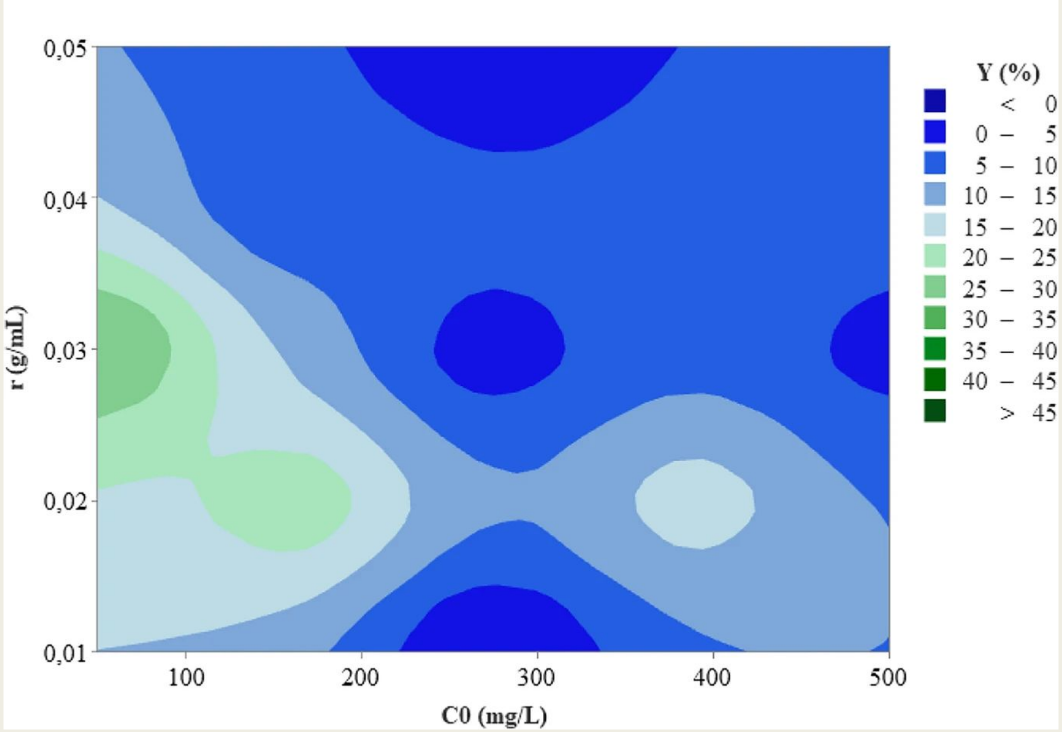


↑ ToC/r/Cphenolics → ↓ Y(%)

pH 4.0 & pH 8.0 → ↑ Y(%)

