



Olive Mill Wastewater Transformation from Pollutant to Sun Protection Paste

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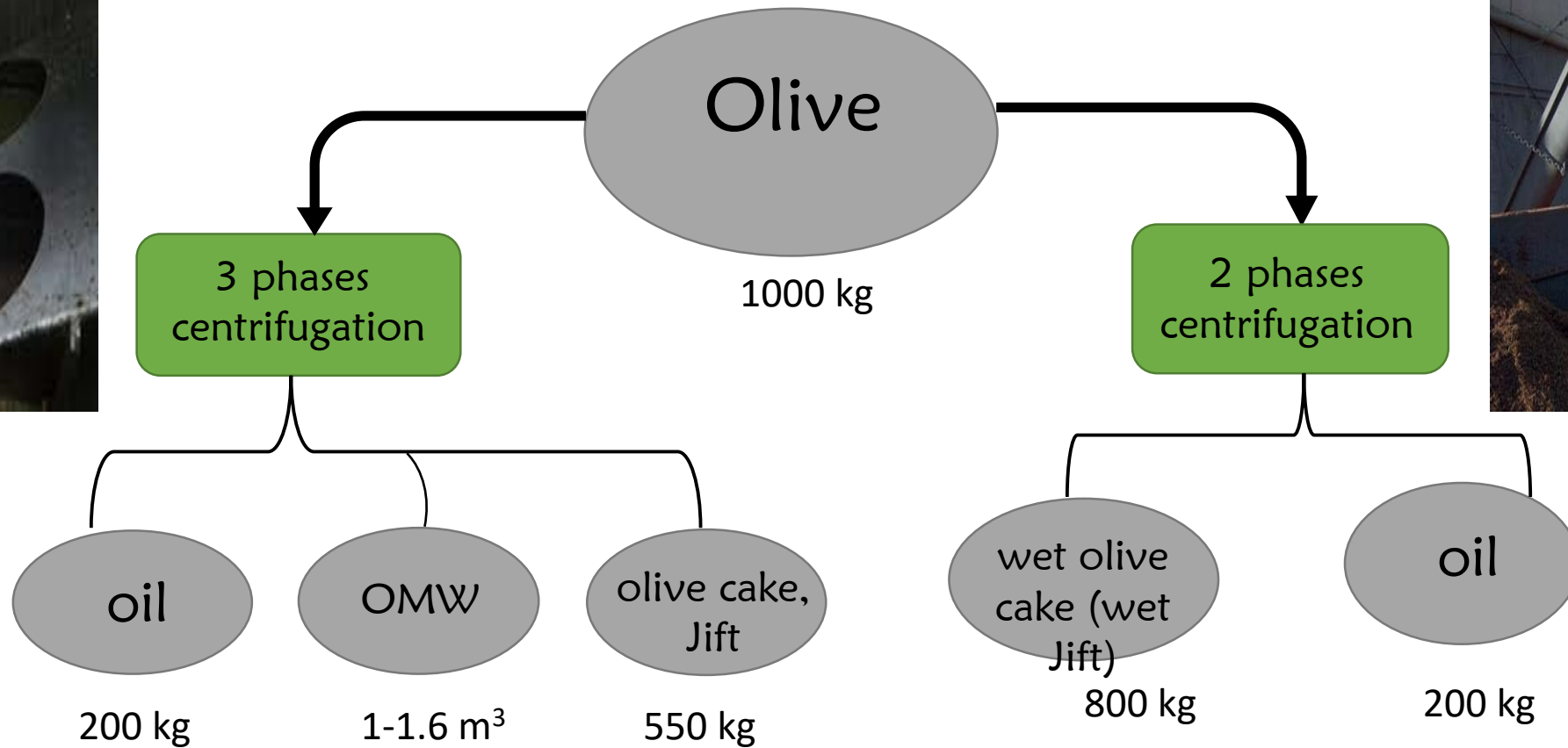
The Institute of Applied Research, The Galilee Society, Shefa-Amr, 20200, Israel



Olive oil extraction system



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OMW: Olive Mill Wastewater

Olive Mill Wastewater (OMW)

Current situation

In Israel:

- 140 olive mills – 80% three phase system
- 150,000 m³/year OMW.
- 30,000 tons “Jift” OMSW wet.
- 12,000 “Jift” OMSW dry .

World wide:

- Two phase system - 30 million tons of solids and liquid waste.
- Three phase system - 15 million m³/year of OMW.

OMW – A Pollutant!

Sample	pH	COD (gr O ₂ /l)		TP (gr/l) eq to Caffeic acid
		Total	Soluble	
OMW	4.5 – 5.5	90 - 220	50 - 150	3.0-15

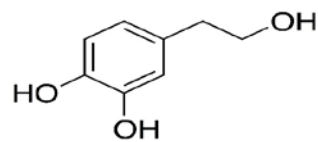
It can pollute water bodies and the environment because of its composition:

- ❖ High BOD (up to 50 g/l) and COD (up to 200 g/l).
- ❖ Low pH (≤ 5).
- ❖ High EC (7-11 dS/m) and ion content (mostly K).
- ❖ High phenolic content.
- ❖ Smell and color.
- ❖ Toxic properties for living organisms



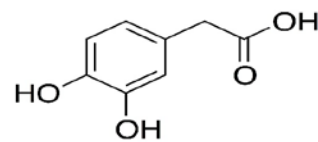


Structures of some bioactive phenols and phenolic glycosides in OMW



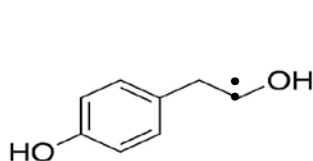
Hydroxytyrosol (HT)

