DEPARTMENT OF FOOD SCIENCE AND TECHNOLOGY,
SCHOOL OF AGRICULTURE,
ARISTOTLE UNIVERSITY OF THESSALONIKI

" *Improving the recovery of phenolic compounds from olive mill wastewater by using activated spent coffee grounds* "

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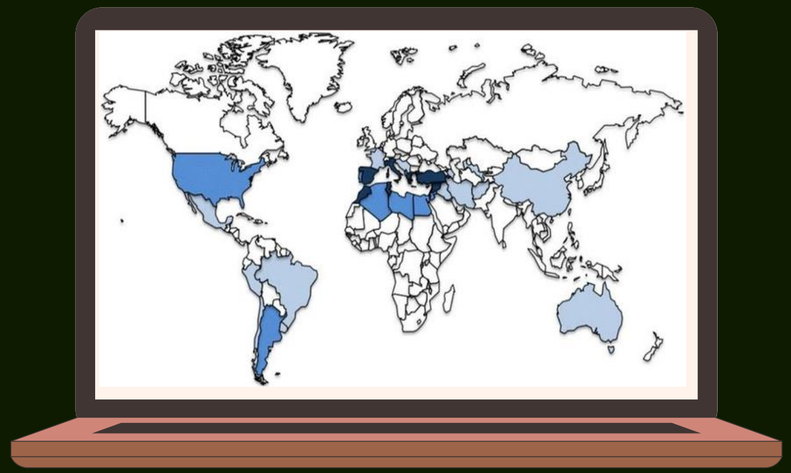
CHANIA, JUNE 2023

OLIVE OIL PRODUCTION

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

2.4 million tons of olives/year



>1 million tons

1-10 million tons

>10 million tons

Guo *et al.*, 2018

Solomakou and Goula, 2021

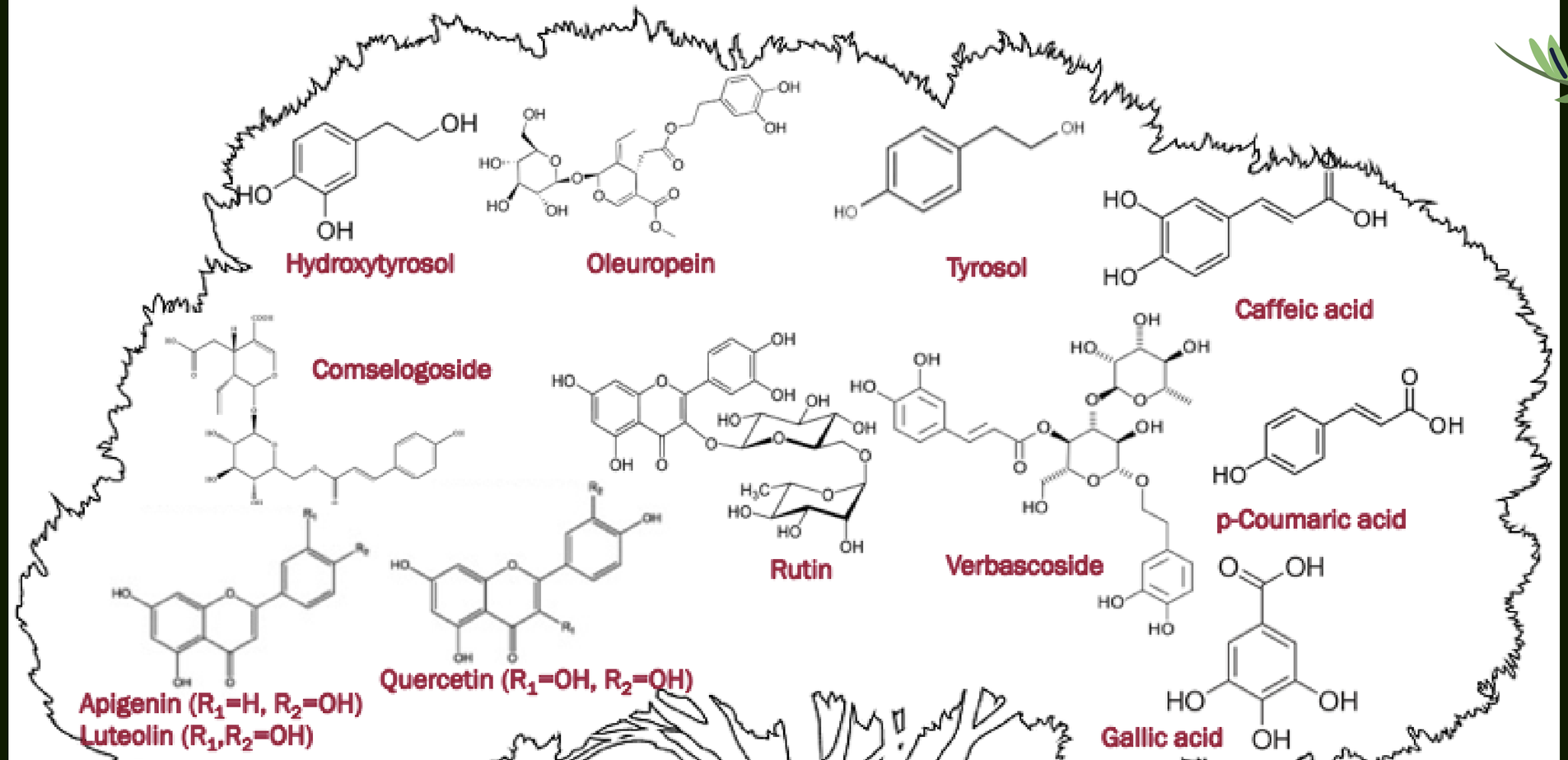
1. Olive collection
2. Purification-Washing
3. Olive crashing
4. Oil separation

OLIVE MILL WASTEWATER (OMW)

