# Pomegranate peel and orange juice by-product as new biosorbents of phenolic compounds from olive mill wastewaters

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# Olive oil production

- The extraction of olive oil consists of three steps:

1. Olive crashing, where the fruit is broken down and the oil is exported
2. Mixing, where the remaining paste is slowly mixed to increase the oil extraction
3. Oil separation from the remaining wastes
   1. Traditional pressing
   2. 3- phases centrifugal extraction system
   3. 2- phases centrifugal extraction system

(Klen & Vodopivec, 2012)

## Traditional pressing

- Obsolete technology
- A solid fraction, “olive husk”, is obtained as a by- product with an emulsion containing the olive oil
- The olive oil is separated from the remaining olive mill wastewater by decanting

## Three – phase extraction process

- Predominant process in modern olive mills
- Two streams of waste
  - i. a wet solid cake (~30% of raw material weight) called “orujo” or “olive cake”
  - ii. a watery liquid (50% of raw material weight) called “alpechin” or “olive mill wastewater (OMW)

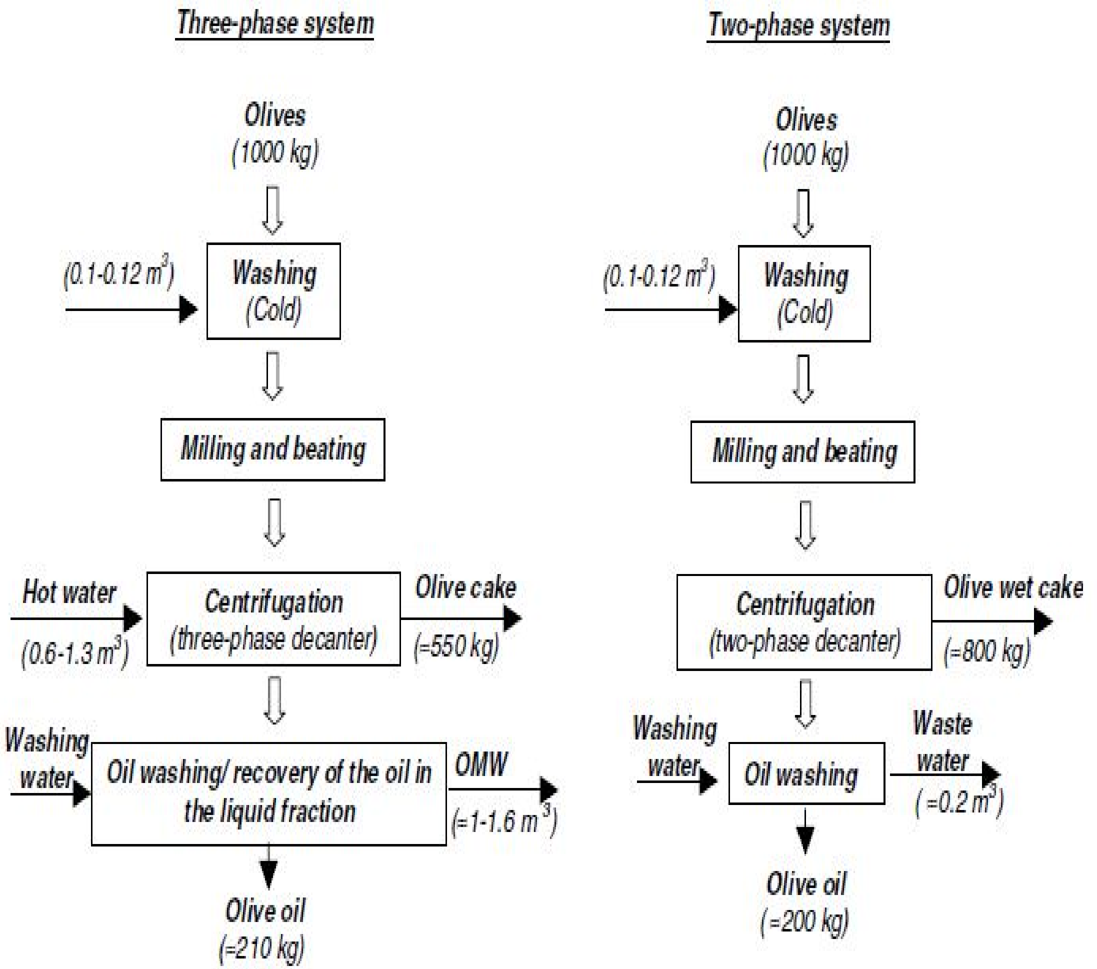
## Two – phase extraction process

- ‘‘Ecological’’ method, reduces the olive mill waste by 75%
- Two fractions
  - i. A solid called “alperujo” or “olive wet husk” or “wet pomace” or “two-phase olive mill waste” (TPOMW)
  - ii. A liquid (olive oil)

(Tsagaraki et al., 2007)

# Olive oil extraction by- products

(Goula et al., 2016)




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

## Three- and two-phase centrifugation systems

(Alburquerque et al., 2004)

# The management of waste from olive mills

- **Olive cake**
  - i. **Solid fuels**
  - ii. **Animal feed supplement**
  - iii. **Return to the olive grove as mulch**

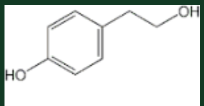
- **Olive mill wastewater (OMW)**
  - i. **Disposal of OMW in nearby aquatic receivers**
  - ii. **Physical and physicochemical processes**
  - iii. **Biological processes**
  - iv. **Coupled physicochemical and biological treatments**

(Tsagaraki et al., 2007; Goula et al., 2016)

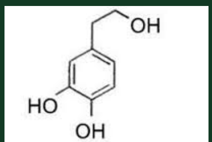
## Composition of olive mill wastewaters and solid residues

| Component | Olive mill by-product | | | Reference |
|---|---|---|---|---|
| | OMW | Olive cake | TPOMW | |
| **Total carbon (%)** | 2.0-3.3 | 29.0-42.9 | 25.4 | Vlyssides et al., 1998; Garcia-Castello et al., 2010 |
| **Total nitrogen (%)** | 0.63 | 0.2-0.3 | 0.25-1.85 | Saviozzi et al., 2001; Di Giovacchino et al., 2006; Dermeche et al., 2013 |
| **Ash (%)** | 1.0 | 1.7-4.0 | 1.4-4.0 | Vlyssides et al., 1998; Di Giovacchino et al., 2006; Lafka et al., 2011 |
| **Lipids (%)** | 0.03-4.25 | 3.5`0-8.72 | 3.76-18.00 | Vlyssides et al., 1998; Paredes et al., 1999; Di Giovacchino et al., 2006; Dermeche et al., 2013 |
| **Total sugars (%)** | 1.50-12.22 | 0.99-1.38 | 0.83-19.30 | Vlyssides et al., 1998; Caputo et al., 2003; Vlyssides et al., 2004 |
| **Total proteins (%)** | | 3.43-7.26 | 2.87-7.20 | Vlyssides et al., 1998; Alburquerque et al., 2004 |
| **Total phenols (%)** | 0.63-5.45 | 0.200-1.146 | 0.40-2.43 | Vlyssides et al., 1998; Caputo et al., 2003; Dermeche et al., 2013 |
| **Cellulose (%)** | | 17.37-24.14 | 14.54 | Vlyssides et al., 1998 |
| **Hemicellulose (%)** | | 7.92-11.00 | 6.63 | Vlyssides et al., 1998 |
| **Lignin (%)** | | 0.21-14.18 | 8.54 | Vlyssides et al., 1998 |

