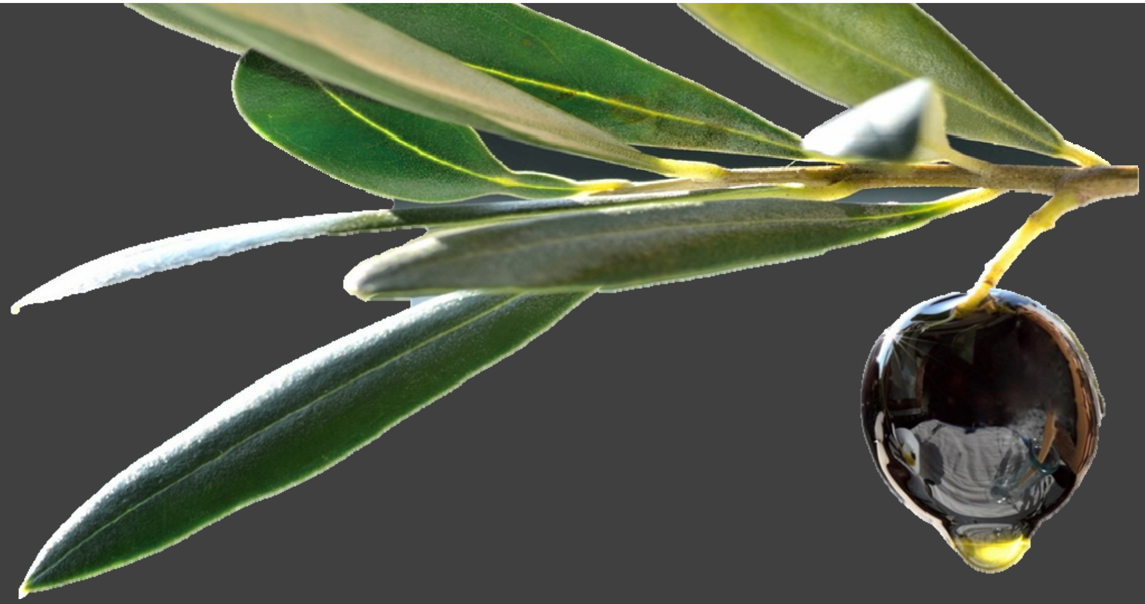

Low cost biosorbents of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies

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Olive oil production

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

Olive oil extraction

1. Traditional pressing

- 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

2. 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 "olive cake"

  ii. a watery liquid (50% of raw material weight) called "olive mill wastewater" (OMW)

3. Two – phase extraction process

- ''Ecological'' method, reduces the olive mill waste by 75%

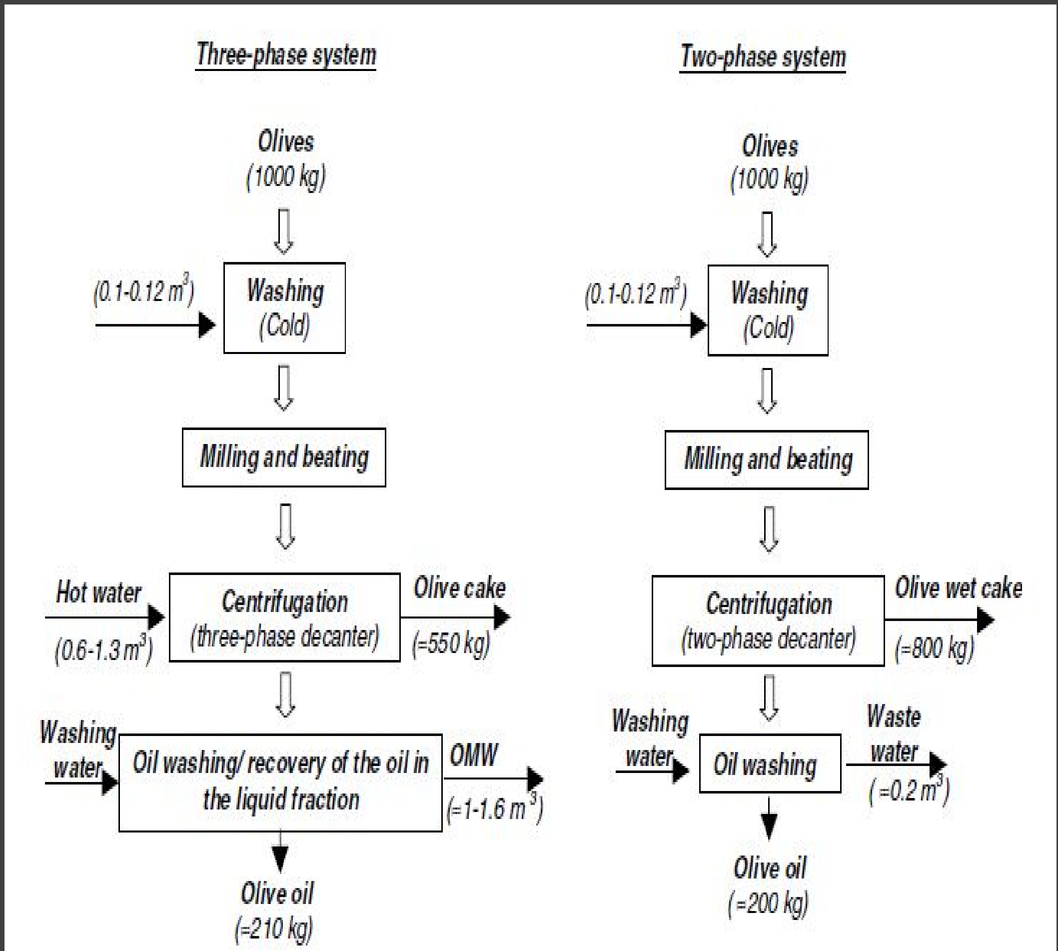
- Two fractions

  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



Comparison of the three and two-phase centrifugation systems for olive oil extraction (Alburquerque et al., 2004)

Olive oil extraction by- products (Goula et al., 2016)

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 kg)