1



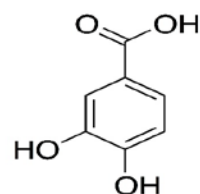
3,4-dihydroxyphenylacetic acid

2



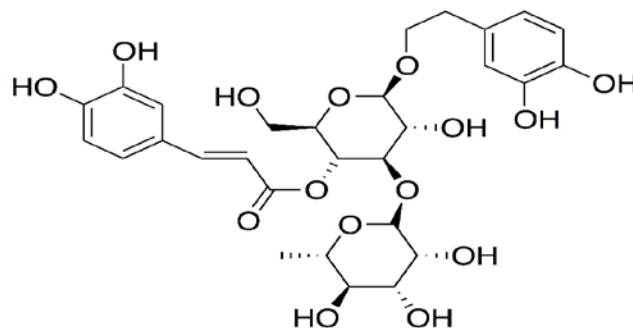
Tyrosol

3



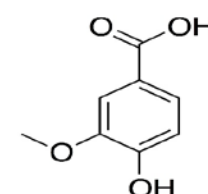
Protocatechuic acid

4



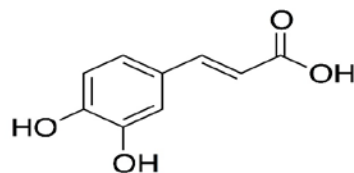
Verbascoside

5



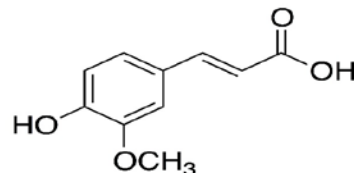
Vanillic acid

6



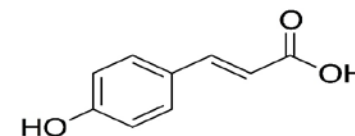
Caffeic acid

7



Ferulic acid

8



p-coumaric acid

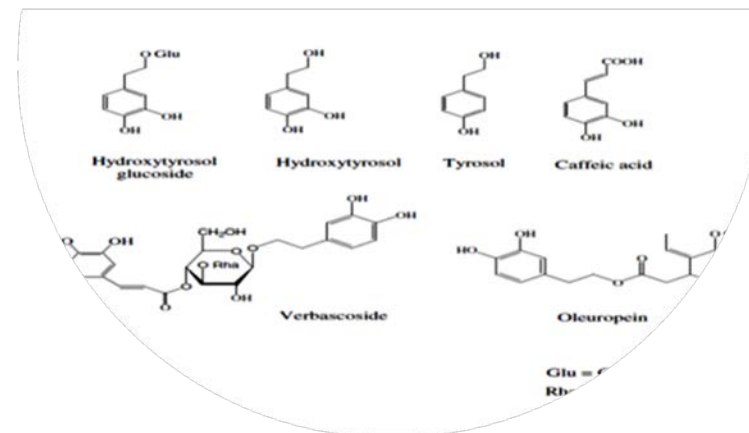
9

OMW from a pollutant to a resource

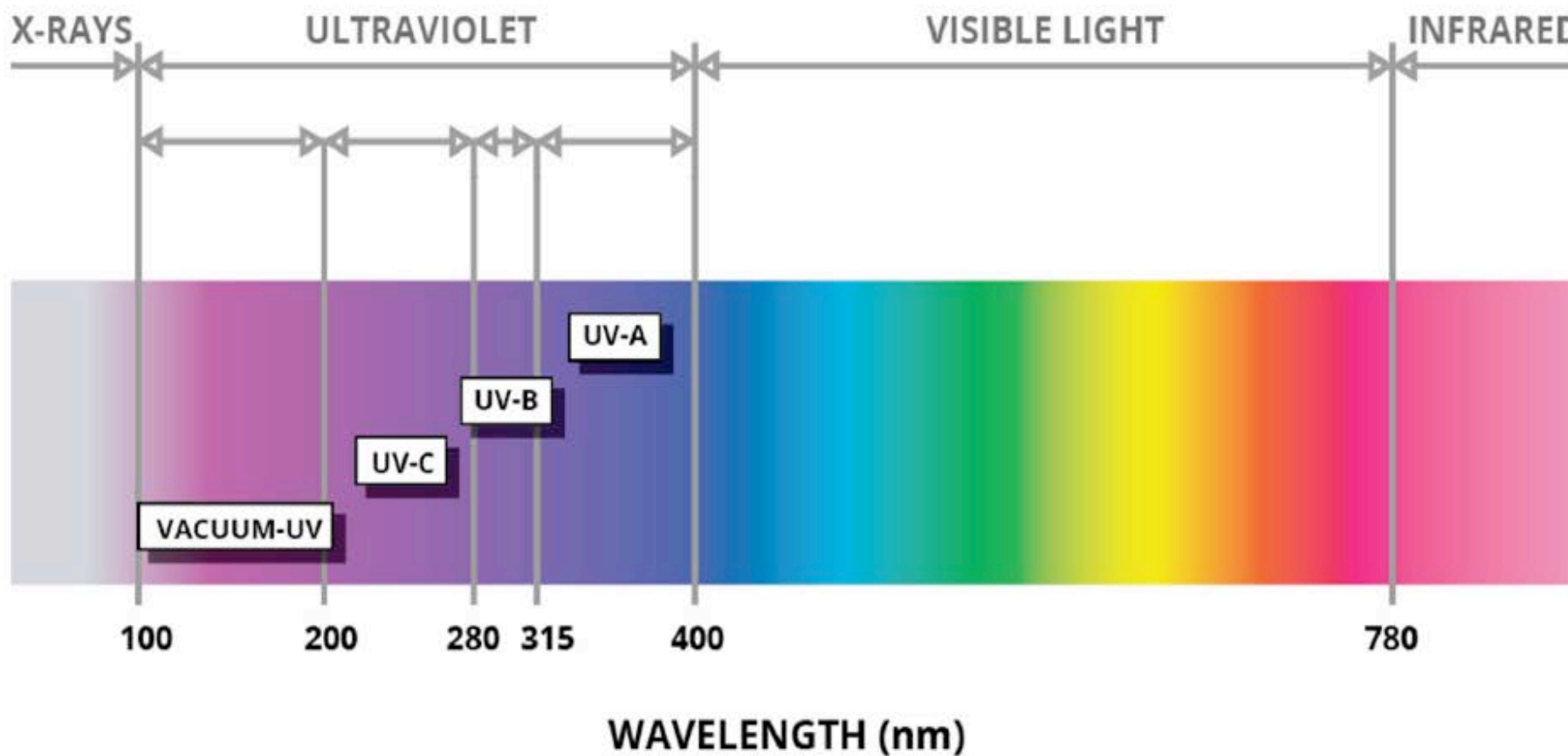
- ❖ For a long time, OMW has been regarded as a hazardous waste with negative impact on the environment.
- ❖ However, this view is changing, and the potential of OMW to become a starting material, rich in bioactive compounds, is being recognized.
- ❖ In particular, polyphenols, abundant in OMW, are natural antioxidants for the food and pharmaceutical industries. A number of studies have also shown that polyphenols are effective as antibacterial, antiviral, and antifungal compounds.

Objective and Aim

The objective and aim of the proposed study is to produce, optimize and characterize an organic extract from OMW in order to obtain a prototype product composed of natural materials with high activity to protect the skin from UV rays.