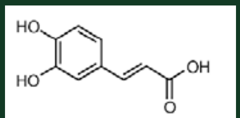
# Phenolics of OMW



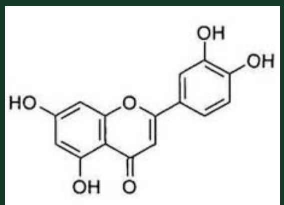
Tyrosol



Hydroxytyrosol

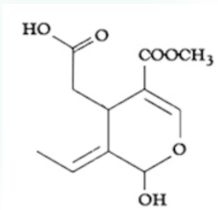


Caffeic Acid

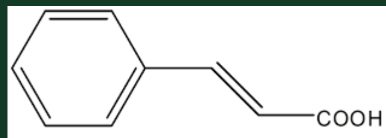


Luteolin

| Phenolic compound | Content (mg/L) | Reference |
|---|---|---|
| Tyrosol | 5-100 | Navrozidis, 2008 |
| Hydroxytyrosol | 35-130 | |
| Caffeic acid | 4-12 | |
| Elenileic acid | 17-1430 | |
| Luteolin | 2-623 | |
| Cinnamic acid | 1-118 | |



ELENOLIC ACID



3-Phenyl-acrylic acid
(**cinnamic acid**)

# Characterization of OMW

- **OMWW**
  - Aqueous, dark, foul smelling, turbid liquid, includes emulsified grease, easily fermentable
  - High organic content(57.2-62.1%)
  - Acidic character (pH 2.2 -5.9)
  - High concentrations of phenolic compounds (up to 80 g/L)
  - High content of solid matter (total solids up to 20 g/L)

→

- high phytotoxicity with strong negative impact on soil quality and plant growth, due to phenolic compounds, low pH and toxic fatty acids
- strong discoloration and pollution of natural waters, resulting in surface and ground water pollution
- threatening the aquatic life
- problems with offensive odors

**Potential source of phenolic compounds and other natural antioxidants**

# Recovery of functional components from OMW

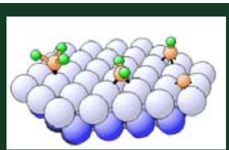
- Membrane separation
- Extraction
- Chromatographic separation
- Adsorption

**Phenolic compounds**

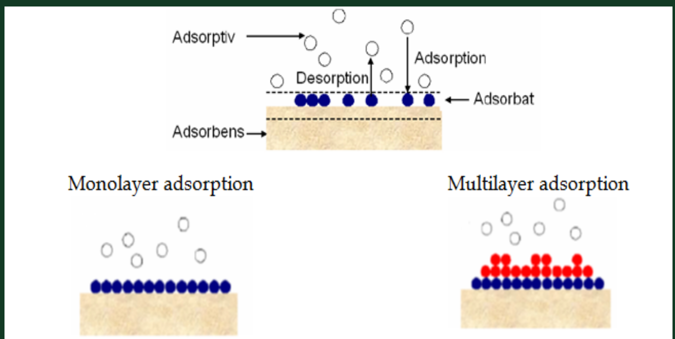
as food additives and/or nutraceuticals

(de Leonardis et al., 2007; Rosello-Soto et al., 2015)

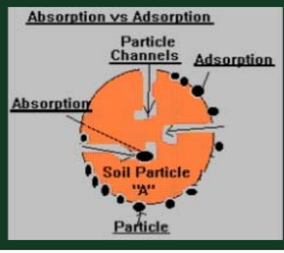
# Adsorption



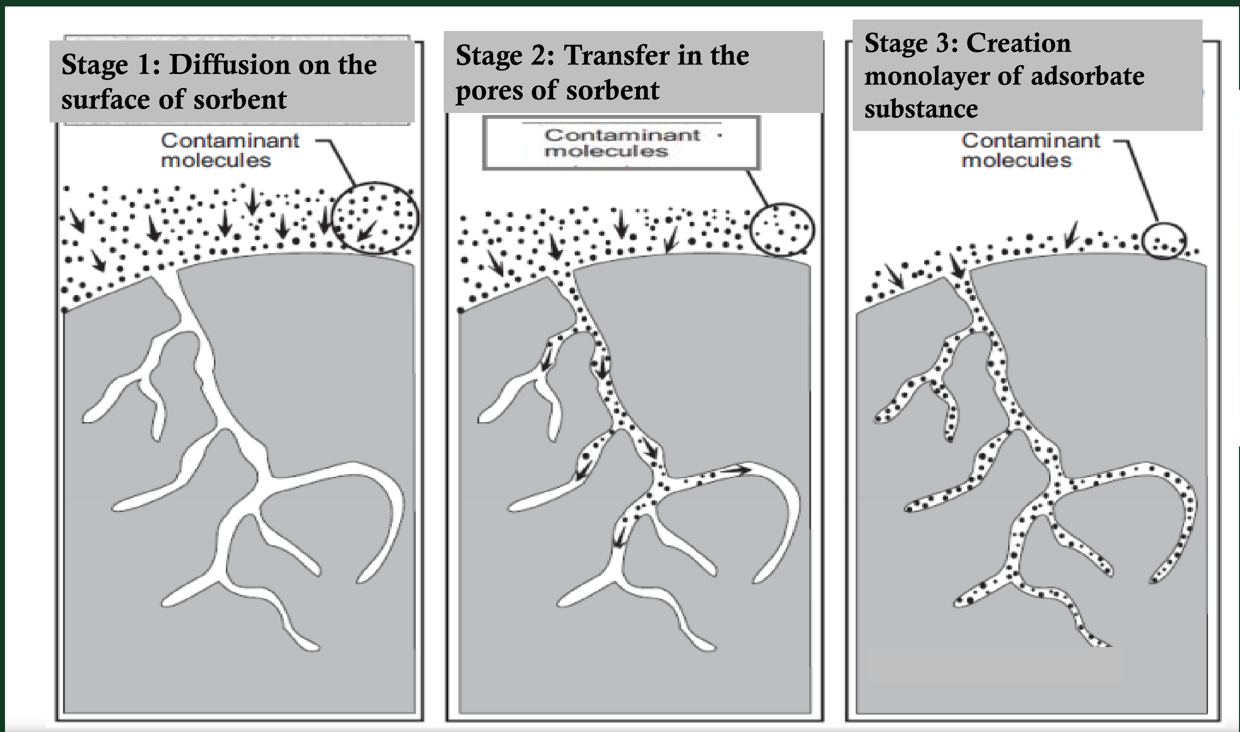
- Adsorption method is generally considered to be the best, effective, low-cost and most frequently used method for the removal of phenolic compounds
- The profitability of an industrial process for the adsorptive purification and concentration of phenolic compounds from OMW depends mainly on the adsorption efficiency and on the recovery rates during desorption




**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 due to intermolecular attraction with the solid molecules.**

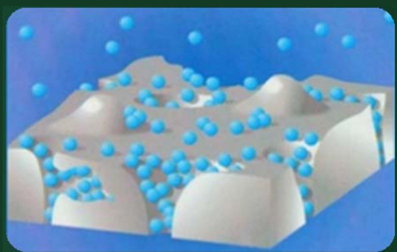



# Stages of adsorption

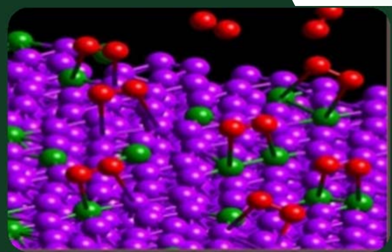


## Mechanisms

- **Exchange adsorption (ion exchange):** electrostatic due to charged sites on the surface
- **Physical adsorption:** Van der Waals attraction between adsorbate and adsorb
- **Chemical adsorption:** Some degree of chemical bonding between adsor te and adsorbent characterized by strong attractiveness. Adsorbed molecules ar not free to move on the surface.