The management of waste from olive mills

Olive cake
- Solid fuels
- Animal feed supplement
- Return to the olive grove as mulch

Olive mill wastewater (OMW)
- Disposal of OMW in nearby aquatic receivers
- Physical and physicochemical processes
- Biological processes
- Coupled physicochemical and biological treatments

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

Characterization of OMW

OMW

- 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)

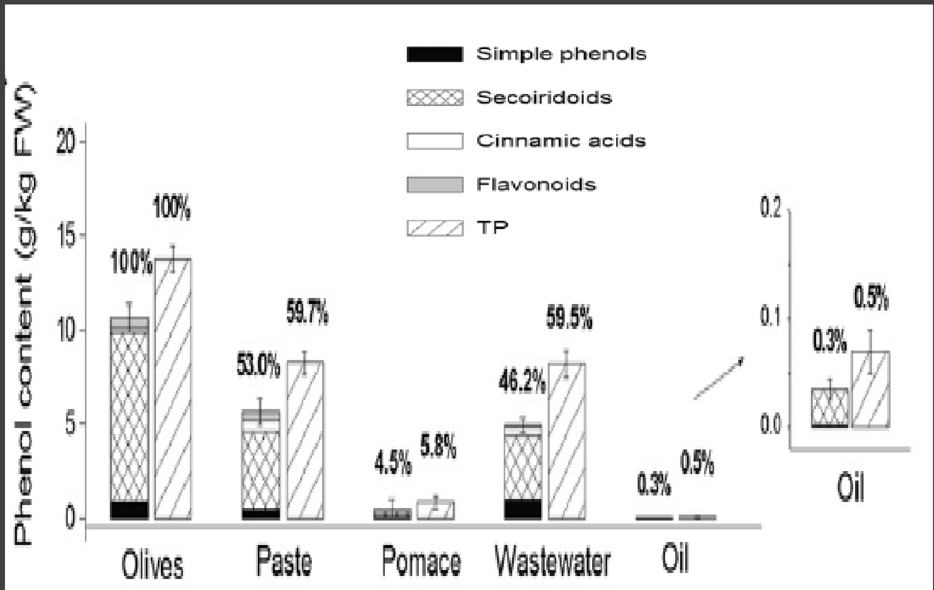
- high **phytotoxicity** with strong neg...ive impact on soil quality and ... h, due to phenolic co... toxic fatty...
- ...ace and
- ...ening the aquatic life
- **problems** with offensive odors

Potential source of phenolic compounds and other natural antioxidants

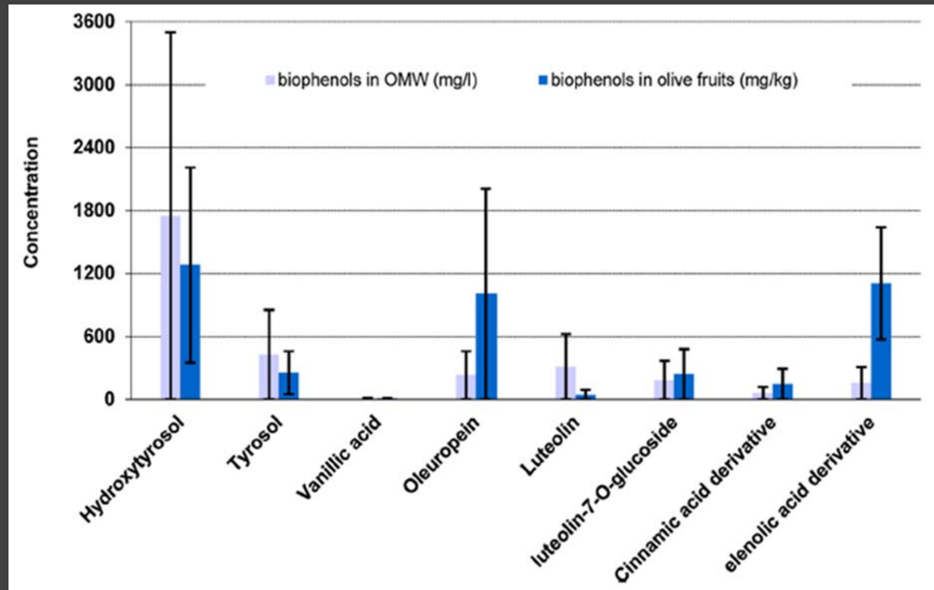
Composition of olive mill wastewaters and solid residues

Characteristic	Olive mill by-product			Reference
	OMW	Olive cake	TPOMW	
pH	2.2-5.9		4.9-6.8	Galiatsatou et al., 2002; Dermeche et al., 2013
Total carbon (%)	2.0-3.3	29.0-42.9	25.4	Vlyssides et al., 1998; Garcia-Castello et al., 2010
Organic matter (%)	57.2-62.1	85.0	60.3-98.5	Aktas et al., 2001; Vlyssides et al., 2004
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	3.50-8.72	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

Comparison of phenolic concentration between olive fruit and OMW



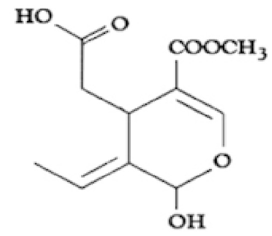
Phenols transfer rates between individual olive matrices in three-phase centrifuge. (Klen et al., 2012)



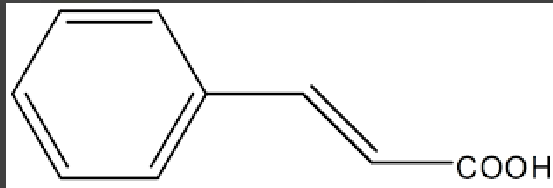
Reported concentrations of biophenols in OMW and olive fruits. (Kaleh et al., 2016)

Phenolics of OMW

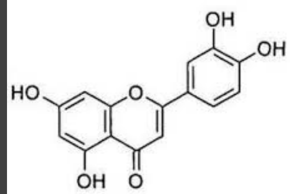
Phenolic compound	Content (mg/L)	Reference
Hydroxytyrosol	35-1600	Navrozidis, 2008 Kaleh et al., 2010 Allouche et al., 2014
Tyrosol	35-1200	
Caffeic acid	4-498	
Elenileic acid	17-1430	
Luteolin	2-623	
Cinnamic acid	1-118	