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



RECOVERY OF PHENOLIC COMPOUNDS

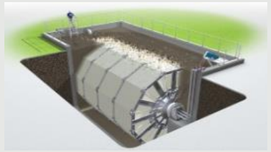
Olive fruits

Olive leaves

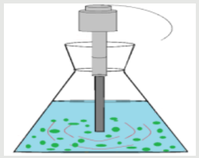
Olive oil

RECOVERY OF BIOACTIVE COMPOUNDS

Membrane separation

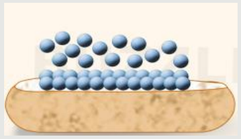


Extraction

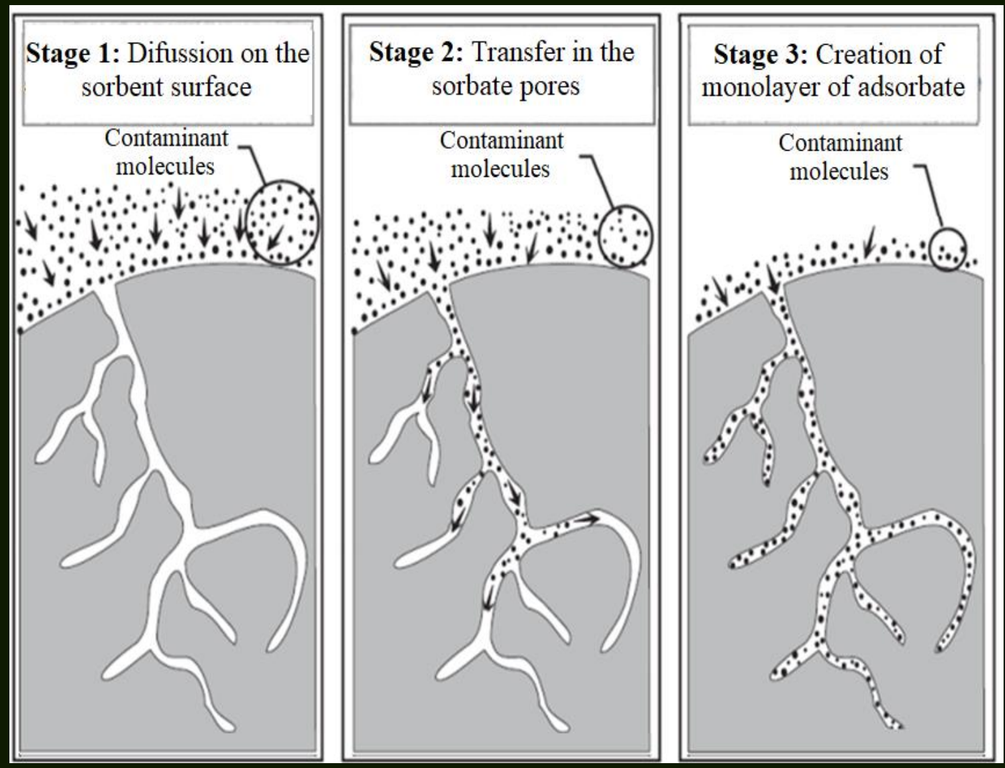


Chromatographic separation

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

ADSORBENTS

ACTIVATED CARBON

GRAPHITE

SILICA GEL

ZEOLITE

POLYMER RESINS

- **HIGH INITIAL COST**
- **NEED FOR REGENERATION**

BIOSORBENTS

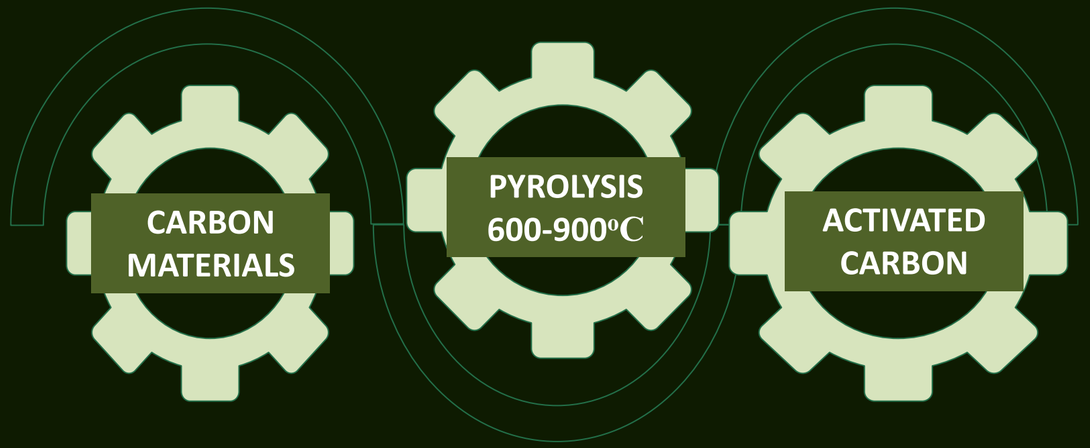
✓Natural materials from food industry

✓Low cost & abundant

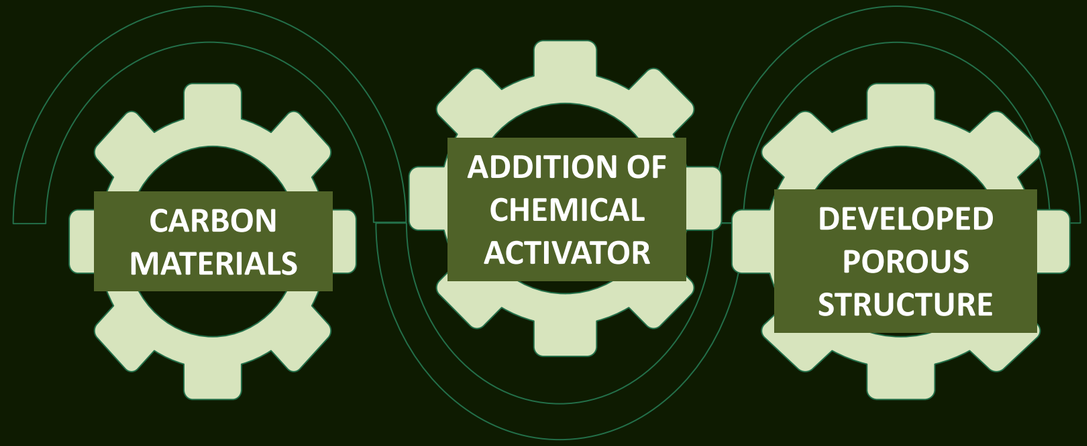
✓Environmentally friendly

ADSORBENT/BIOSORBENT PRODUCTION

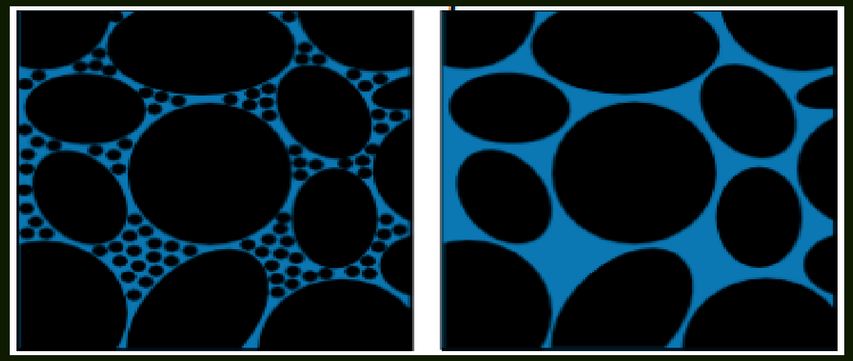
PHYSICAL ACTIVATION-PYROLYSIS



CHEMICAL ACTIVATION



***Chemical Activators: Phosphoric acid, Potassium hydroxide, Sodium hydroxide, Calcium chloride and Zinc chloride**



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

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

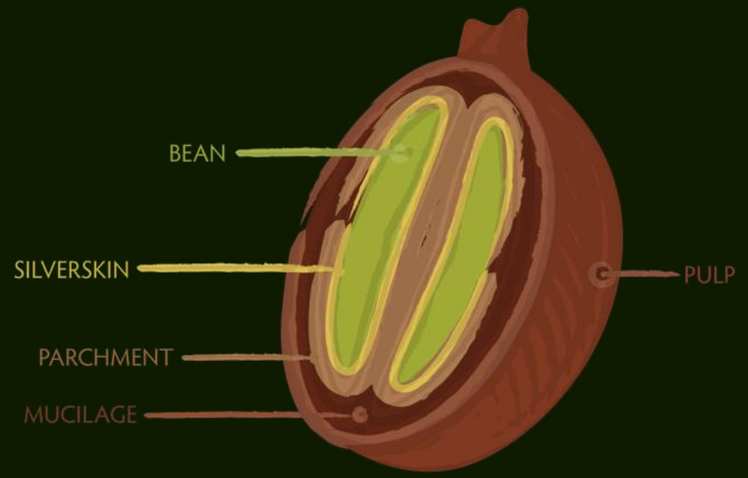
- 1 kg of soluble coffee ➡ 2 kg of wet SCG