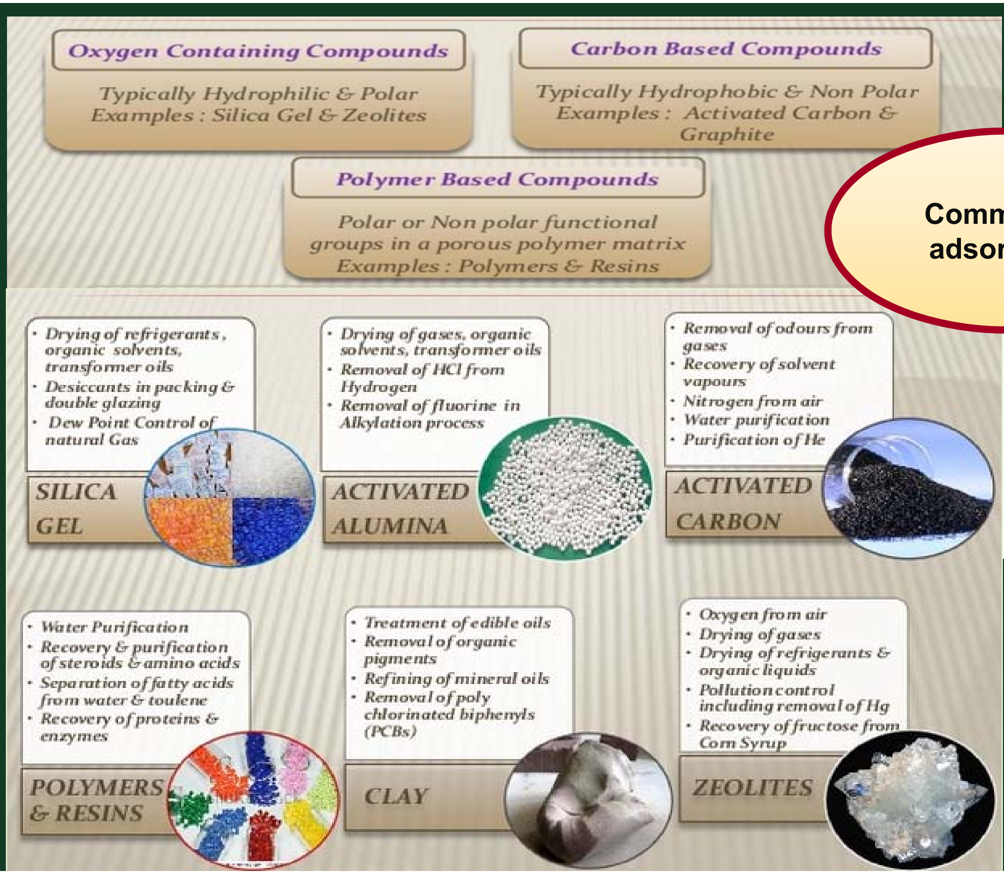


*Physical adsorption*



*Chemical adsorption*

# Commercial adsorbents



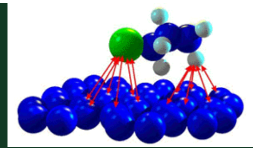
## Commercial adsorbents used for recovery of phenolics from OMW

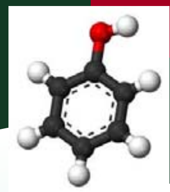
| Adsorbent | | Yield (%) | Reference |
|---|---|---|---|
| Resin | XAD-4 | 3.5- 97.5 | (Kaleh et al., 2016) |
| | XAD-16 | 4.5- 99.0 | |
| | XAD-761 | 2.1- 87.2 | |
| | Xad-7hp | 3.1- 98.0 | |
| | FPX-66 | 4.5- 98.0 | |
| | PVPP | 0.9-100 | |
| | AF5 | 31.7-91.4 | |
| | AF6 | 90- 100 | |
| | AF7 | 92.4- 100 | |
| | GAC | 71- 100 | |
| | PAC | 93.5- 100 | |
| Val d' Orsia soil | | 27- 67 | (Santi, 2007) |
| Zeolite | | 37- 45 | |
| Bentonite | | 29-45 | |
| Banana peel | | 34 -66 | (Achaka et al.,2009) |
| Wheat bran | | 12-63 | (Achak et al., 2014) |

## Biosorbents used for recovery of various components

| Adsorbent | Recovery | 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, 2010) |
| | Pb from water | 76.0 -58.3 | |
| | Cr from leather tanning | 99.1- 100 | (Jamil et al., 2008) |
| Coir pith carbon | Congo red | 30.5-66.5 | (Namasivayam et al., 2002) |
| 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) |

# Objective





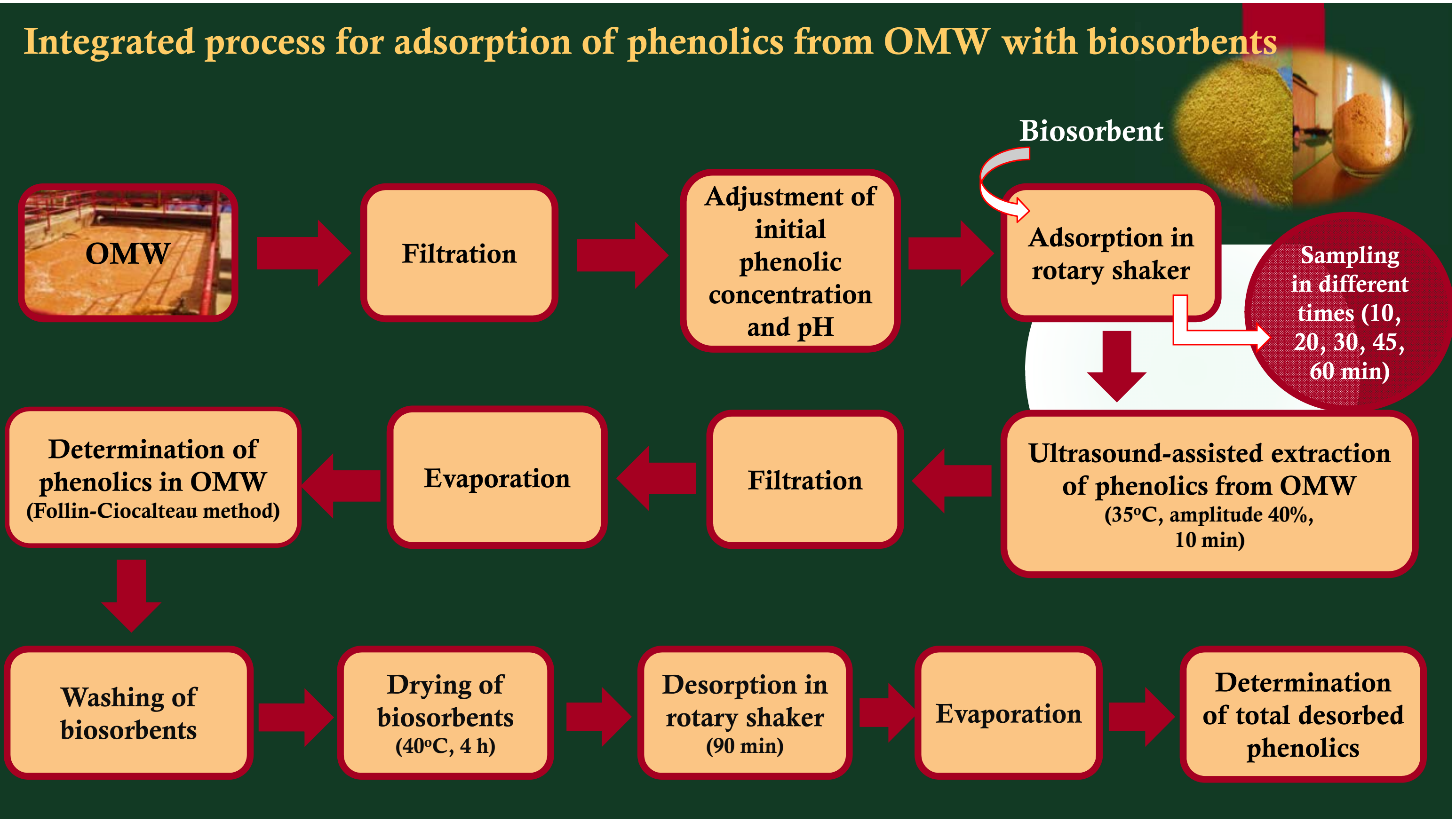
- Investigation of the efficiency of two food wastes:
    - *pomegranate peel*
    - *orange juice by-product*