ELENOLIC ACID

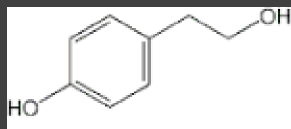


3-Phenyl-acrylic acid
(**cinnamic acid**)

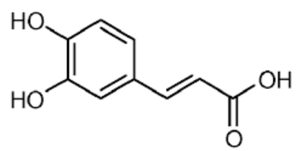


Luteolin

Hydroxytyrosol

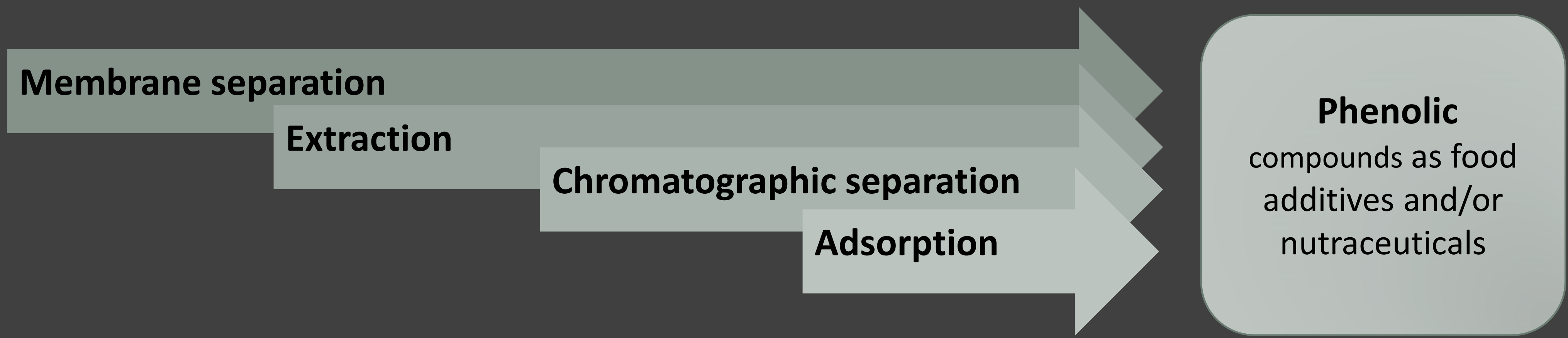


Tyrosol



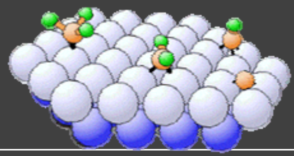
Caffeic Acid

Recovery of functional components from OMW

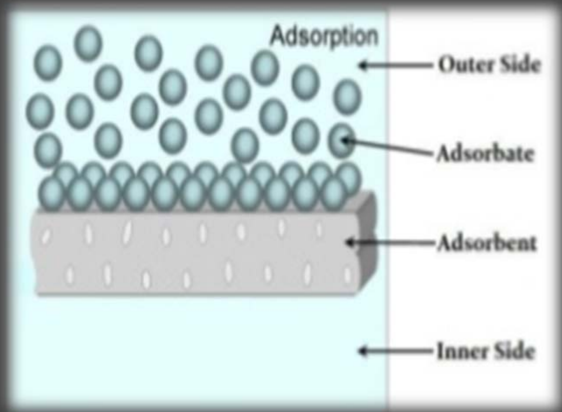


(Leonardis et al., 2007; Rosello-Soto et al., 2015)