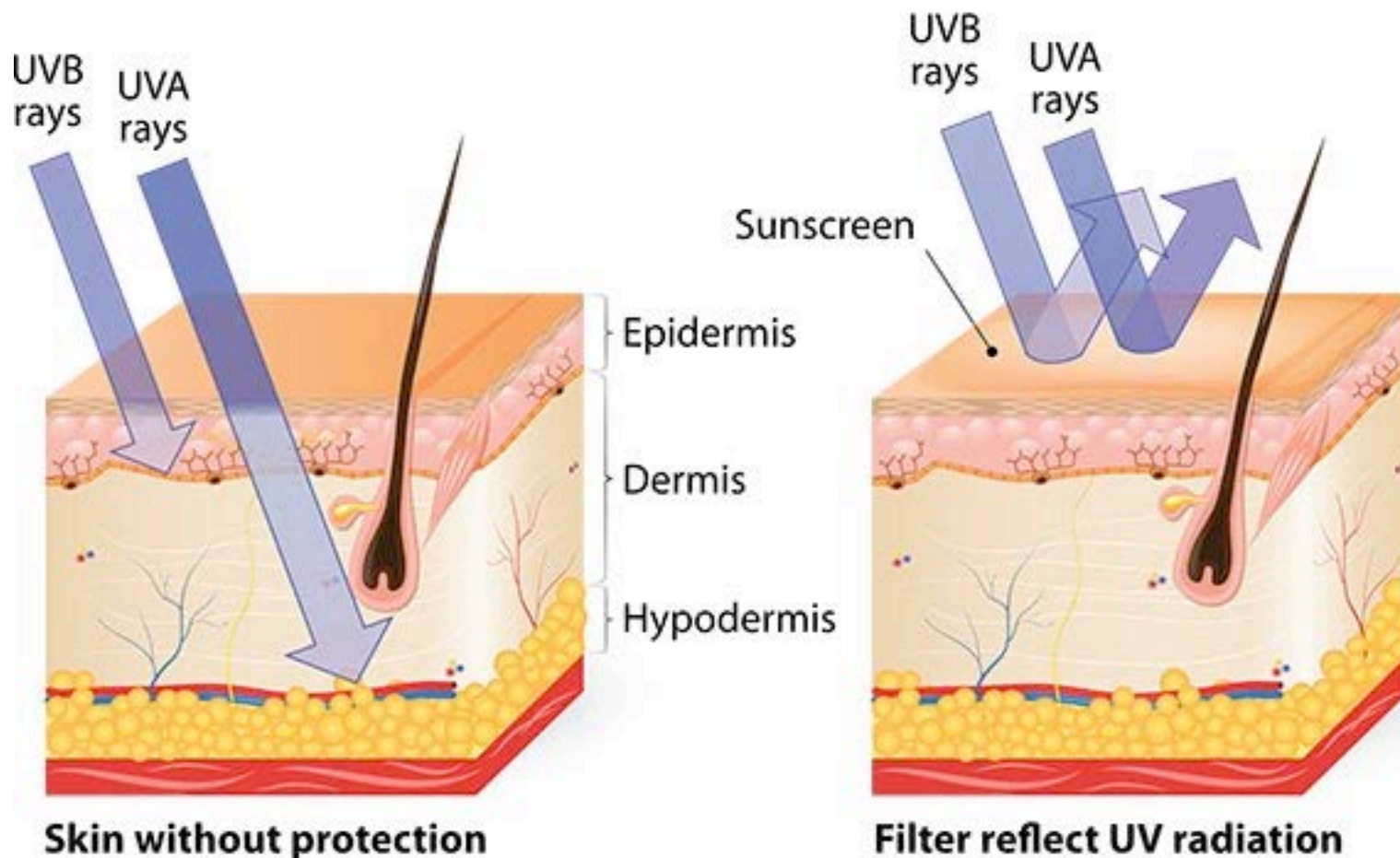


THE ELECTROMAGNETIC SPECTRUM





UV penetration into the layers of the skin





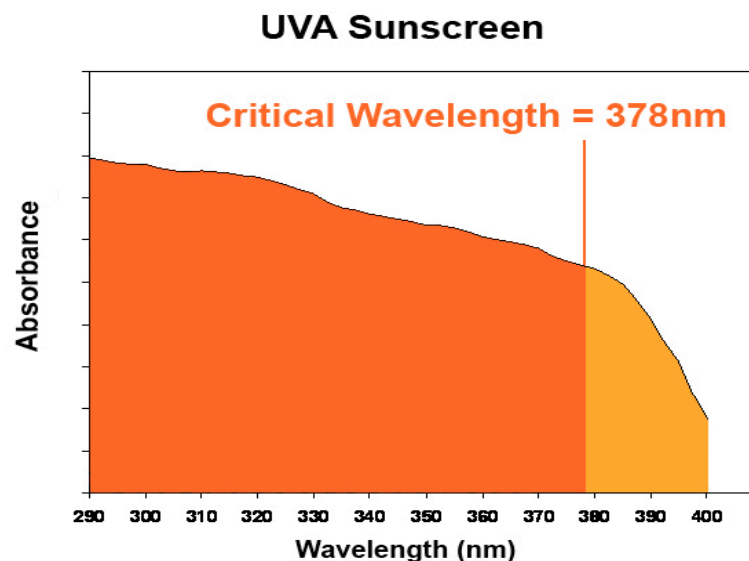
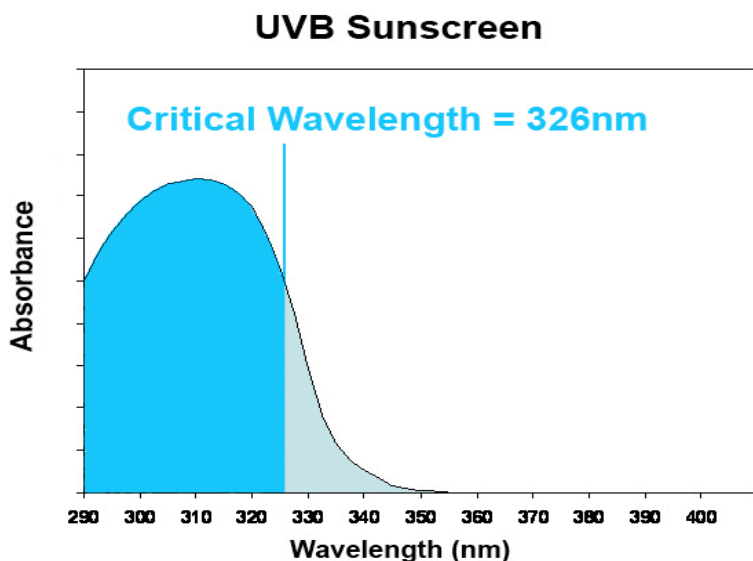
Sun Protection Factor (SPF) and Critical Wavelength (CW)

SPF: is a relative value of how long a sunscreen will protect us from UVB rays relatively to a non protected skin (Mansur, J.S; et al 1986).