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

  - ICO: > $9{,}9 \times 10^6$ Kg of coffee consumption in 2021

ICO, 2022

COFFEE INDUSTRY'S BY-PRODUCTS



DRY PROCESSING

WET PROCESSING

COFFEE HUSK

~15%

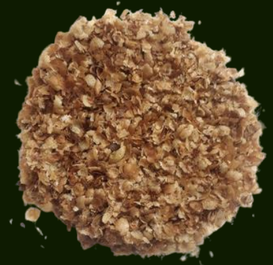
COFFEE HUSK

~15%

COFFEE PULP

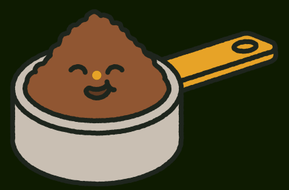
29-35%

ROASTING



COFFEE SILVERSKIN

1-3%

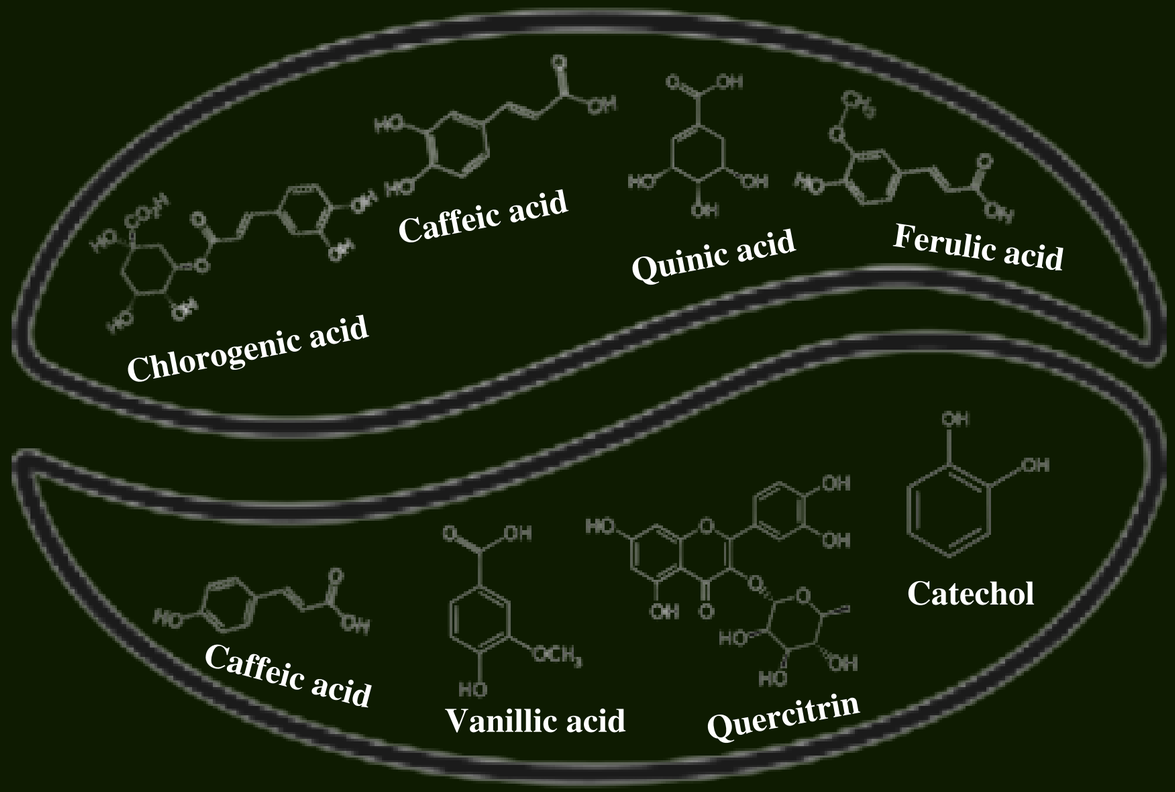


Spent Coffee Grounds

45-55 %

SCG CHEMICAL COMPOSITION

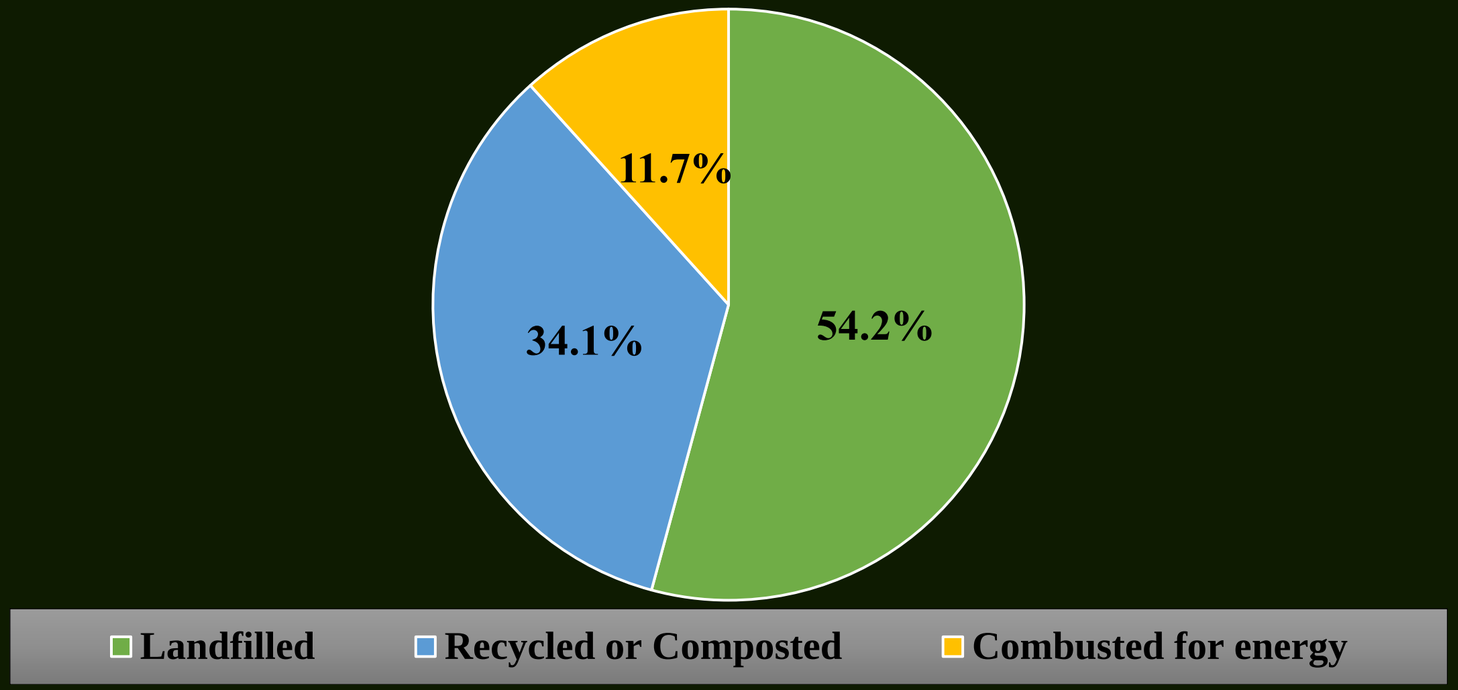
Component	Concentration
Moisture	1.18 – 74.72 (%)
Cellulose	12.40 ± 0.79 (g/100 g d.b.)
Hemicellulose	39.10 ± 1.94 (g/100 g d.b.)
Arabinose	3.60 – 6 (g/100 g d.b.)
Mannose	19.07 – 47 (g/100 g d.b.)
Galactose	16.43 – 30 (g/100 g d.b.)
Lignin	23.90 ± 1.70 (g/100 g d.b.) Insoluble 17.59 ± 1.56 Soluble 6.31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