Adsorption

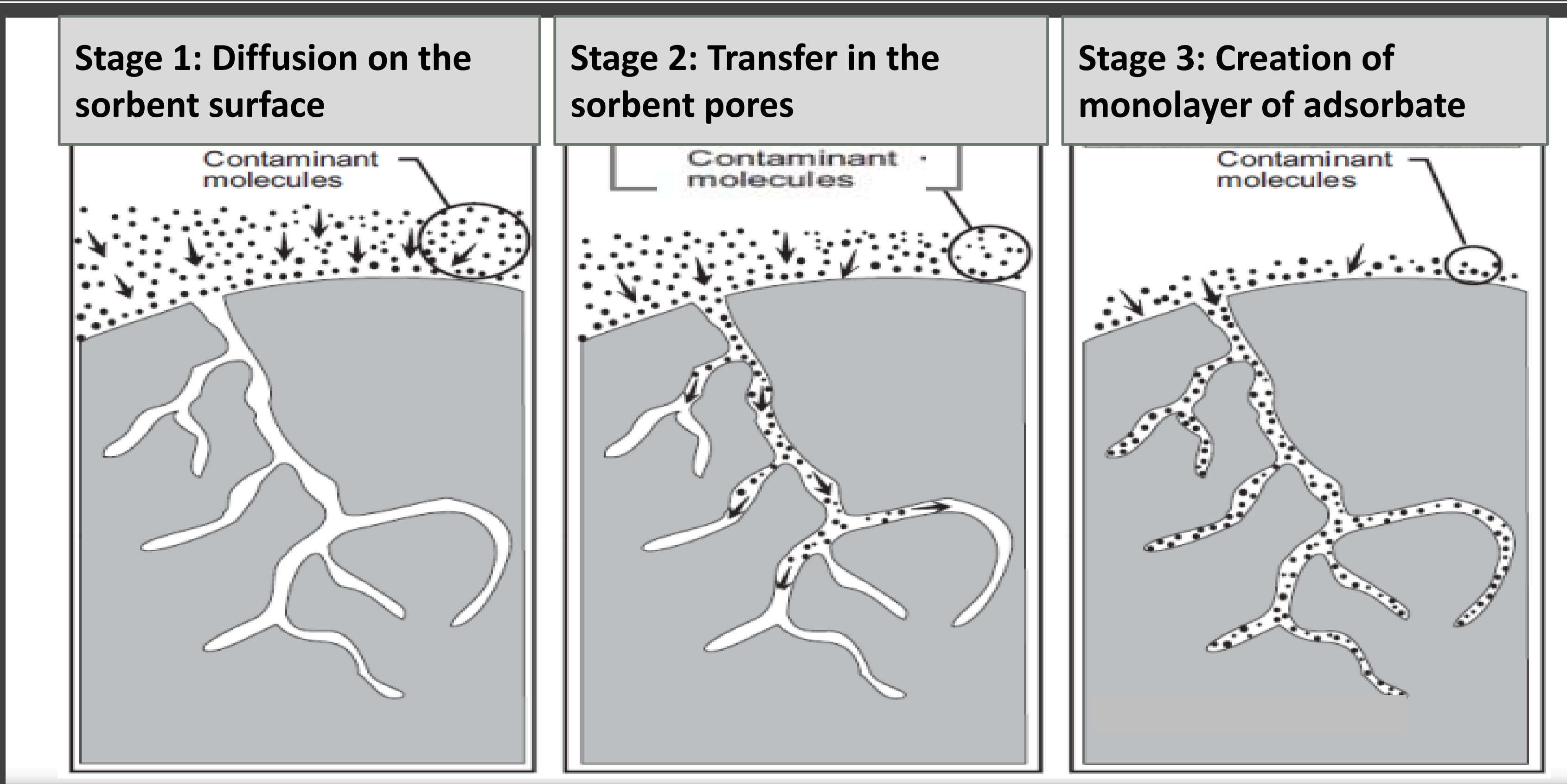


- Adsorption is generally considered to be the best, effective, low-cost and most frequently used method for the removal of phenolic compounds
- The profitability of an industrial process for the adsorptive purification and concentration of phenolic compounds from OMW depends mainly on the adsorption 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 intermolecular attraction with the solid molecules.

Stages of adsorption

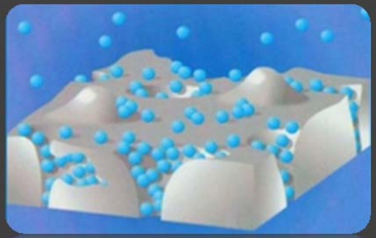


Mechanisms

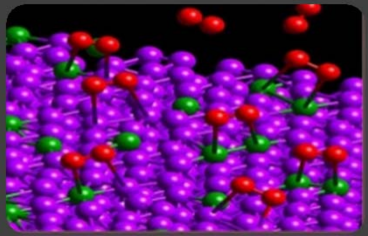
- **Exchange adsorption (ion exchange):** electrostatic due to charged sites on the surface

- **Physical adsorption:** Van der Waals attraction between adsorbate and adsorbent

- **Chemical adsorption:** Some degree of chemical bonding between adsorbate and adsorbent characterized by strong attractiveness. Adsorbed molecules are not free to move on the surface.

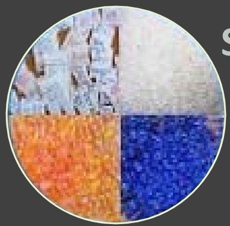


Physical adsorption

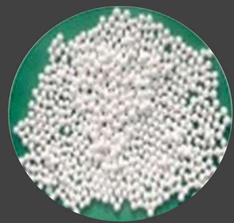


Chemical adsorption

Commercial adsorbents



Silika gel



Activated alumina

Clay

Polymers & resins

Zeolites

Activated carbon

Polymer Based Compounds

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

Oxygen Containing Compounds

Typically Hydrophilic & Polar
Examples : Silica Gel & Zeolites

Carbon Based Compounds

Typically Hydrophobic & Non Polar
Examples : Activated Carbon & Graphite

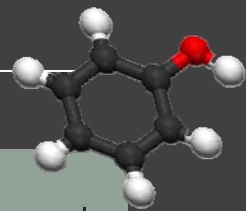
Commercial adsorbents used for recovery of phenolics from OMW

Adsorbent	Yield(%)	Reference
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	
Betonite	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 et al., 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



- In this work two food wastes
  - pomegranate peel
  - orange juice by-product

  were used as biosorbents

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

- Adsorption isotherms
  - Langmuir
  - Freundlich
  - Temkin
- Kinetic models
  - pseudo-first-order
  - pseudo-second-order
  - intraparticle diffusion model

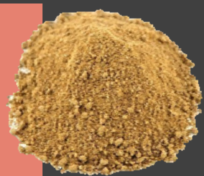
Models used for experimental data fitting

Materials & Methods

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 juice waste

Orange → Washing → Juice production → Orange wastes → Drying 40°C, 48 h → Grinding → Sizing → Orange wastes powder