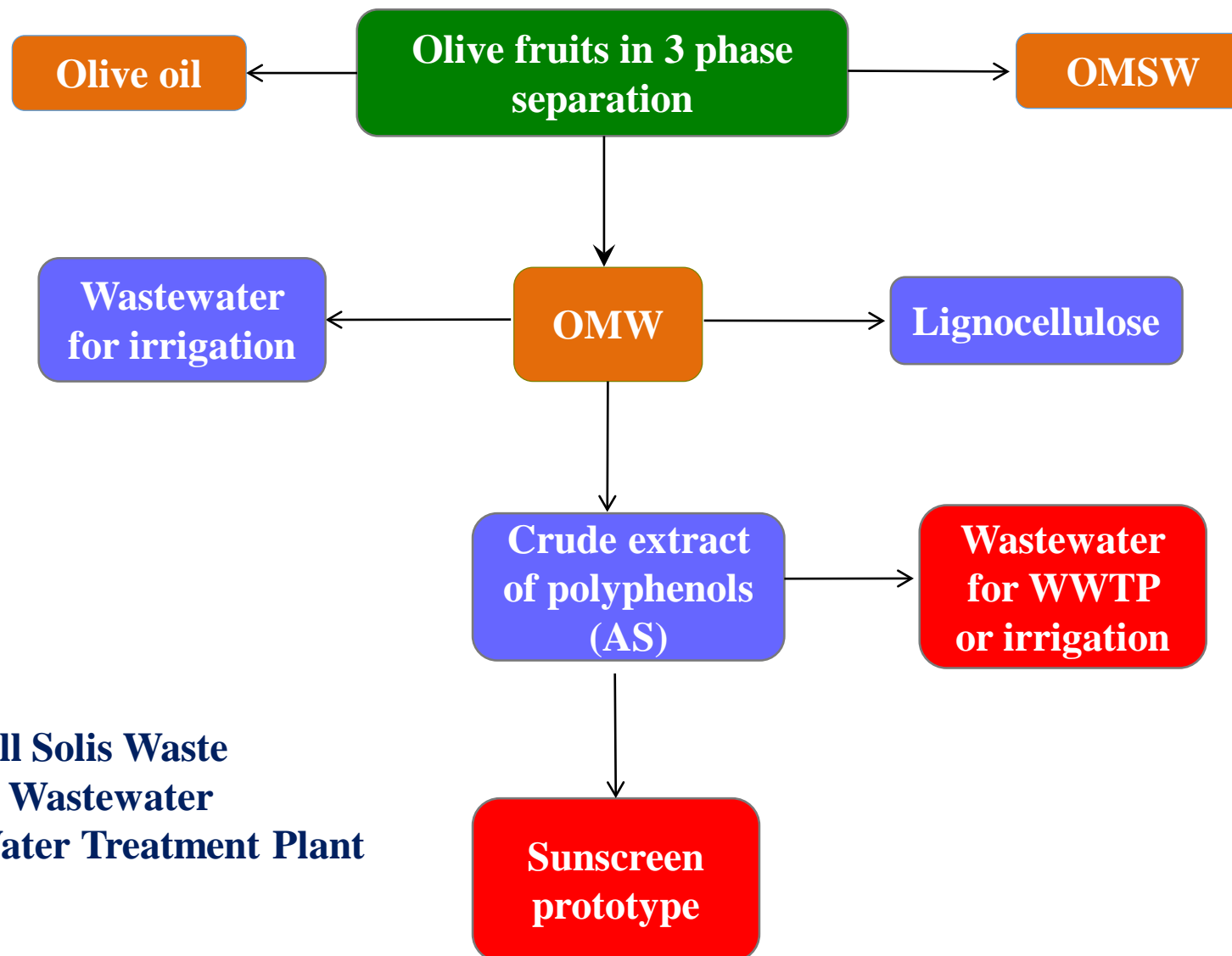
$$SPF = CF \times \sum_{290}^{320} EE(\lambda) \times I(\lambda) \times Abs(\lambda)$$

CW: The “Critical Wavelength” (λ_c) is the wavelength below which 90% of the area under the absorbance curve resides (COLIPA).

$$\int_{290}^{\lambda_{CW}} Abs(\lambda) \times d(\lambda) = 0.9 \int_{290}^{400} Abs(\lambda) \times d(\lambda)$$