***d.b.: dry basis**

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

WASTE MANAGEMENT

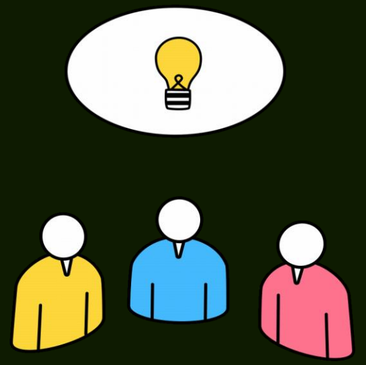


Waste management of coffee by-products (U.S. Environmental Protection Agency (EPA, 2017).

⬆ 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
- ✓ Potential increase of adsorption efficiency after biosorbent pre-treatment (thermal or chemical activation)
- ✓ Development of a **novel, low cost** method for the recovery of phenolic compounds and their exploitation as **food additives** in food industry

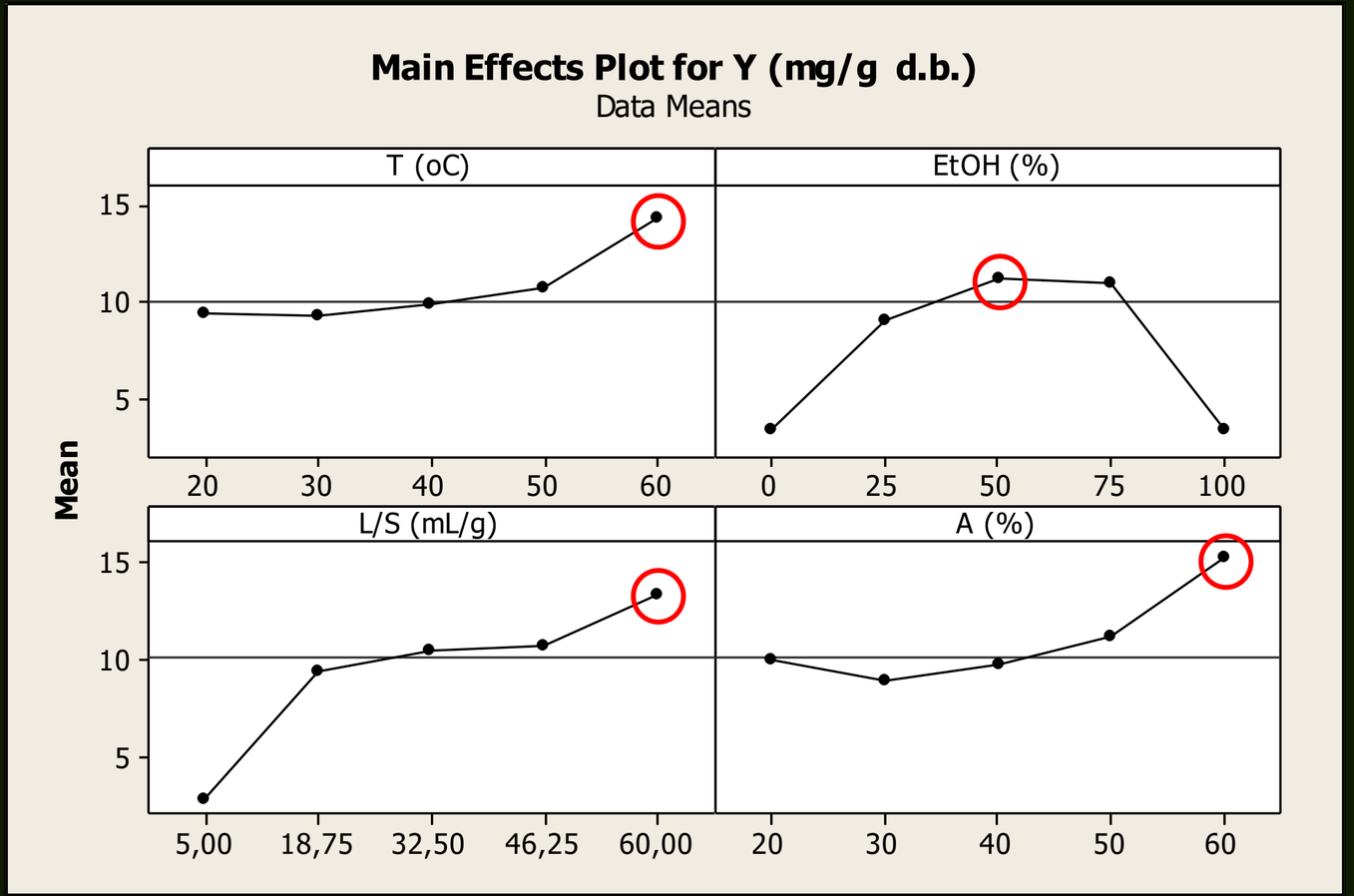
MATERIALS AND METHODS

SAMPLES PREPARATION

SCG PHENOLICS EXTRACTION

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

Solomakou *et al.*, 2022*a*



Optimum Yield: 18.54 mg/g d.b.