Composition of biosorbents

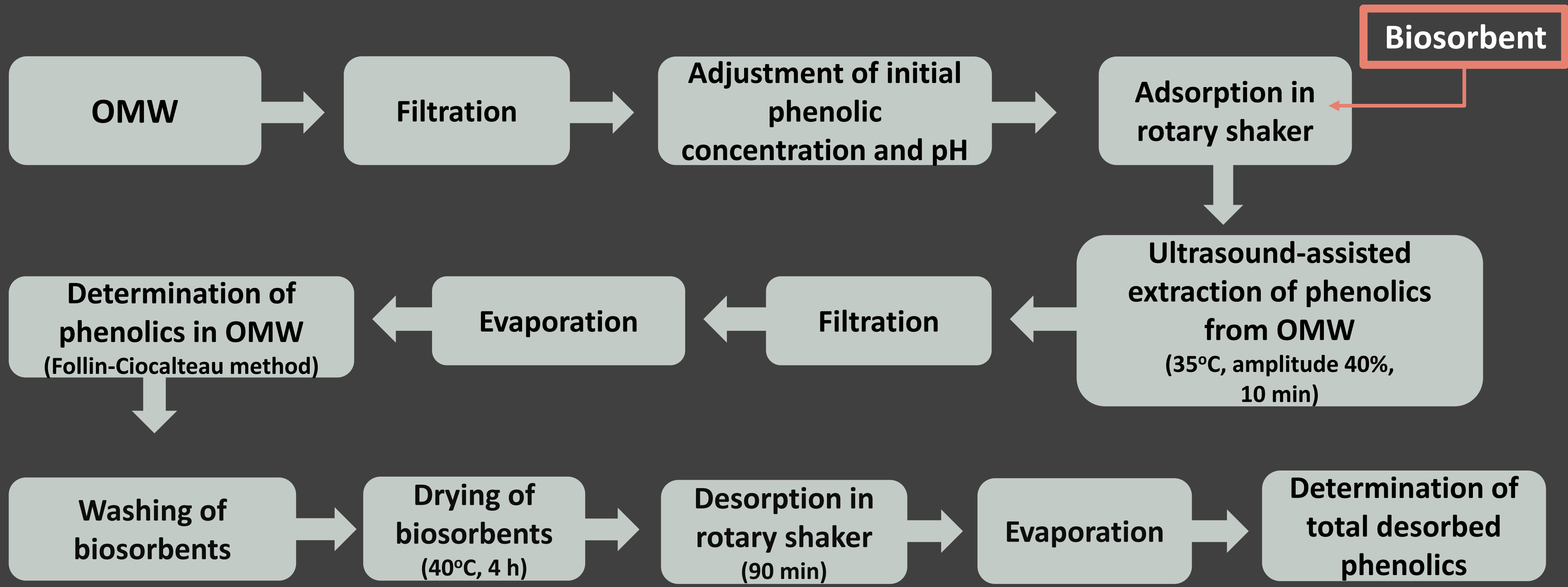
Pomegranate peel

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

Integrated process for adsorption of phenolics from OMW with biosorbents



Factors Affecting the Adsorption Process

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

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)

Desorption

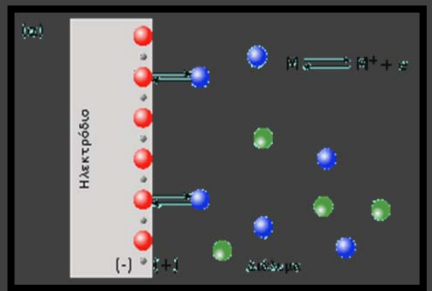
Water (pH 7)

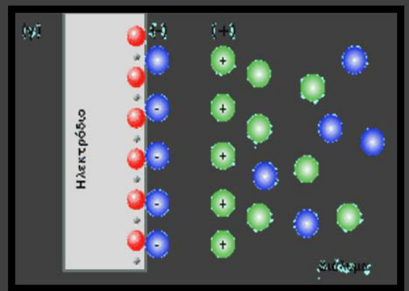
50% acetic acid (pH 1.2)

Alkaline water (pH 12)

Yield desorption= $\frac{C_1}{C_0 - C}$

C_0: concentration of phenolics in OMW before adsorption
C: concentration of phenolics in OMW after adsorption
C_1: concentration of phenolics in solvent after desorption





Regeneration

➢ **Thermal regeneration**

Heating biosorbent (after desorption) for 2 h at:

- 100 ºC
- 150 ºC
- 200 ºC
- 250 ºC

➢ **Chemical regeneration**

Stirring biosorbent (after desorption) for 2 h with 20% methanol and drying at 50 ºC

Adsorption Isotherms

- Isotherm **Langmuir**

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}$$

- Isotherm **Freundlich**

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

- Isotherm **Temkin**

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

- C_e **(g/L)**: the amount of the unadsorbed phenolic compounds concentration in solution at equilibrium
- q_e **(mg/g)**: the amount of adsorbed phenolic compounds per unit weight of adsorbent at equilibrium.
- **b (L/g)**: the equilibrium constant or Langmuir constant related to the affinity of binding sites
- Q_m **(mg/g)**: represents 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 that shows adsorption capacity of adsorbent
- ***n**:* constant which shows greatness of relationship between adsorbate and adsorbent
- B_T **(kJ/mol)**: heat of sorption
- K_T : Temkin isotherm parameters

(Achak et al., 2009; Anwar et al., 2010)