Work Plan

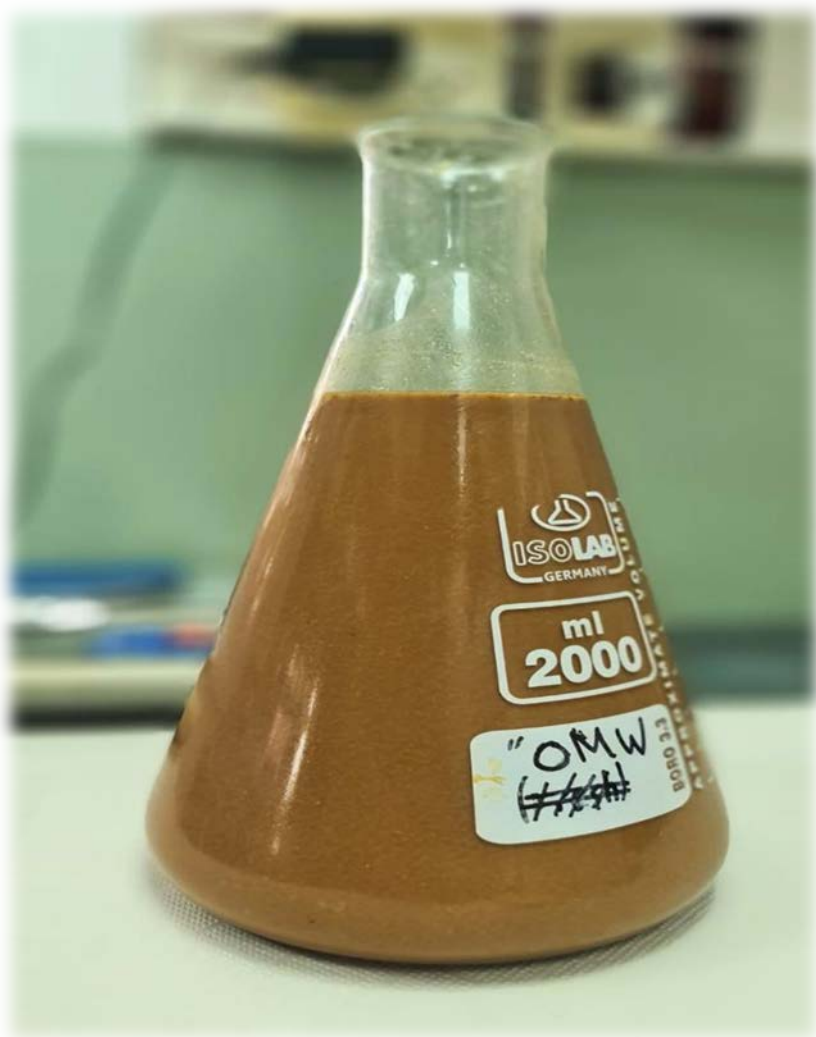


OMSW: Olive Mill Solis Waste

OMW: Olive Mill Wastewater

WWTP: Waste Water Treatment Plant

AS: Antisolvent



OMW

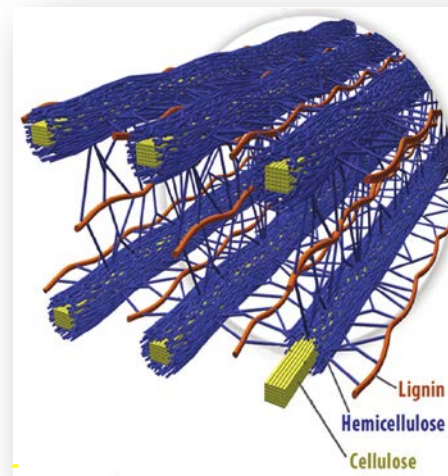


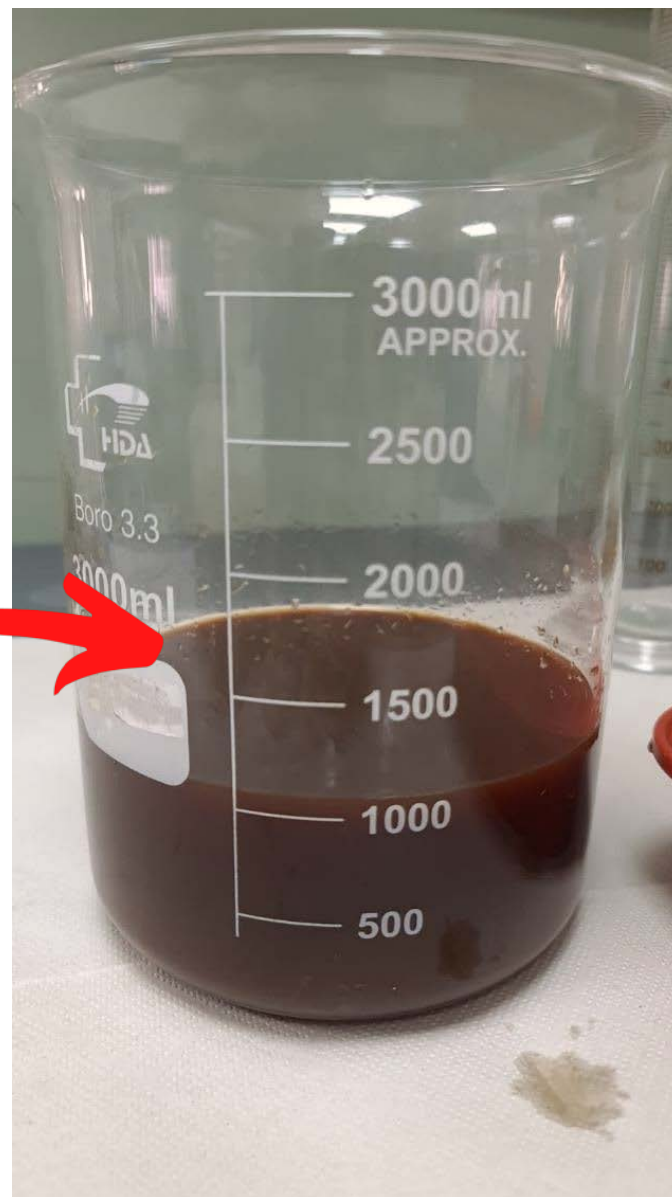
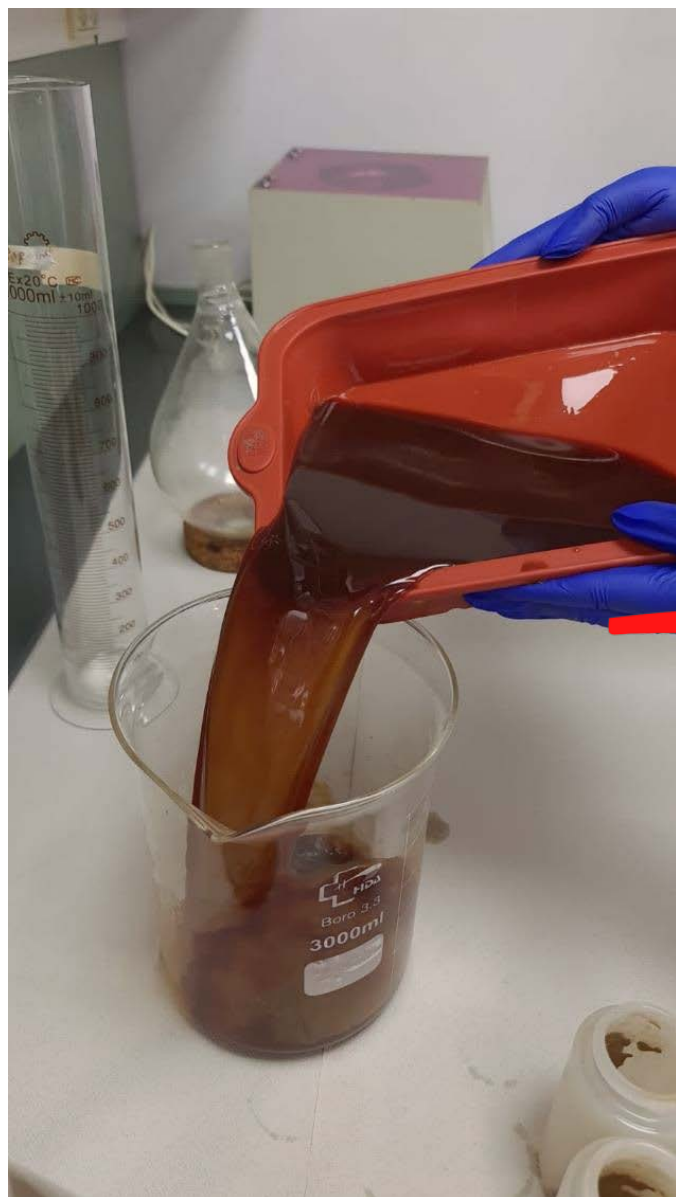
After Centrifuge