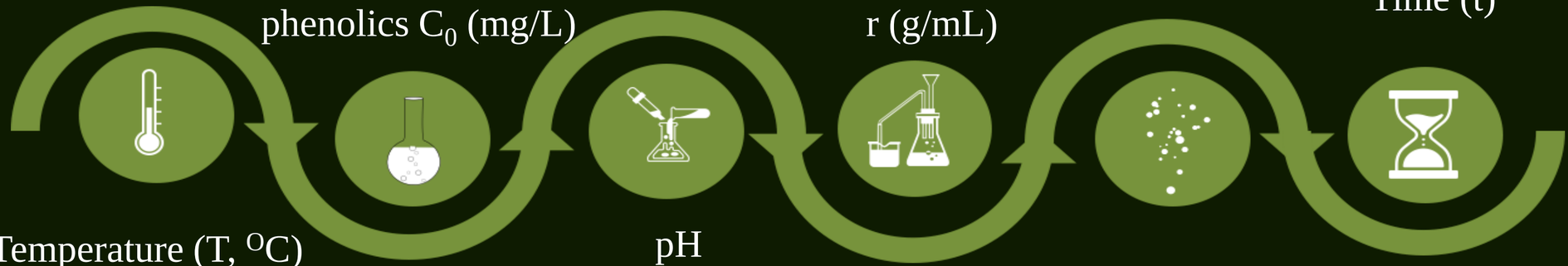
Optimum extraction conditions			
L/S	**Solvent (% aq. EtOH)**	**T°C**	**Amplitude**
53 mL/g	50.5% EtOH v/v	60°C	60%

ADSORPTION AFFECTING PARAMETERS

Initial concentration of phenolics C_0 (mg/L)

Solvent/Sorbent ratio r (g/mL)

Time (t)



Temperature (T, ^{O}C)

pH

Particle size of biosorbent

INVESTIGATED PARAMETERS

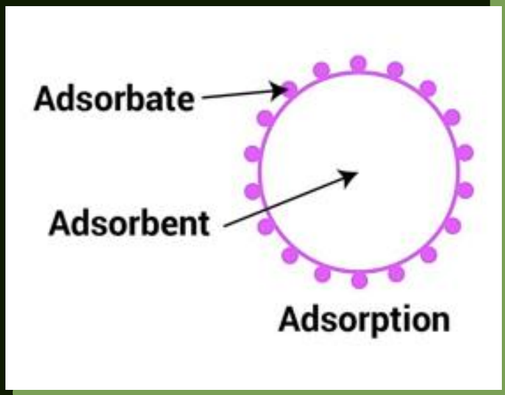
- **T: 20-60^{o}C**
- **pH: 2-10**
- **r: 0.01-0.05 mL/g**
- **C_0 : 50-500 mg/L**

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

C_0 : Initial phenolic concentration in solution

C : Remaining phenolic concentration in solution after adsorption

Parameters Levels (RSM Methodology)			
T (^{o}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



BIOSORBENT ACTIVATION

Physical activation

Drying of biosorbent: 100-250^{o}C for 2 h

Chemical activation

Activation with NaOH

SCG + NaOH, 2M (25^{o}C for 24 h)- ratio: 2g/33mL → Stirring at 45^{o}C for 2h → Washing with distilled water → Drying at 80^{o}C for 4 h

Activation with MeOH

SCG + MeOH+ 5.4 mL HCl 0.1M → Stirring at 60^{o}C for 24 h → Washing with distilled water → Drying at 40^{o}C for 24 h

Chemical activated biosorbents

BIOSORBENT ACTIVATION

Protein coating

Skim milk + EtOH (1:2)

Protein precipitation

Stirring (2 min)

Centrifugation

Precipitate + aqueous solution pH 9.0

Adsorbent (SCG) + HCl 2N (12 h)

Filtration, washing and drying (100°C)

Protein particles

Treated SCG

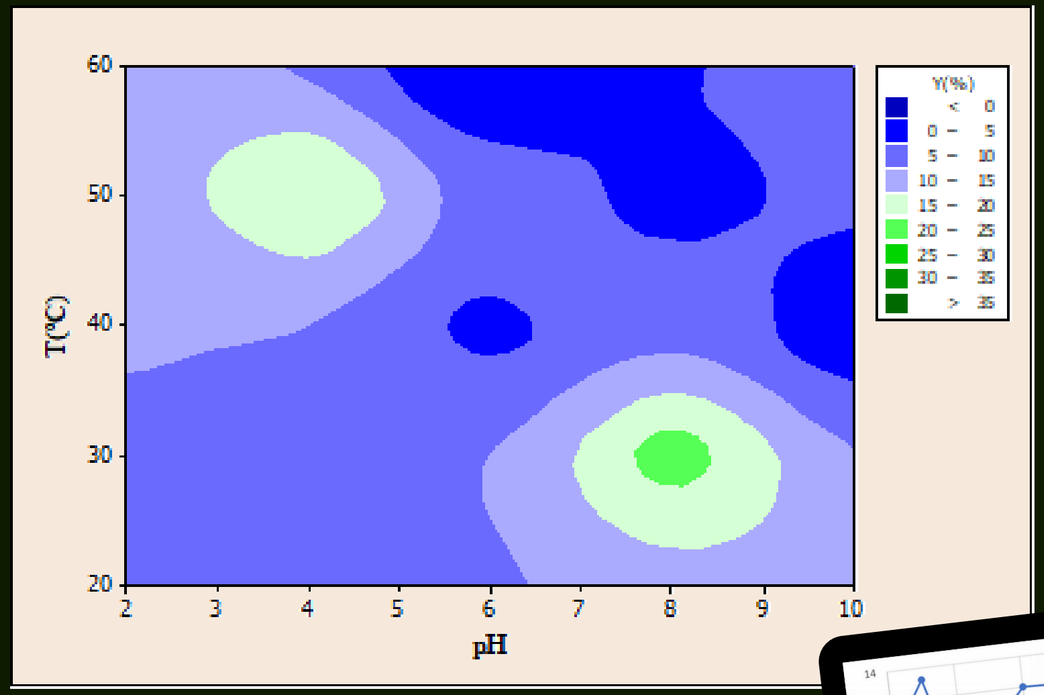
Stirring (37°C, 2 h)