Kinetics of the adsorption

- Pseudo-first-order

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$

- Pseudo-second-order

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

- Diffusion model

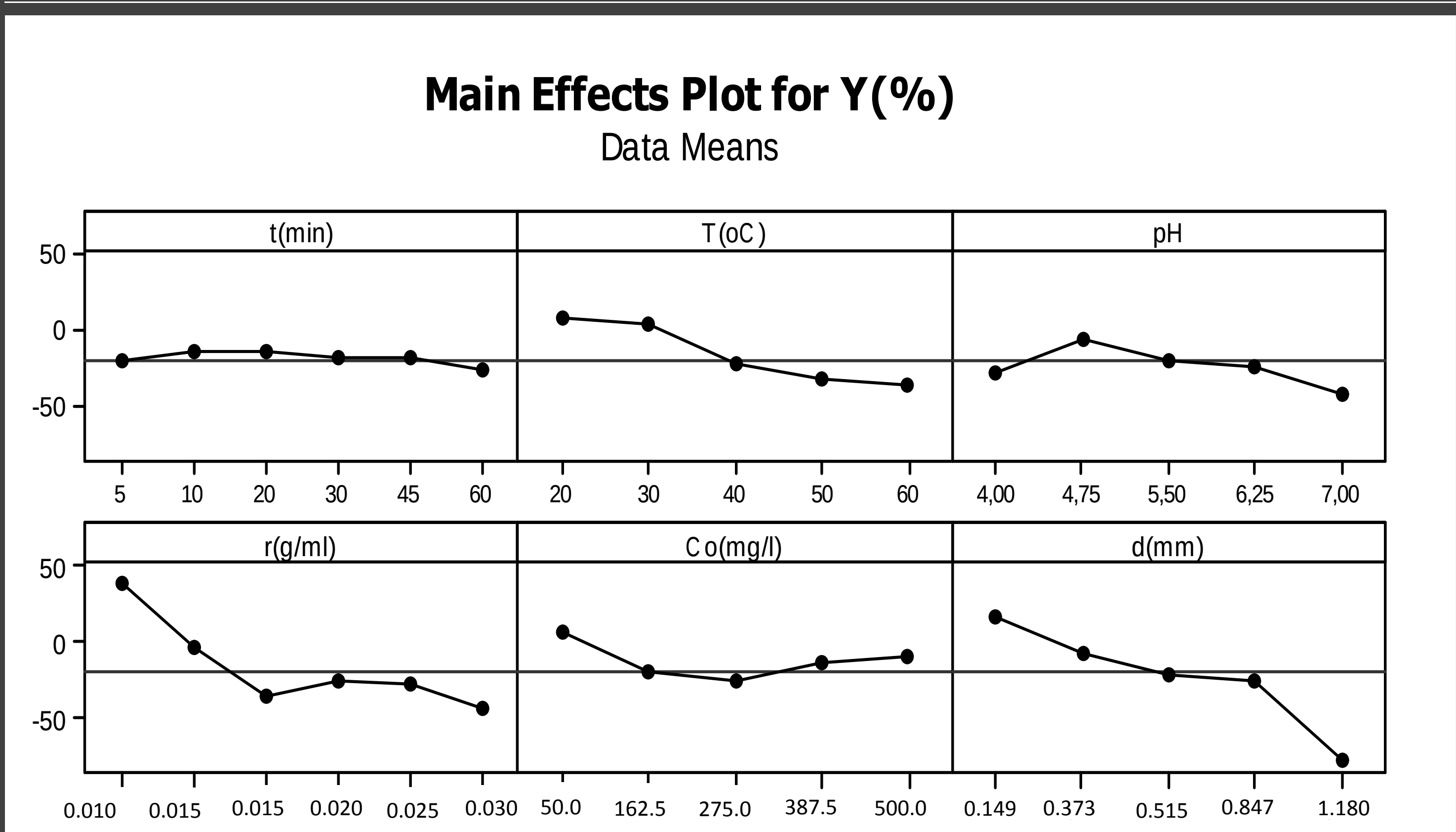
$$q_t = k_p\, t^{\frac{1}{2}} + C$$

- $\boldsymbol{q_e}$ (mg/g): the amount of phenolic compounds adsorbed at equilibrium
- $\boldsymbol{q_t}$ (mg/g): the amount of phenolic compounds adsorbed at any time, t (min)
- $\boldsymbol{K_1}$ (min^{-1}): the equilibrium rate constant of pseudo-first-order sorption
- $\boldsymbol{K_2}$ (g/g min): the rate constant for pseudo-second-order kinetics

- $\boldsymbol{q_t}$ (mg/g): the amount of phenolic compounds adsorbed at equilibrium at time, *t* (min)
- $\boldsymbol{k_p}$ (g/g $min^{\frac{1}{2}}$): is the intraparticle diffusion rate constant
- **C** (mg/g): the intercept

Results

Factors Affecting the Adsorption Process



Max adsorption yield:

T : 20ºC
pH : 4.75
r : 0.01 g/mL
C_o : 50mg/L
D : 0.149 mm

Yield adsorption= $\frac{C_0 - C}{C_0}$

Biosorbent	Max Yield
Pomegranate peel	93.13%
Orange-juice waste	89.60%

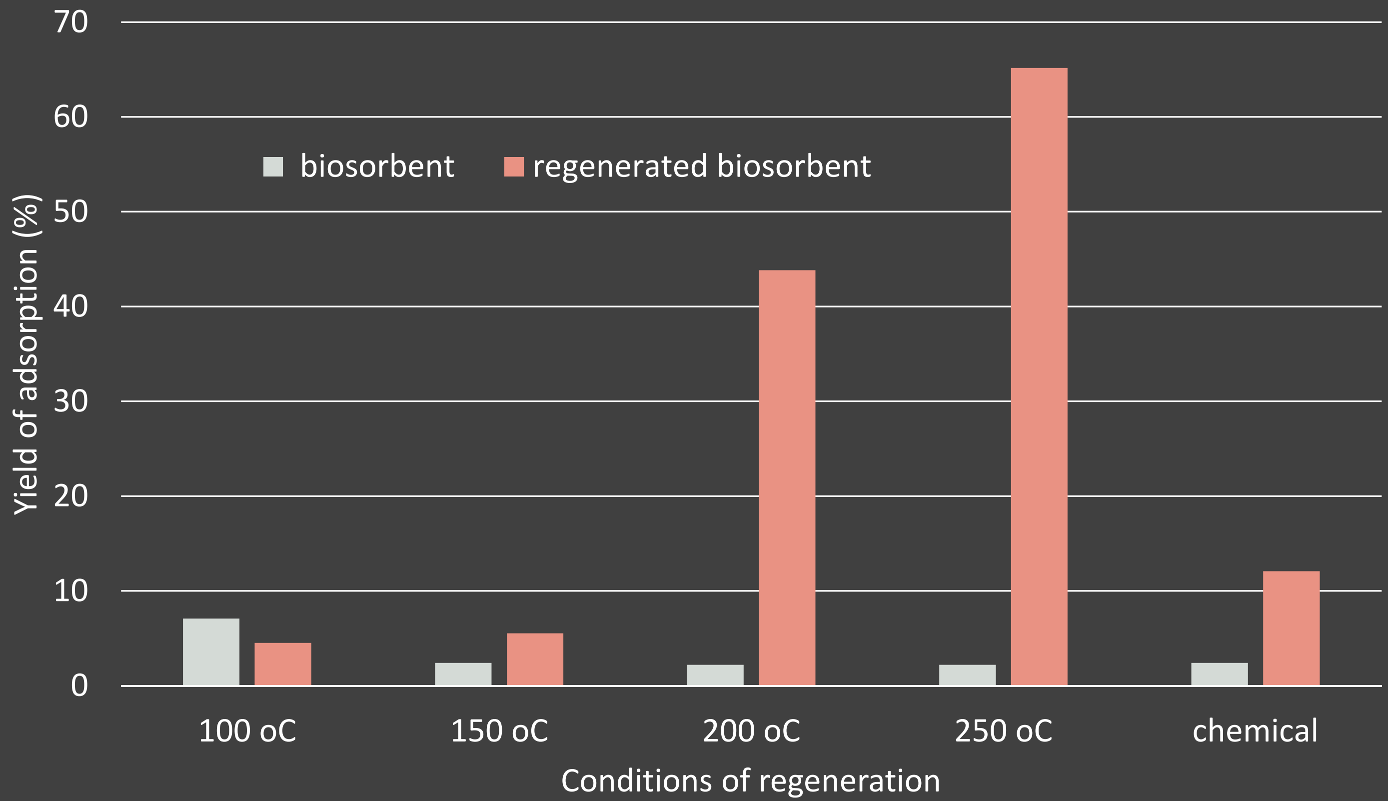
Desorption

	Pomegranate peel	Orange juice waste
50% acetic acid	59.34%	5.33%
Water	13.04%	2.17%
Alkaline water	67.31%	1.33%