Sieving (106MIC) – solid phase removal



Removal of unwanted solids





Measuring volume

1200ml OMW

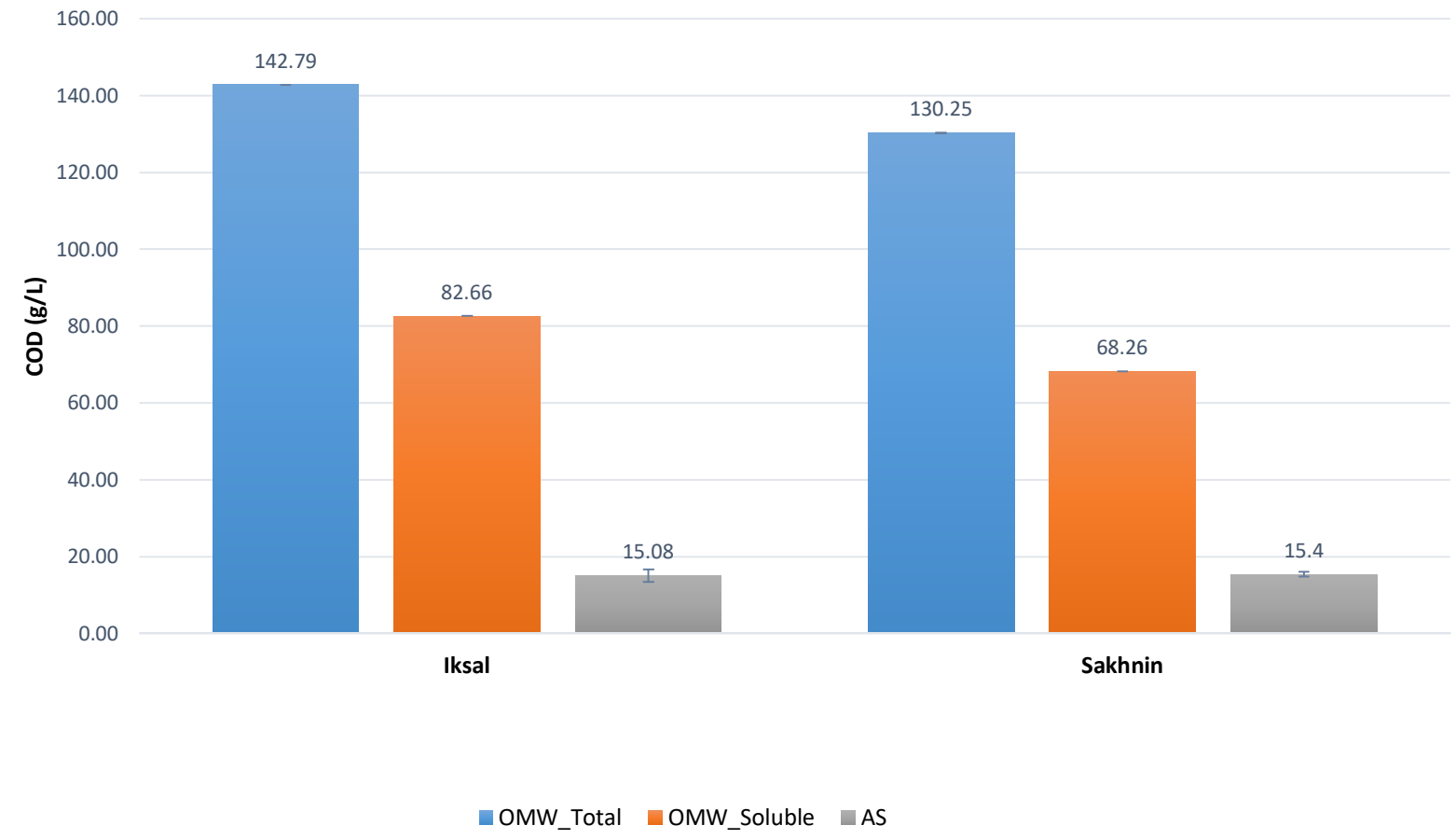


$V_{OAC} = 1050\text{ml}$



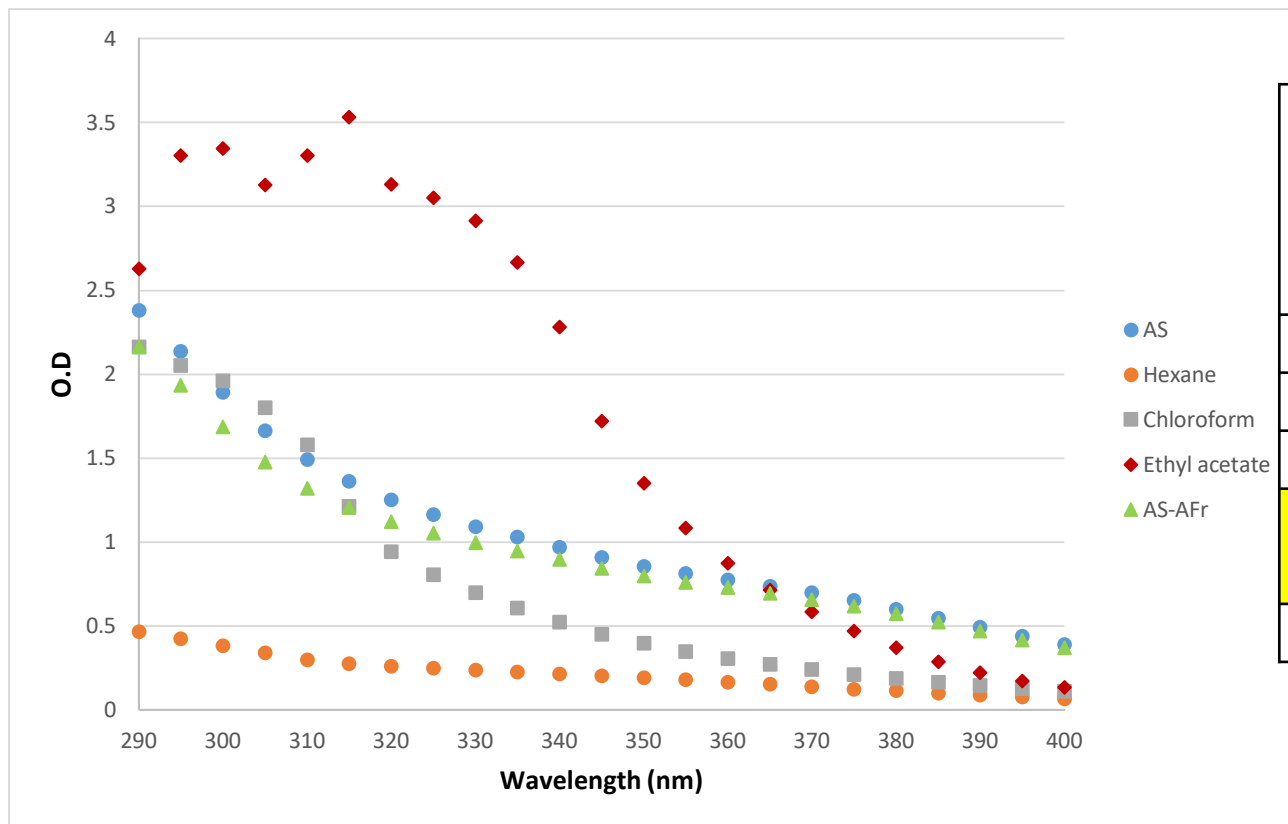
Results

COD reduction through OMW treatment





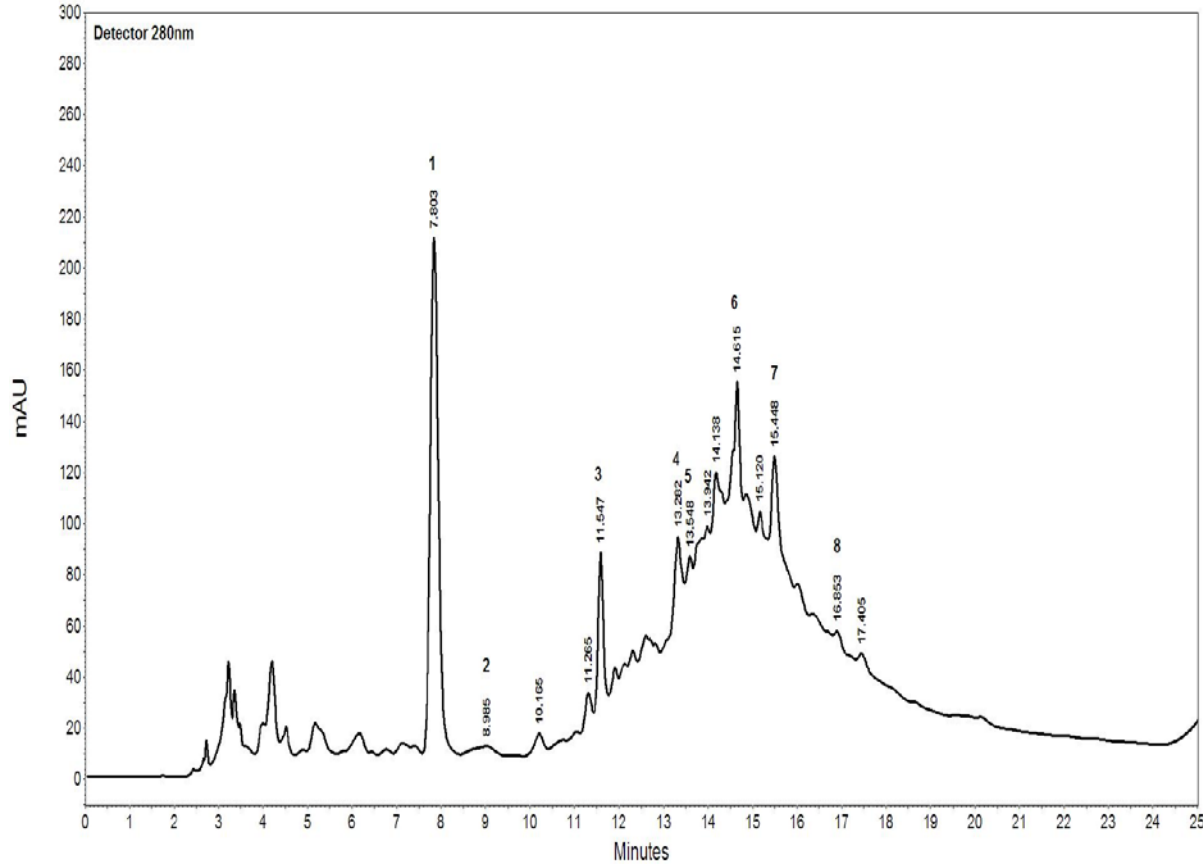
UV activity of the fractions obtained by Fractionation Guided Assay (FGA)



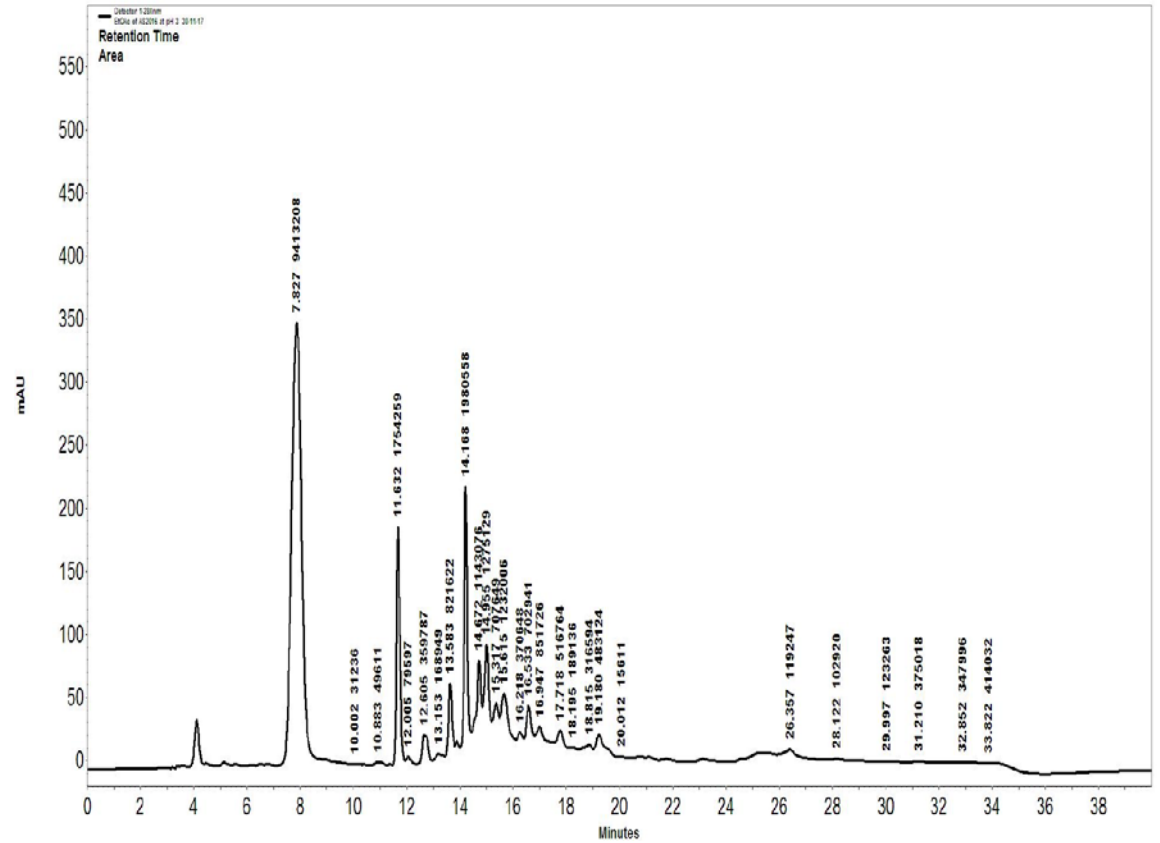
Fraction 800 ppm	SPF \pm 3std	CW \pm 3std	TP \pm 3std [mg/l] eq to Caffeic acid	Sugars \pm 3std [mg/l] eq to D-(+)- Glucose
AS	11.27 \pm 0.70	375 \pm 0.00	68.82 \pm 0.95	152.762 \pm 0.040
Hex Ext	3.48 \pm 0	320 \pm 3.54	10.74 \pm 1.90	ND
CLF Ext	12.23 \pm 0.23	355 \pm 3.54	80.98 \pm 0.22	ND
EtOAc Ext	35.72 \pm 0.79	360 \pm 7.07	350.46 \pm 1.68	86.452 \pm 0.019
AS_AFr	10.53 \pm 0.29	380 \pm 0.00	57.68 \pm 0.22	139.682 \pm 0.032