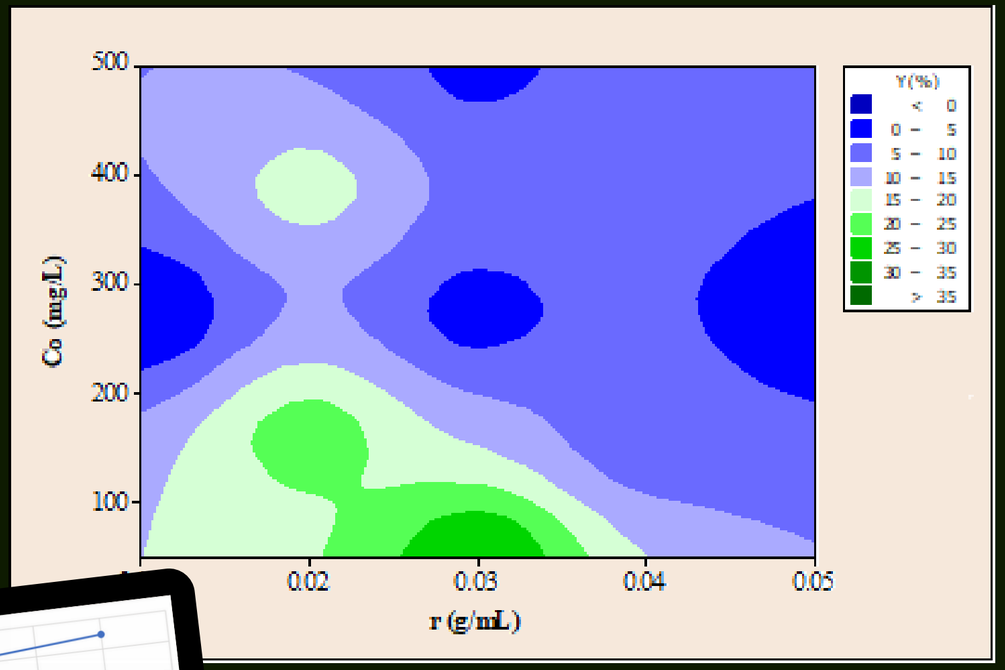
Filtration, washing and drying (55°C)

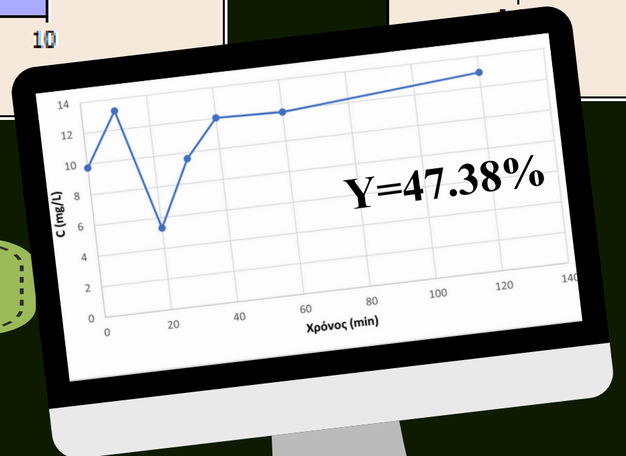
RESULTS AND DISCUSSION

PHENOLICS ADSORPTION

Non activated SCG







Solomakou *et al.*, 2022*b*

T=30°C, pH= 8.0, r=0.02 g/mL, C_0=250 mg/L

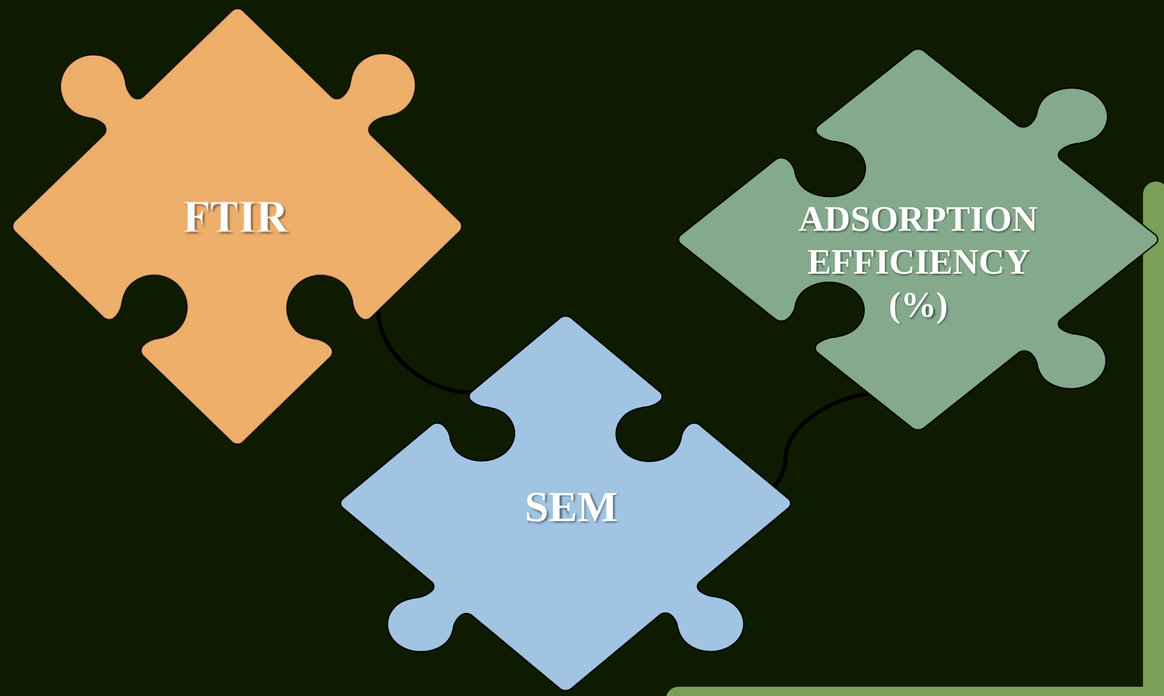
PHENOLICS ADSORPTION

Experiments with higher adsorption efficiency

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

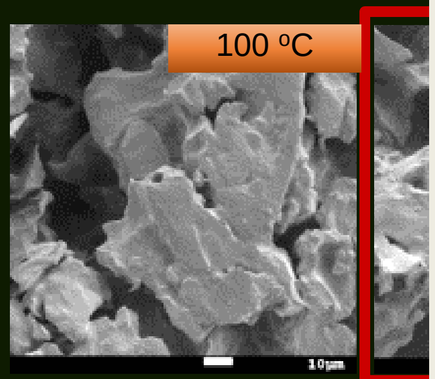
Exp B : T=30°C, pH= 8.0, r=0.02 g/mL, C_0=250 mg/L