Adsorption mechanism: ion exchange

Adsorption mechanism: chemisorption

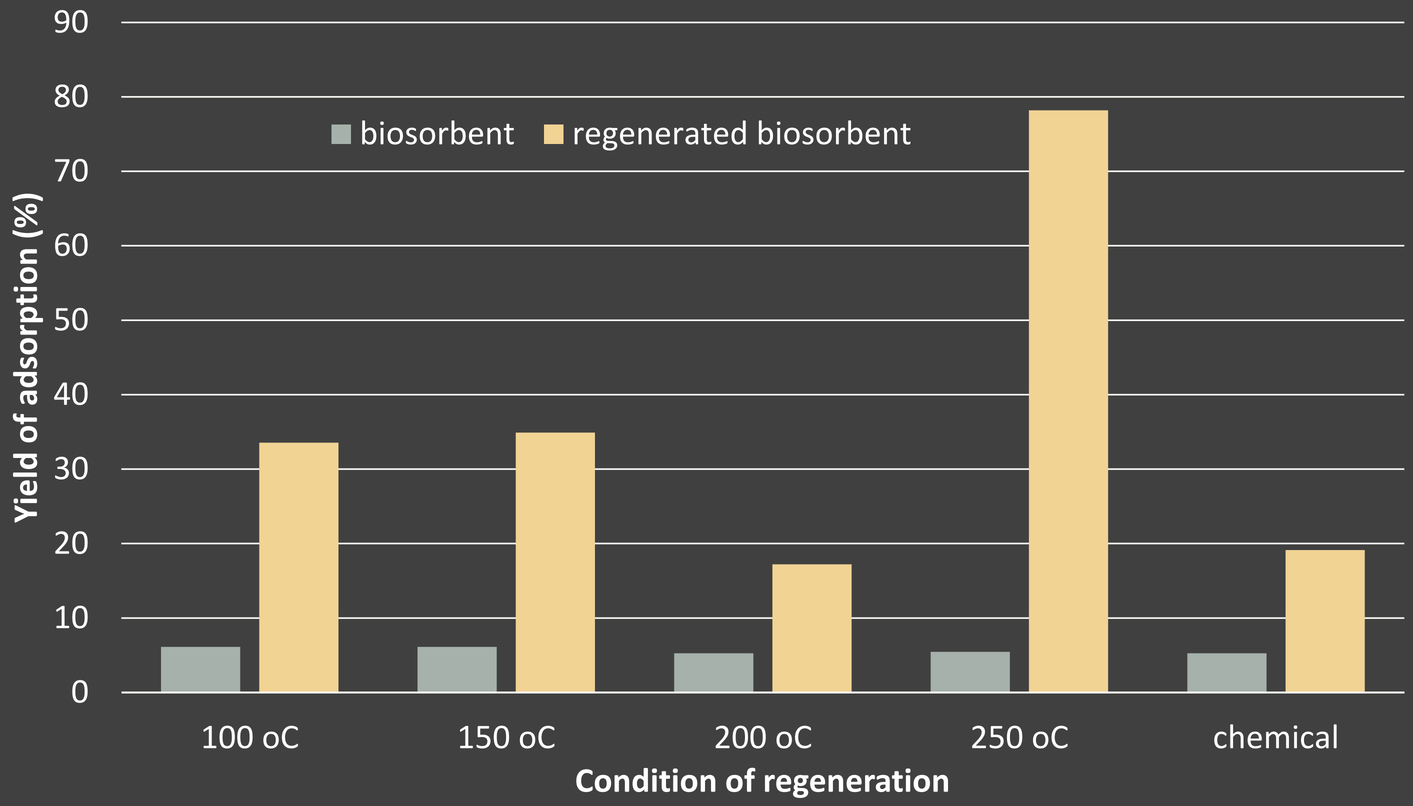
Regeneration of pomegranate peel



The most effective method of regeneration

Thermal regeneration, **250º C for 2 h**

Regeneration of orange juice waste



The most effective method of regeneration

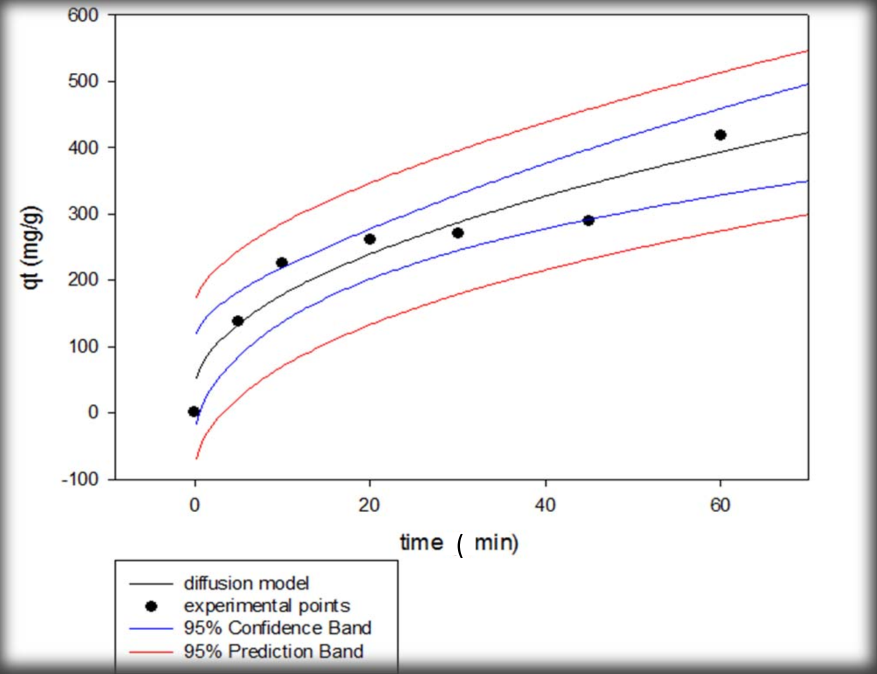
Thermal regeneration, **250° C for 2 h**