  as biosorbents for removal of phenolic compounds from OMW

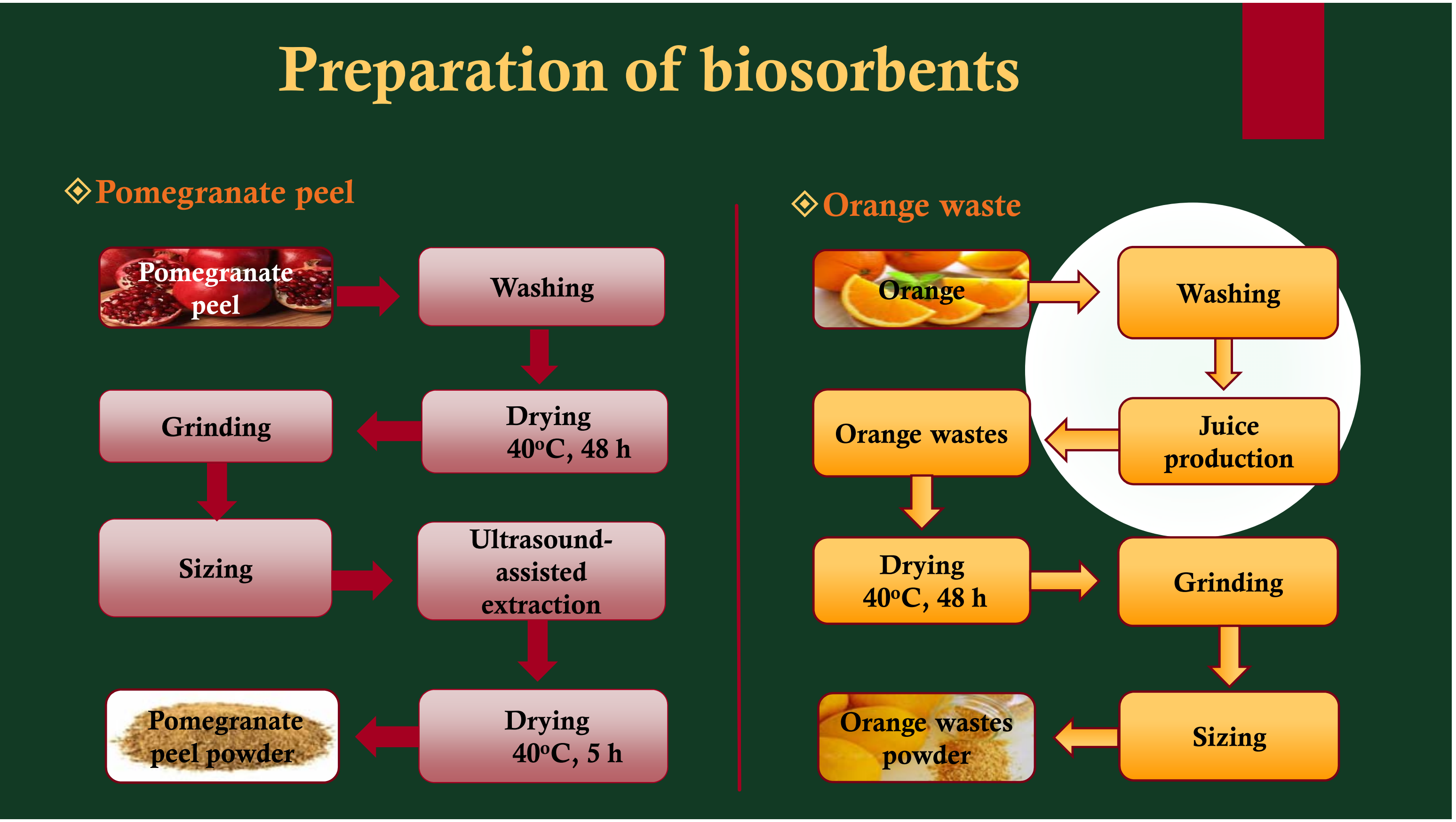
- Optimization of adsorption process using biosorbents

- Development of a new, low cost method for removal of phenolic compounds from OMW

# Materials and Methods



Integrated process for adsorption of phenolics from OMW with biosorbents
Biosorbent
OMW
Filtration
Adjustment of initial phenolic concentration and pH
Adsorption in rotary shaker
Sampling in different times (10, 20, 30, 45, 60 min)
Ultrasound-assisted extraction of phenolics from OMW
(35°C, amplitude 40%, 10 min)
Filtration
Evaporation
Determination of phenolics in OMW
(Follin-Ciocalteau method)
Washing of biosorbents
Drying of biosorbents
(40°C, 4 h)
Desorption in rotary shaker
(90 min)
Evaporation
Determination of total desorbed phenolics


Preparation of biosorbents
Pomegranate peel
Pomegranate peel
Washing
Drying 40°C, 48 h
Grinding
Sizing
Ultrasound-assisted extraction
Drying 40°C, 5 h
Pomegranate peel powder
Orange waste
Orange
Washing
Juice production
Orange wastes
Drying 40°C, 48 h
Grinding
Sizing
Orange wastes powder

# Composition of biosorbents

## POMEGRANATE PEEL

| Component | Content (%) |
|---|---|
| Total solids | 96.00 |
| Moisture | 4.00 |
| Total sugars | 31.38 |
| Protein | 8.72 |
| Crude Fiber | 21.06 |
| Fat | 9.40 |
| Ash | 5.00 |
| Total phenolics | 8.10 |

## ORANGE JUICE WASTE

| Component | Content (g/100 g DM) |
|---|---|
| Moisture | 8.52 |
| Protein | 13.25 |
| Lipid | 2.12 |
| Ash | 4.25 |
| Carbohydrate | 80.38 |
| Total dietary fiber | 65.7 |
| Insoluble dietary fiber | 48.9 |
| Soluble dietary fiber | 16.8 |

# Factors Affecting the Adsorption Process

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

# Experimental Design for Optimization of Adsorption

**Levels of variables**

| T (°C) | pH | Sorbent/OMW ratio (r) (g/mL) | Initial phenolic concentration in OMW ($C_o$) (mg/L) | Sorbent particle size (d) (mm) | Biosorbent type |
|---|---|---|---|---|---|
| 20 | 4.00 | 0.010 | 50.0 | 0.149 | Pomegranate peel |
| 30 | 4.75 | 0.015 | 162.5 | 0.373 | |
| 40 | 5.50 | 0.020 | 275.0 | 0.515 | Orange juice wastes |
| 50 | 6.25 | 0.025 | 387.5 | 0.847 | |
| 60 | 7.00 | 0.020 | 500.0 | 1.180 | |