HPLC of AS and EtOAc fractions



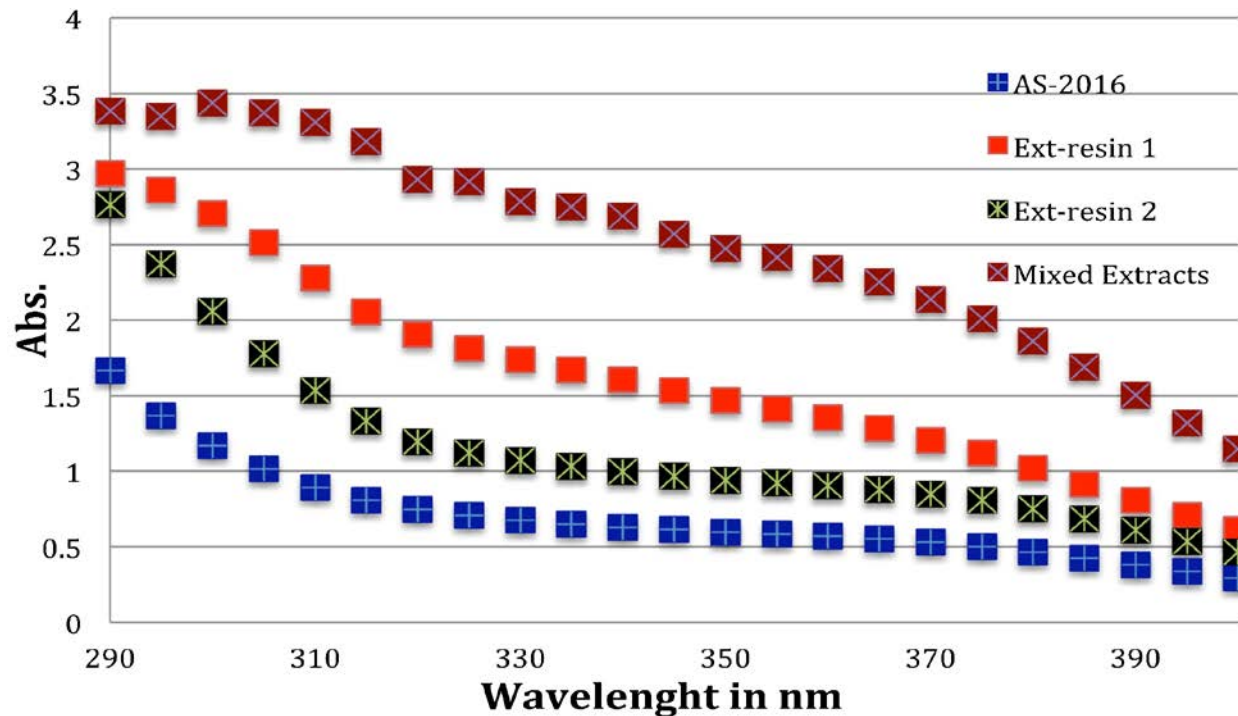
HPLC chromatogram of AS extract at a concentration of 1000 ppm



HPLC chromatogram of EtOAc fraction of AS at a concentration of 1000 ppm



UV activity of the resins' extracts in comparison to Antisolvent



Fraction 800 ppm	SPF \pm 3std	CW \pm 3std	TP \pm 3std [mg/l] eq to Caffeic acid	Sugars \pm 3std [mg/l] eq to D-(+)- Glucose
AS	11.27 \pm 0.70	378 \pm 1.15	68.82 \pm 0.95	146.27 \pm 20
Ext-resin 1	26.83 \pm 2.30	377 \pm 0.57	105.39 \pm 23.55	146.30 \pm 11.78
Ext - resin 2	18.78 \pm 0.51	377 \pm 1.10	75.28 \pm 17.95	122.05 \pm 36.16
Mixed Ext 1+2	31.21 \pm 2.32	382 \pm 1.50	189.27 \pm 45.71	293.3 \pm 47.84

Sample	Amount
OMW	1 L
AS	35 gr
Ext-resin 1	4.88 gr
Ext-resin 2	4.22 gr
Mixed Ext 1+2	9 gr



SPF and CW of FGA extracts versos resins

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Conclusions:

- ❖ Polyphenols in OMWW are responsible for the SPF values and active against UVB radiation, while phenolic glycosides in OMWW are active against UVA radiation and responsible for the CW values.
- ❖ The fractions obtained from FGA process are active against UVB rays only and they could no longer be considered as broad spectrum.
- ❖ Adsorbent resins were a breakthrough in this research because they could adsorb phenols and phenolic glycosides from Antisolvent fraction, with impressive values (SPF > 30 and CW > 380).



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Thank you for your attention





Properties of resins

Resin	Resin 1	Resin 2
Matrix type	acrylate-divinylbenzene	styrene-divinylbenzene
Particle size	20-60 mesh	20-60 mesh
Pore size	0.5 ml/g pore volume 300-400 Å mean pore size	0.55 ml/g pore volume 200 Å mean pore size
Surface area	380 m ² /g	800 m ² /g

The interaction between the resins and :the extract

Hydrogen bonds*

Hydrophobic interactions*

$\pi - \pi$ bonding*