ADSORPTION OF OMW PHENOLIC COMPOUNDS

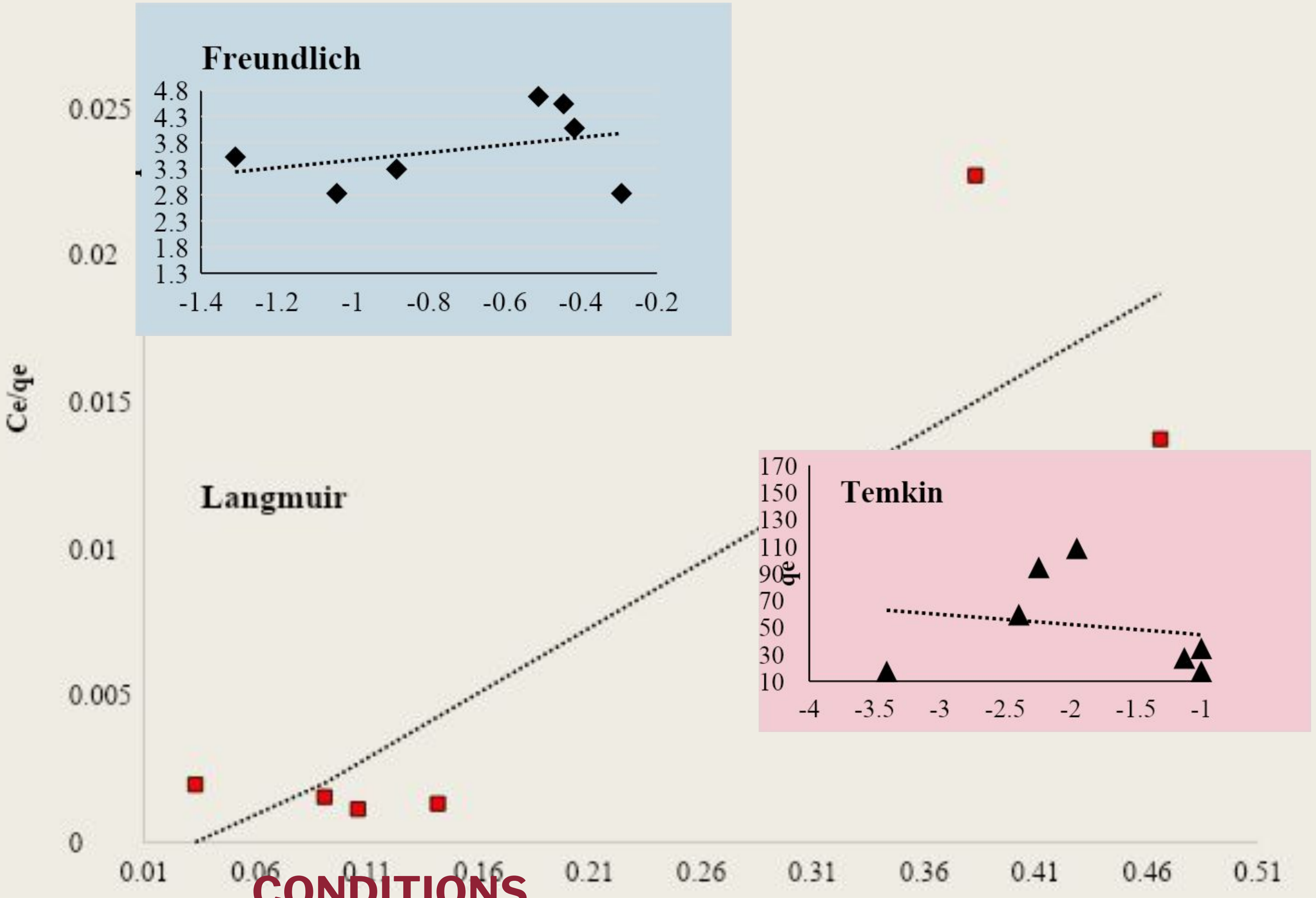




OPTIMUM CONDITIONS

T=30°C, pH= 8.0, r=0.02 g/mL, C_0=162.5 mg/L

ISOTHERMS



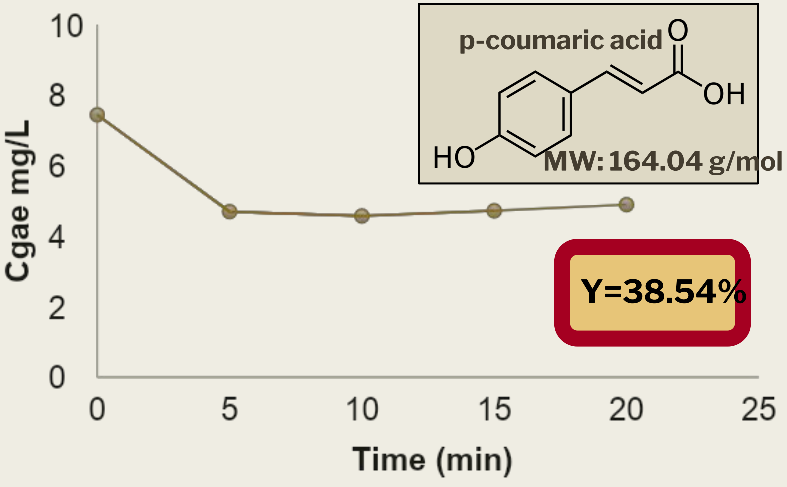
CONDITIONS

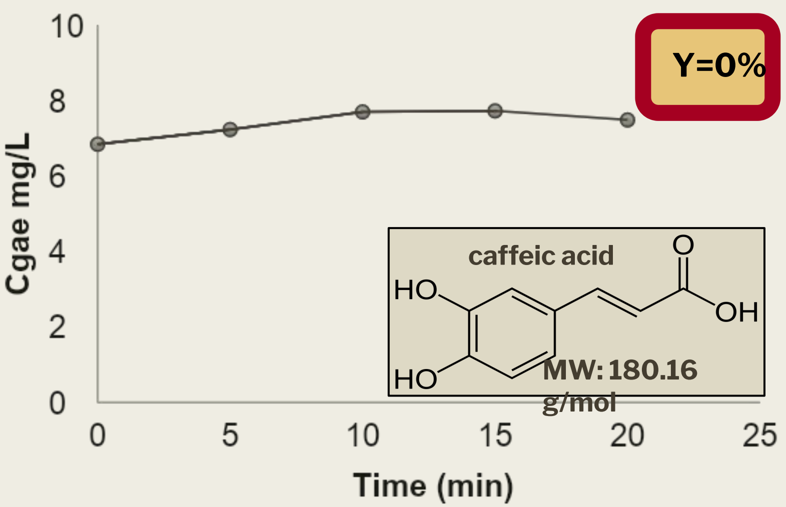
- ✔ T=50°C
- ✔ pH= 4.0
- ✔ r=0.02 g/mL
- ✔ C_0=50-500 mg/L

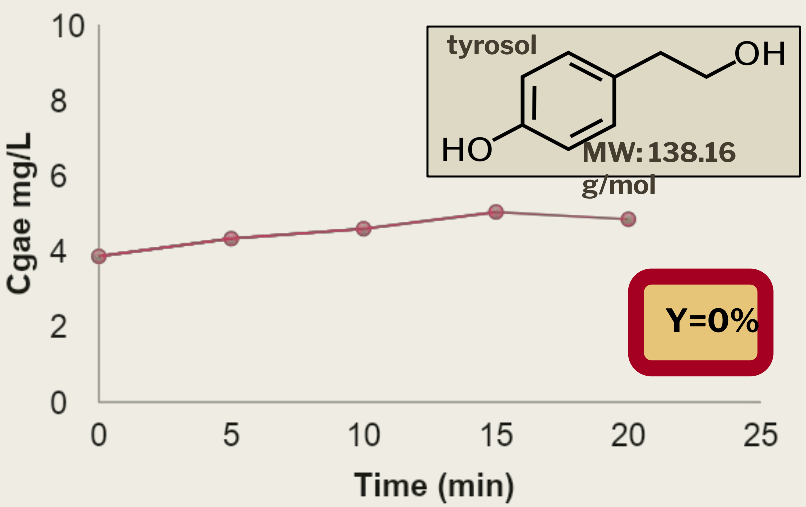
Maximum adsorption capacities (q_{max}) of phenolic compounds from OMW onto various adsorbents (Solomakou and Goula, 2021)

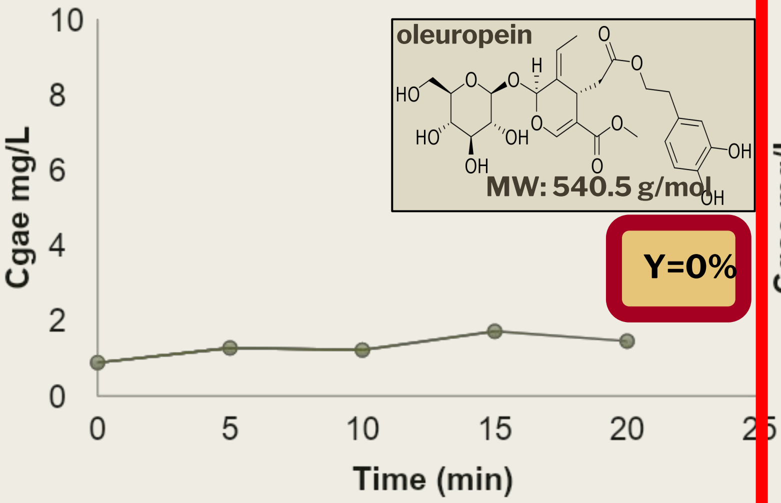
Adsorbent	Adsorption capacities (q_{max}) (mg/g)
Activated carbon	65
Activated carbon	340.6
Activated carbon from olive husk	349.92
Activated carbons from olive stone and pulp	91.74
Active charcoal	390
Banana peel	688.9
Combusted olive pomace	11.4
Commercial activated carbon	308
Commercial starch	32.35
Magnetic nanoparticles	79.09
Milk protein activated carbon	152.4
Olive pit–derived activated carbon	375
Orange juice by product	166.67
Polymeric resins	288
Pomegranate peel	44.44
Pomegranate seed	56.82
Resin	370
Sand	39.01
Spent Coffee Grounds	22.49
Wheat bran	487.3