**Response Surface Methodology (32 experiments for each biosorbent)**

$$\text{Yield} = \frac{C - Co}{Co} \, 100$$

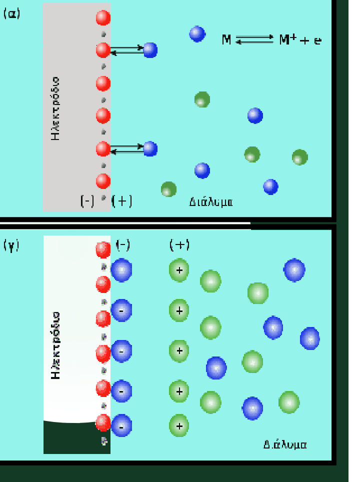
C: concentration of phenolics in OMW after adsorption
$C_o$: initial concentration of phenolics in OMW

Lower Yield value

Higher Adsorption Capacity

# Desorption

1. 50% acetic acid (pH 1.2)
2. Water (pH 7)
3. Alkaline water (pH 12)

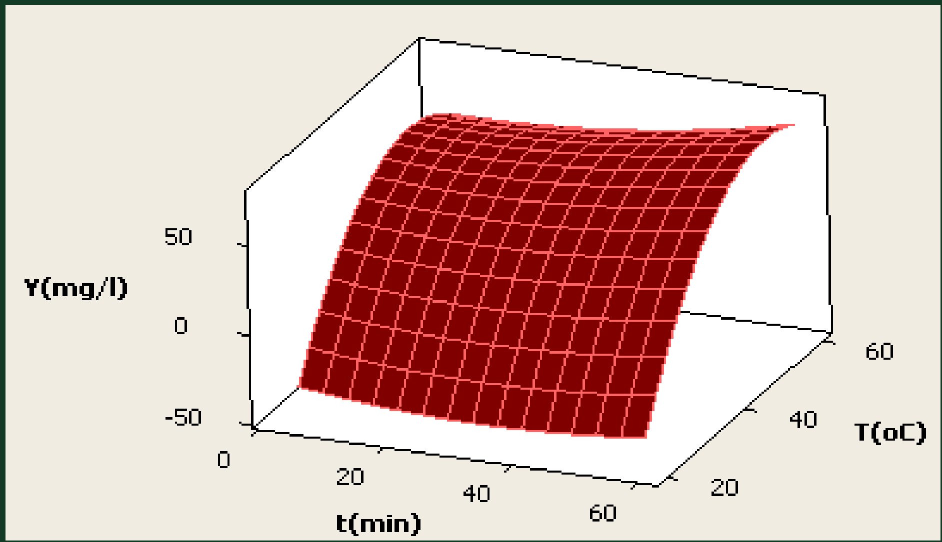


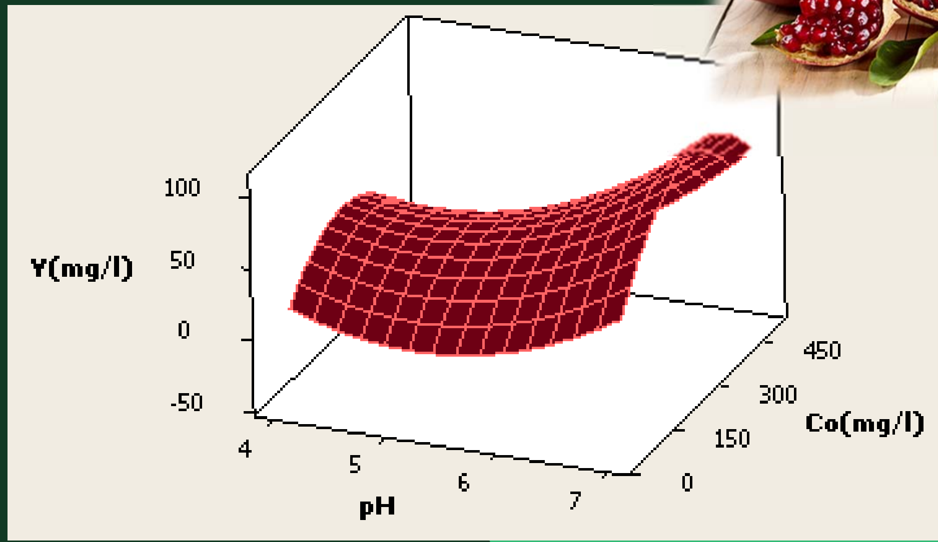
**Yield desorption**= $\frac{C3}{C1-C2}$

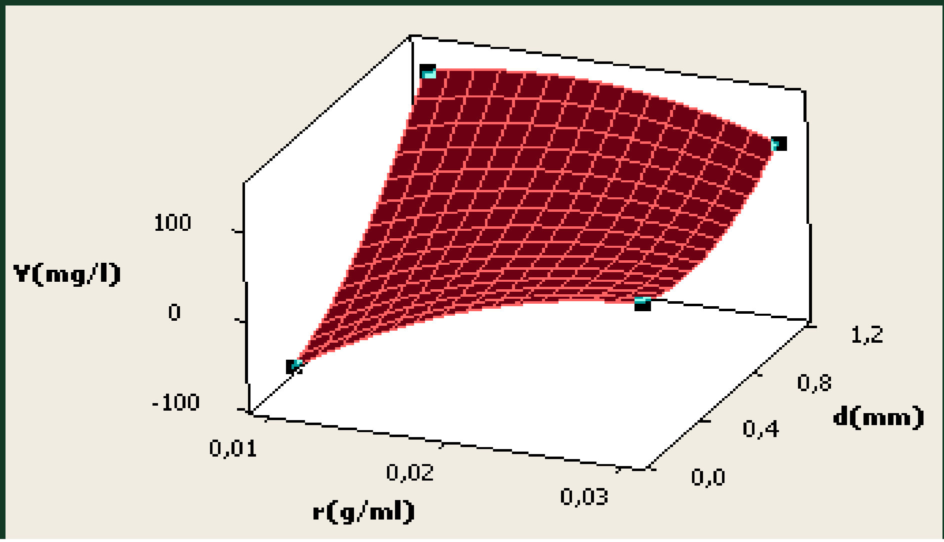
**$C_1$**: concentration of phenolics in OMW before adsorption
**$C_2$**: concentration of phenolics in OMW after adsorption
**$C_3$**: concentration of phenolics in solvent after desorption

# Results

# Pomegranate peel - biosorbent




$$\text{Yield} = \frac{C - Co}{Co}\,100$$

Max adsorption capacity:

- ✓ T : $20^{O}C$
- ✓ pH : 4.75
- ✓ r : 0.01 g/mL
- ✓ $C_O$ : 50 mg/L
- ✓ d : 0.149 mm