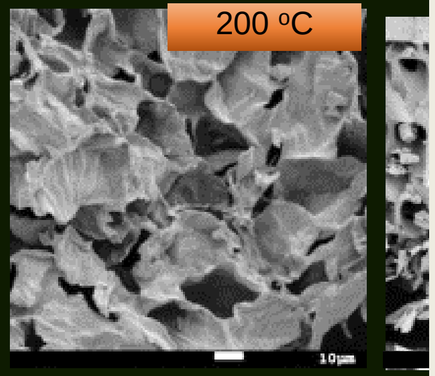
Adsorption experiments: Non treated SCG, thermal and chemical treated SCG

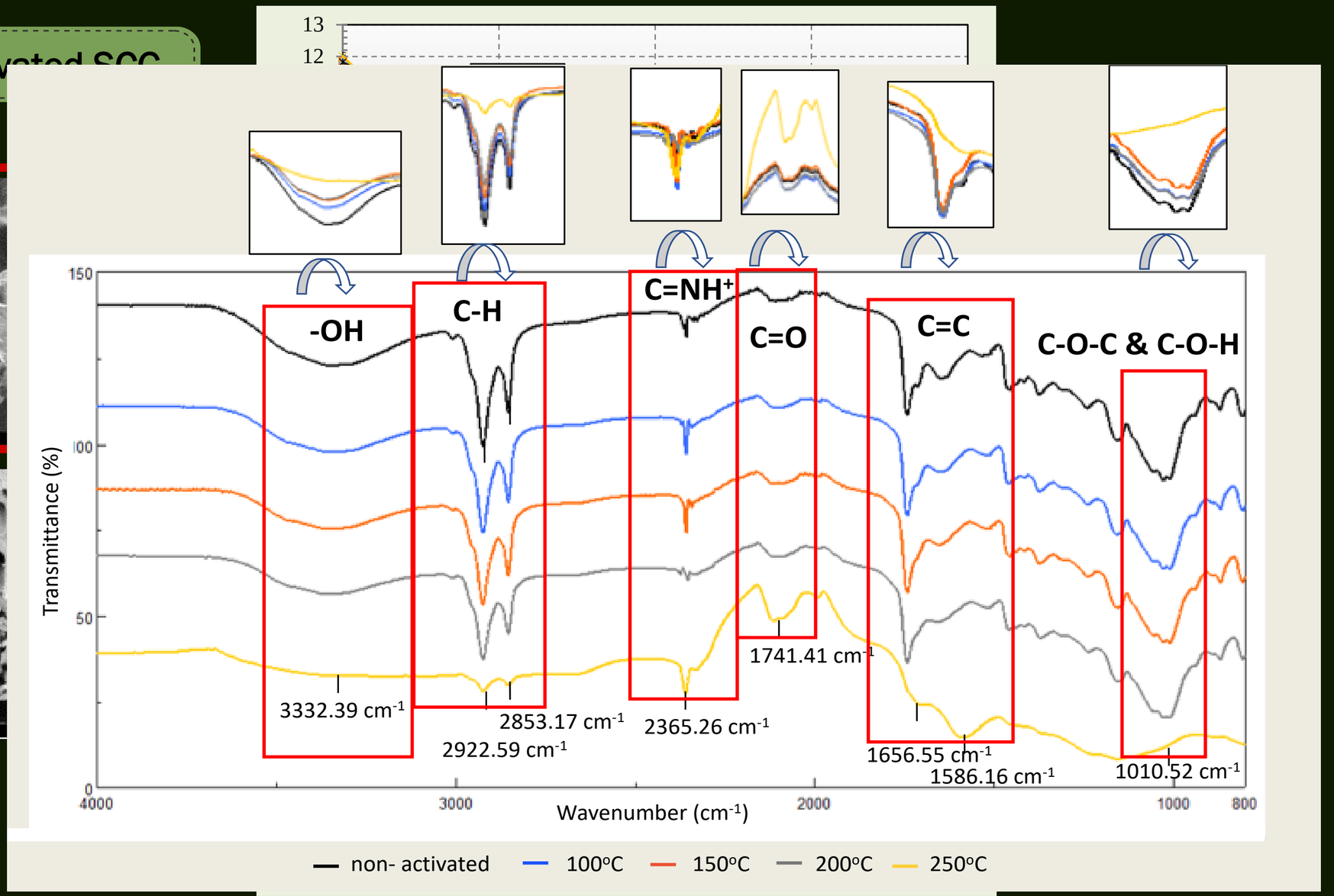


PHENOLICS ADSORPTION

Physical activated SCC

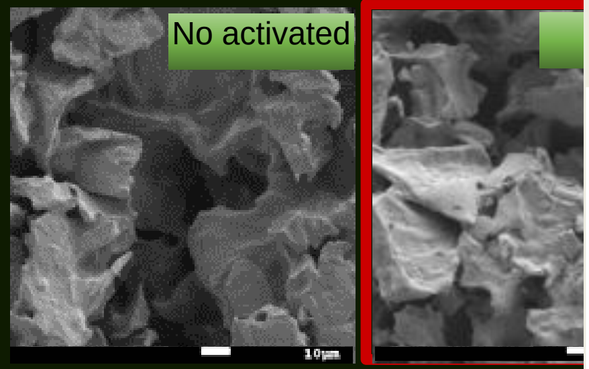


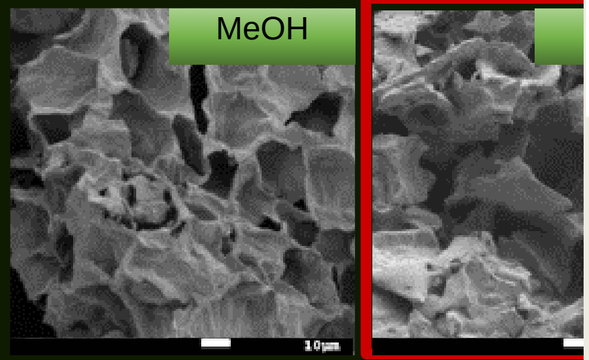


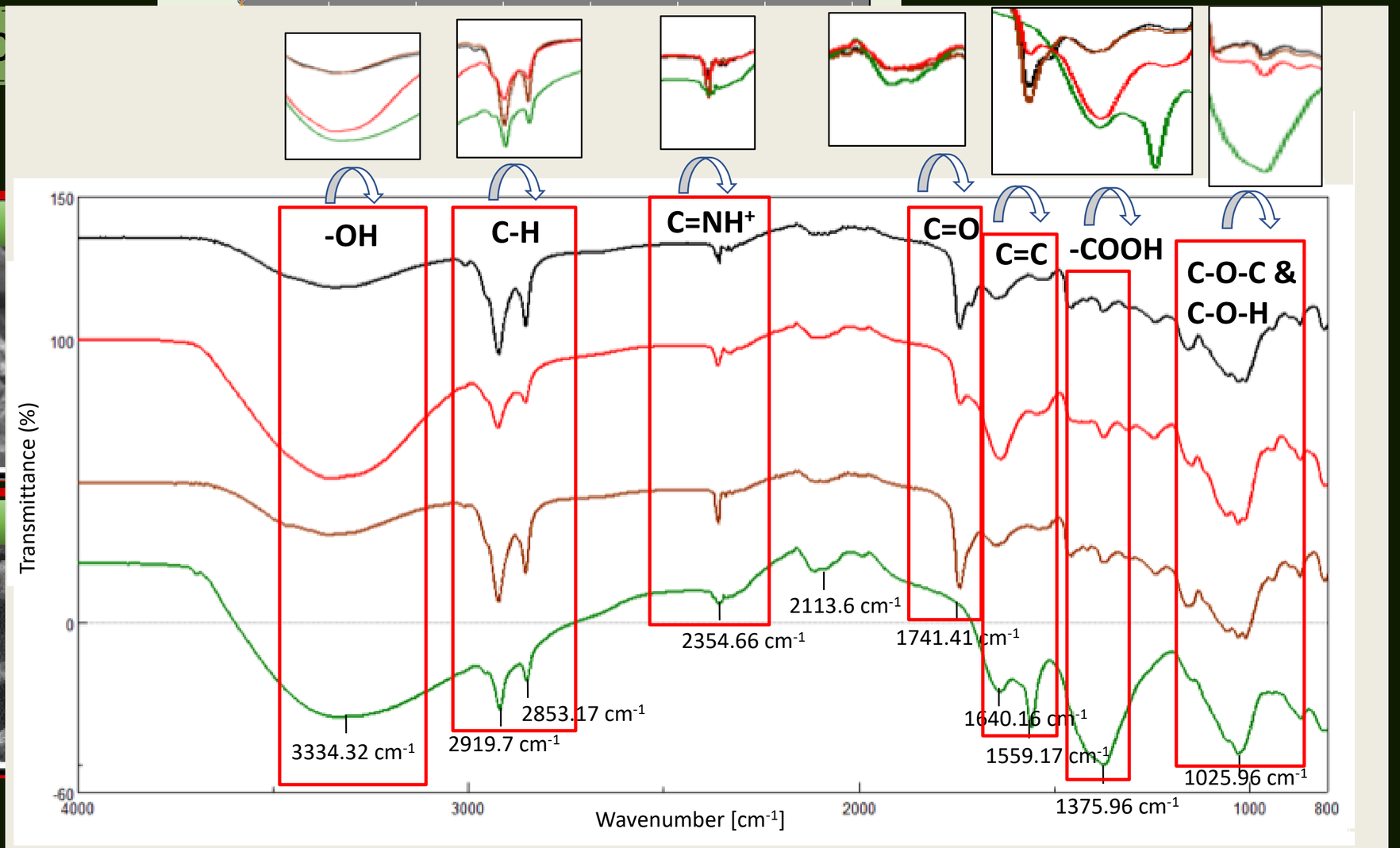


PHENOLICS ADSORPTION

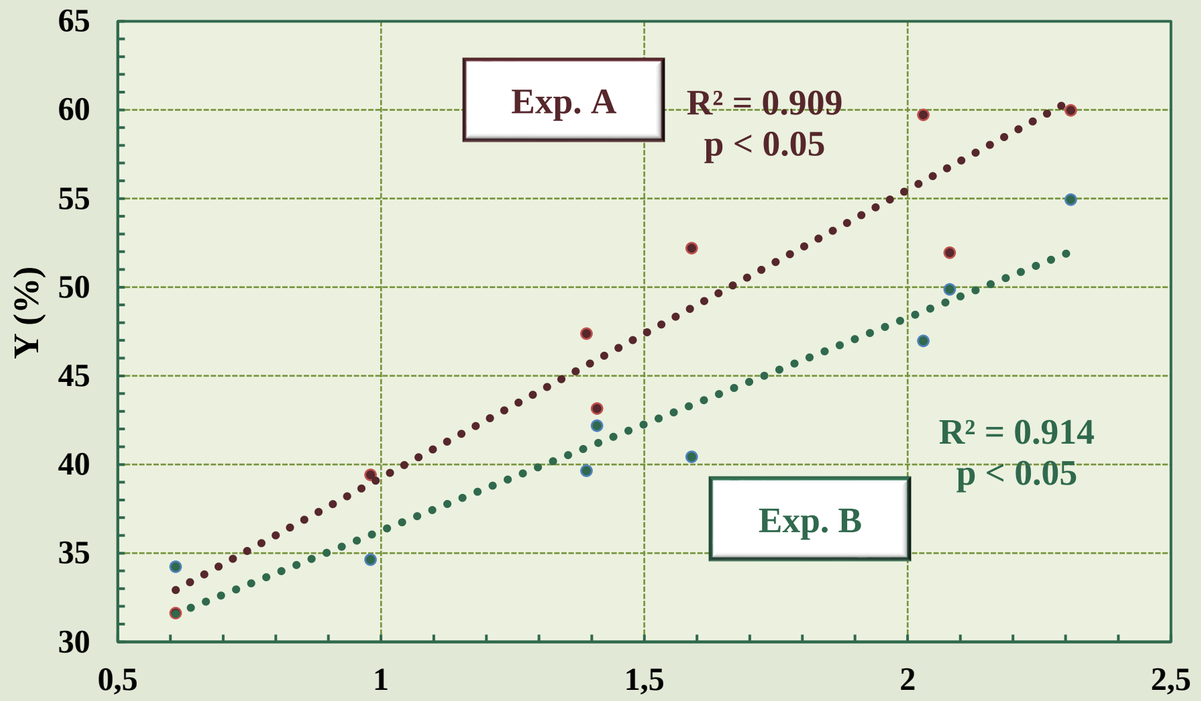
Chemical activated SC







SEM ANALYSIS



Activation method	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Pore width (nm)
No treatment	653	0.315	1.39
Chemical - protein	**920**	**0.446**	**2.08**
Chemical - MeOH	734	0.337	1.41
Chemical - NaOH	**1119**	**0.496**	**2.31**
Thermal – 100°C	468	0.230	0.98
Thermal – 150°C	796	0.356	1.59
Thermal – 200°C	368	0.171	0.61
Thermal – 250°C	**998**	**0.462**	**2.03**

Adsorption Yield %

Protein coated SCG, Chemical-**NaOH** and Thermal **250°C**

CONCLUSIONS

01 **OMW phenolics presented maximum adsorption yield of 47.38% using untreated SCG as biosorbent**

02 **Both physical and chemical pretreatment lead to modification of adsorption yield**

03 **Chemical- protein coating**

Chemical-NaOH

Thermal- 250^{o}C

Adsorption Yield (%)

THANK YOU VERY MUCH FOR YOUR ATTENTION!