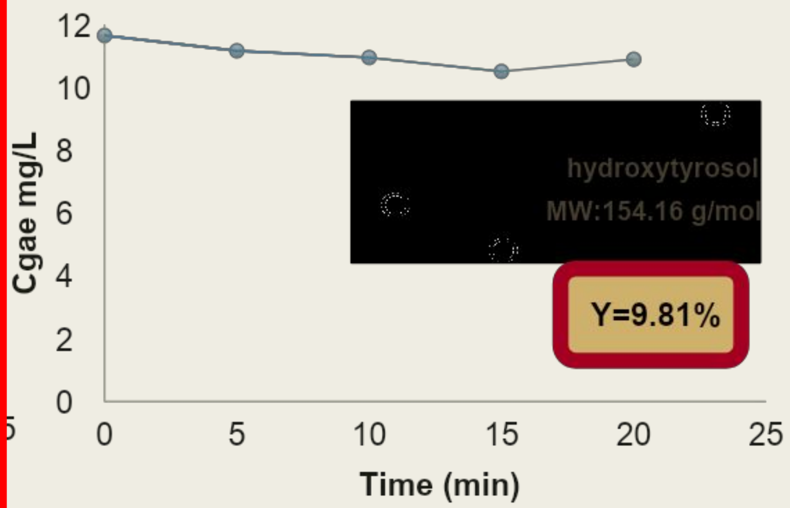
ADSORPTION OF MAIN PHENOLIC COMPOUNDS

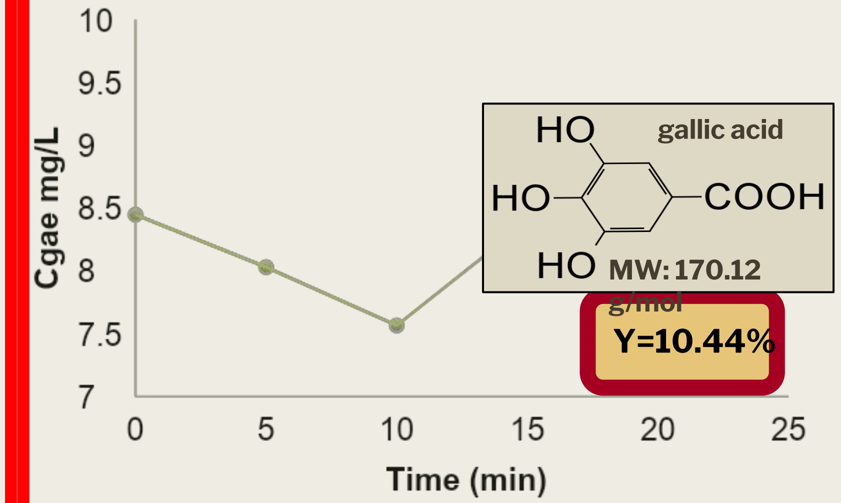






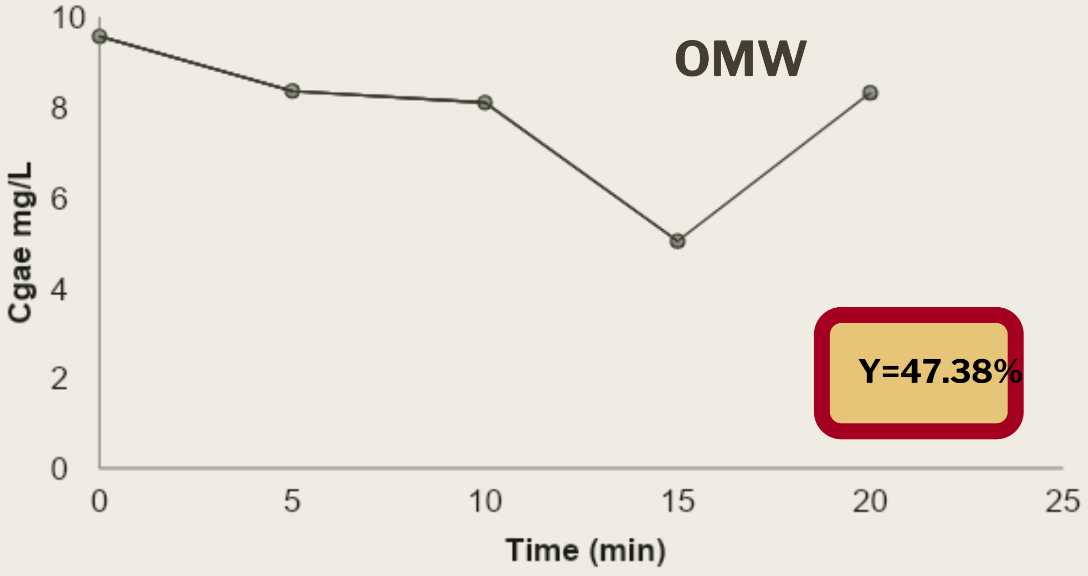


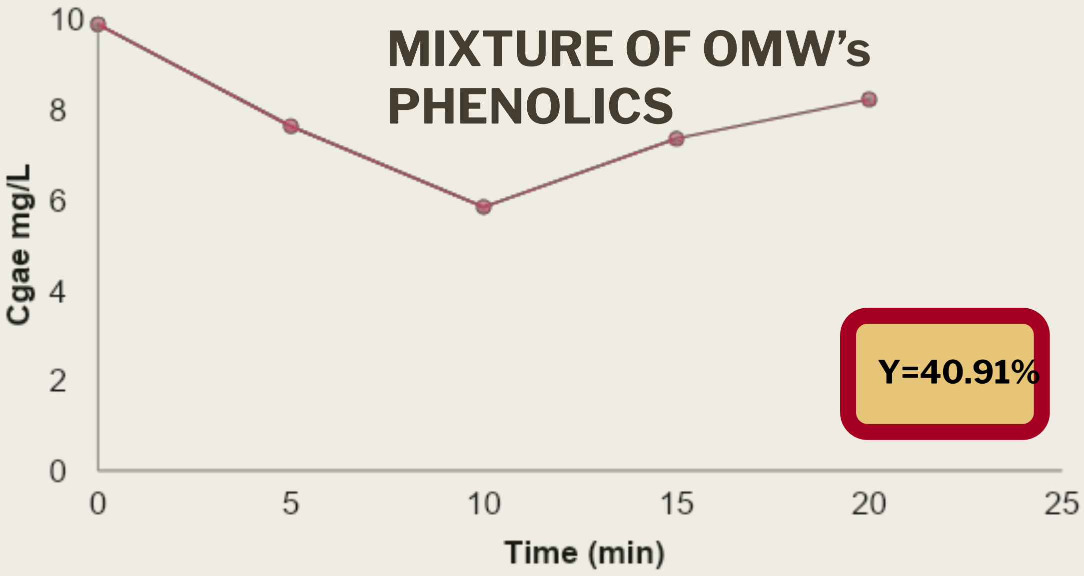




OPTIMUM CONDITIONS

T=50°C, pH= 4.0, r=0.02 g/mL, C_0=200 mg/L





	$X_i = C_i/C_{total}$	Y_i/Y_{total}
p-coumaric	0.012	0.94
caffeic acid	0.12	0
tyrosol	0.48	0
hydroxytyrosol	0.14	0.24
oleuropein	0.12	0
gallic acid	0.12	0.26

$Y_{total} = X_1 * Y_1 + X_2 * Y_2 + \ldots + X_n * Y_n = 0.012*38.54\% + 0\% + 0\% + 0.14*9.81\% + 0\% + 0.12*10.44\% = 3.08\ \%$

CONCLUSIONS

- OMW phenolics presented **maximum adsorption yield of 47.38%** using SCG as biosorbent, value considered satisfactory given the omission of thermal or chemical activation
- Adsorption of model OMW phenolics presented **similar efficiencies**
- Main adsorbed phenolics appeared to be **p-coumaric** and **gallic aci**d and **hydroxytyrosol**
- Adsorption is influenced by the presence of individual phenolic components

THANK YOU FOR YOUR ATTENTION…