Lower C

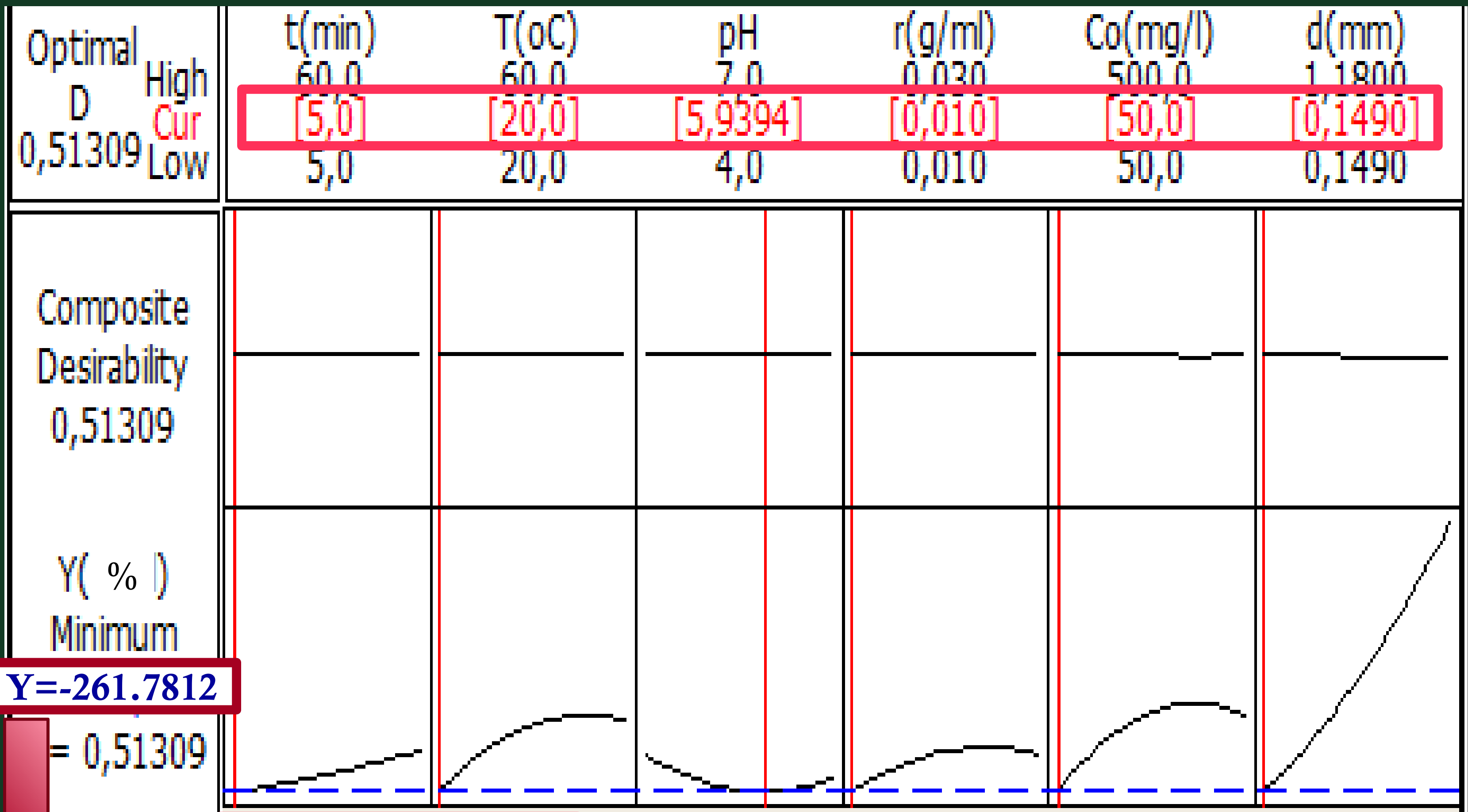
⬇

Lower Yield value

⬇

Higher Adsorption Capacity

# Pomegranate peel as biosorbent – Optimization




Y=-261.7812

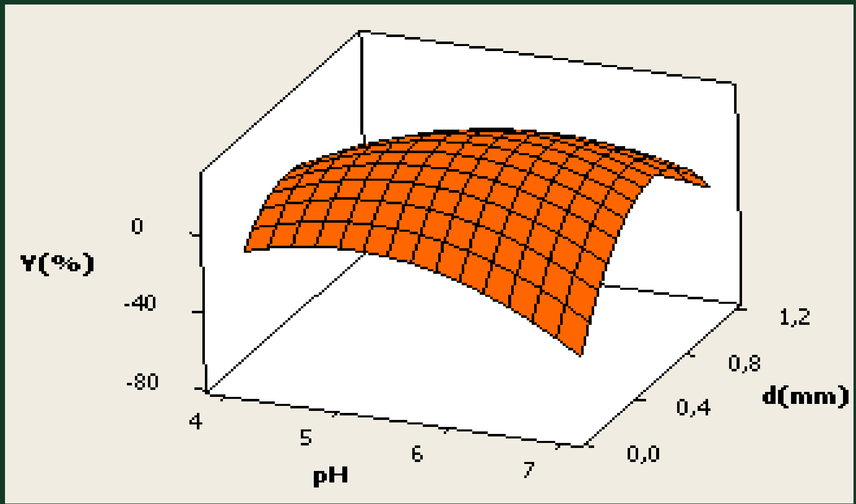
The phenolics concentration reduced by 2.6 times

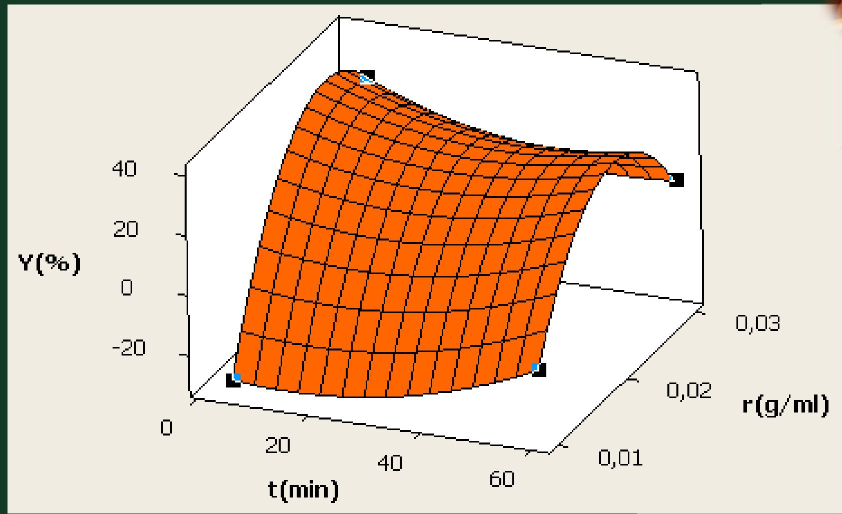
$$\text{Yield}=\frac{C-Co}{Co}100$$

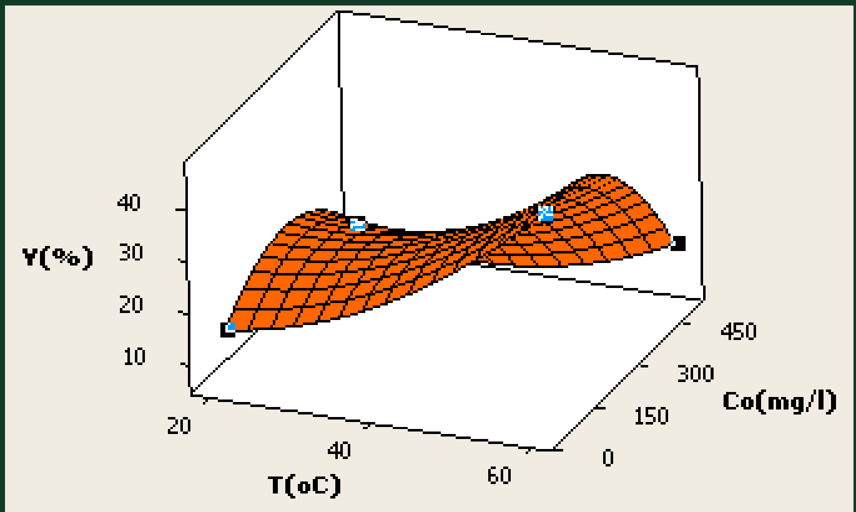
| Statistically significant parameters | p-value |
|---|---|
| pH | 0.034 |
| $T^2$ | 0.003 |
| $pH^2$ | 0.036 |
| $r^2$ | 0.049 |
| $C_o$ | 0.000 |
| $d^2$ | 0.033 |
| T*r | 0.047 |

$$y = -52 + 260d - td + 184Tr - 3Td - 7374rd$$

# Orange juice waste - biosorbent




**Max adsorption capacity:**

- ✓ **T** : 30$^{O}$C
- ✓ **pH** : 7
- ✓ **r** : 0.01 g/mL
- ✓ **$C_O$** :162.5 mg/L
- ✓ **d** : 0.149 mm
- ✓ t: : 20min

Lower C

⇩

Lower Yield value

⇩

Higher Adsorption Capacity

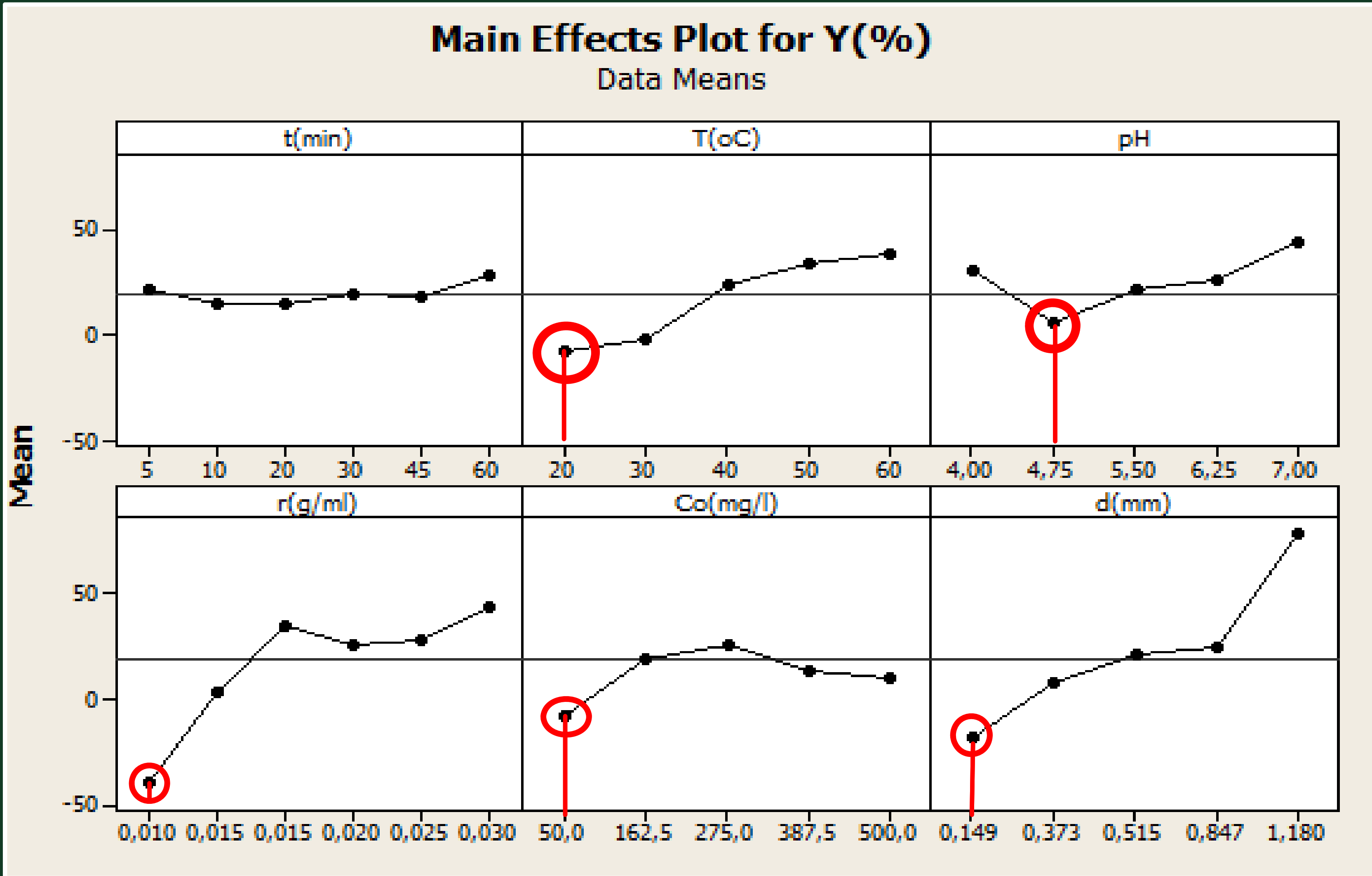
# Orange juice wastes as biosorbent - Optimization

| | |
|---|---|
| t | **60 min** |
| T | **20$^o$C** |
| pH | **4.00** |
| r | **0.03 g/mL** |
| $C_o$ | **500 mg/L** |
| d | **1.18 mm** |

$$y = -777 + 10T + 368d - 337909r^2 - 165d^2 \\ -2TpH - 3Td + 1431pHr$$

| **Statistically significant parameters** | **p-value** |
|---|---|
| T | 0.012 |
| d | 0.014 |
| $pH^2$ | 0.041 |
| $r^2$ | 0.001 |
| $d^2$ | 0.000 |
| T*pH | 0.000 |
| T*r | 0.043 |
| T*d | 0.020 |
| r*d | 0.012 |

# Effects of Various Parameters




Lower phenolics concentration in OMW after adsorption (C)

↓

Lower Yield (Y, %) value

↓

Higher adsorption capacity

**Max adsorption capacity:**

**T** : 20$^{o}$C

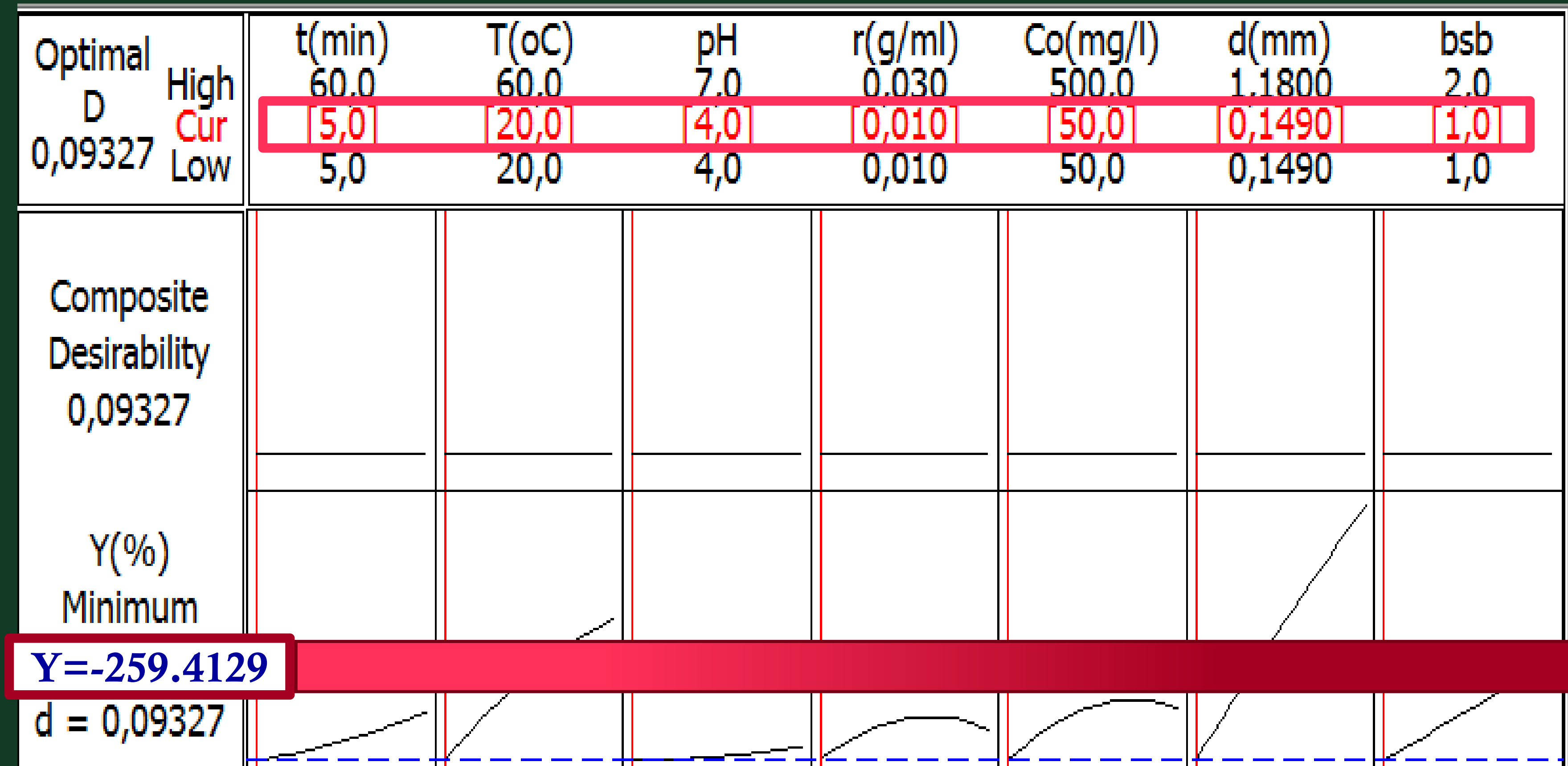
**pH** : 4.75

**r** : 0.01 g/mL

**$C_o$** : 50mg/L

**d**: 0.149 mm

# Adsorption - Optimization




**Biosorbent (bsb)**

1: pomegranate peel

2: orange juice wastes

Yield= $\frac{C-Co}{Co}$ 100

The phenolics concentration reduced by 2.6 times

$$y = -788 + 506d + 249(bsb) - 304383r^2 + 162Tr - 2T(bsb)$$
$$+1185ph\, r - 19ph(bsb) - 7283rd - 128d(bsb)$$

# Desorption

**Adsorption mechanism: ion exchange**

◈ Pomegranate peel powder - biosorbent

| **50% acetic acid** | **Water** | **Alkaline water** |
| --- | --- | --- |
| Desorption efficiency: 59.34% | Desorption Efficiency: 13.04% | Desorption Efficiency: 67.31% |

**Best solute in desorption**

**Adsorption mechanism: chemisorption**

◈ Orange juice waste powder - biosorbent

| **Alkaline water** | **Water** | **50% acetic acid** |
| --- | --- | --- |
| Desorption Efficiency: 1.33% | Desorption Efficiency: 2.17% | Desorption Efficiency: 5.33% |

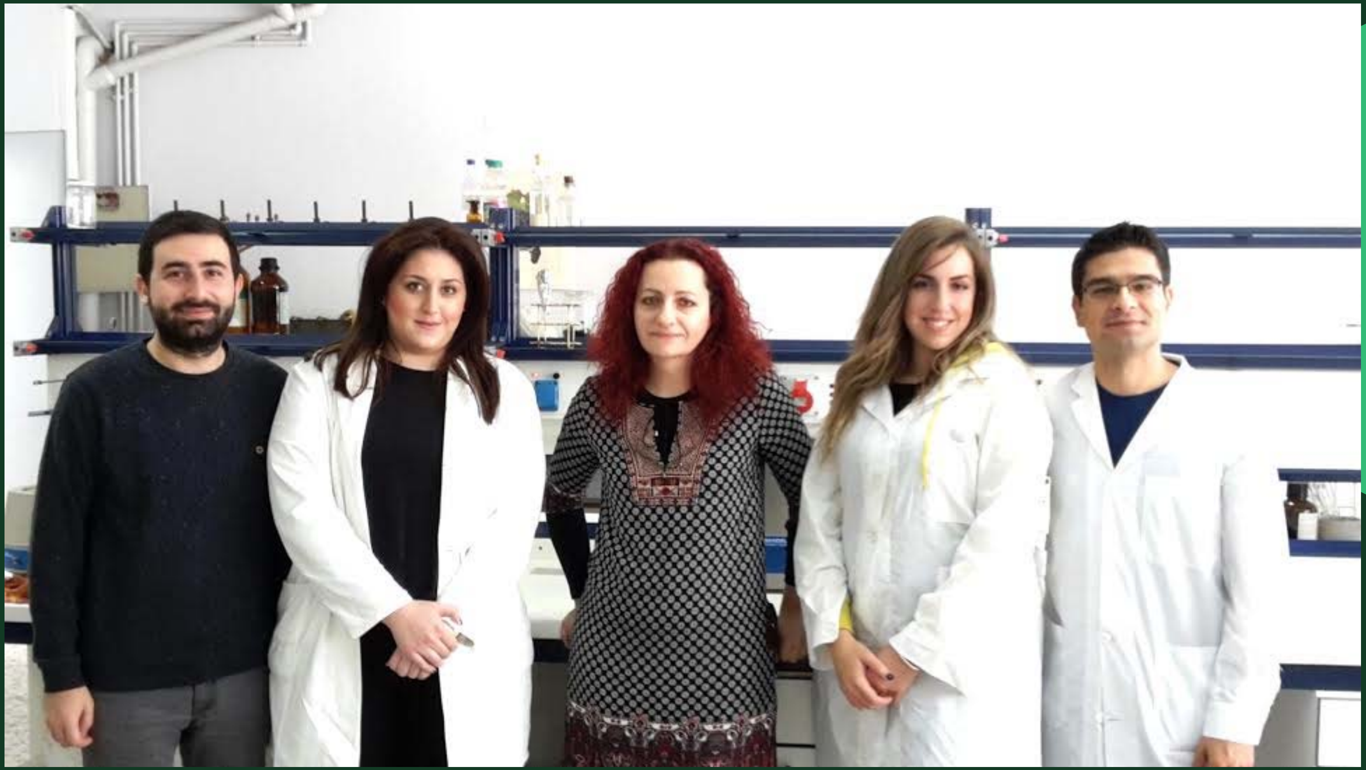
# Conclusions

- ✓ Banana peel and orange juice waste have proven to be promising materials for the removal of contaminants from olive mill wastewaters
- ✓ The adsorption process was very fast, and it reached equilibrium in < 60 min of contact
- ✓ The optimum adsorption conditions were:
    - T: 20°C
    - pH: 4
    - r: 0.01 g/mL
    - $C_o$: 50 mg/L
    - d: 0.149 mm
    - t: 5 min
    - Pomegranate peel powder as biosorbent

reduction of phenolics concentration = 260%

- ✓ All the examined factors had a statistical significant effect on the adsorption capacity
- ✓ Desorption experiments showed an ion change adsorption for pomegranate peel and a chemisorption mechanism for orange waste
- ✓ Kinetic and equilibrium studies should be accomplished

# Thank you for your attention!



Team of food engineering…