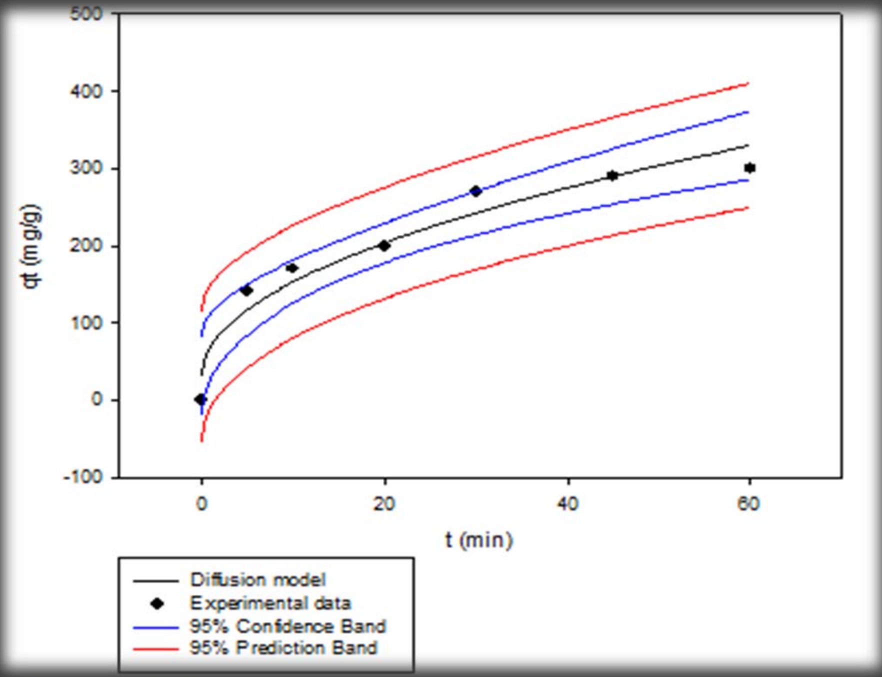
Kinetics models of adsorption

Model	Pomegranate peel		Orange juice waste	
	R^2	SSE	R^2	SSE
Pseudo-first order model	0.2251	155.3953	0.278	95.5524
Pseudo-second order model	0.7099	112.2772	0.5279	80.9984
Diffusion model	0.8129	91.9249	0.7956	70.6179

$$q_t = k_p \, t^{\frac{1}{2}} + C$$

Fitting of Diffusion model for some adsorption experiments





Pomegranate peel

pH = 4.75, T = 20^{o}C, r = 0.015 g/mL, C_o= 387.5 mg/L, D = 1.18 mm

Orange juice waste

pH = 5.5, T = 40^{o}C, r = 0.01 g/mL, C_o= 275 mg/L, D = 0.847 mm

Effect of process variables on kinetic model constants

$$q_t = k_p t^{\frac{1}{2}} + C$$

α b

Diffusion model

- Adsorption with pomegranate peel

$\boldsymbol{a} = -61 - T + 98\, Tr - 0.005\, TCo + 0.012\, pH\, Co - 17\, pH\, d + 0.0004\, Co^2$--52 d^2 R^2=48%

$\boldsymbol{b} = 1285 - 27\, T\ - 68286\, r + Co - 200d + 5\, T\, pH - 34\, pH^2 + 13710\, \mathrm{pH\ r} - pH\, Co - 40\, d^2$ R^2=62%

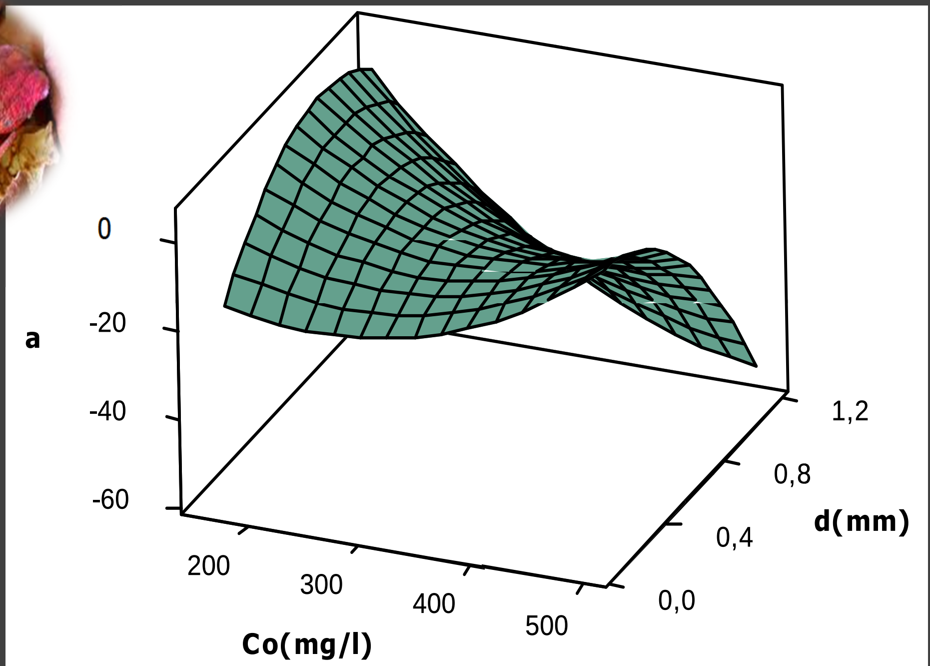
- Adsorption with orange waste

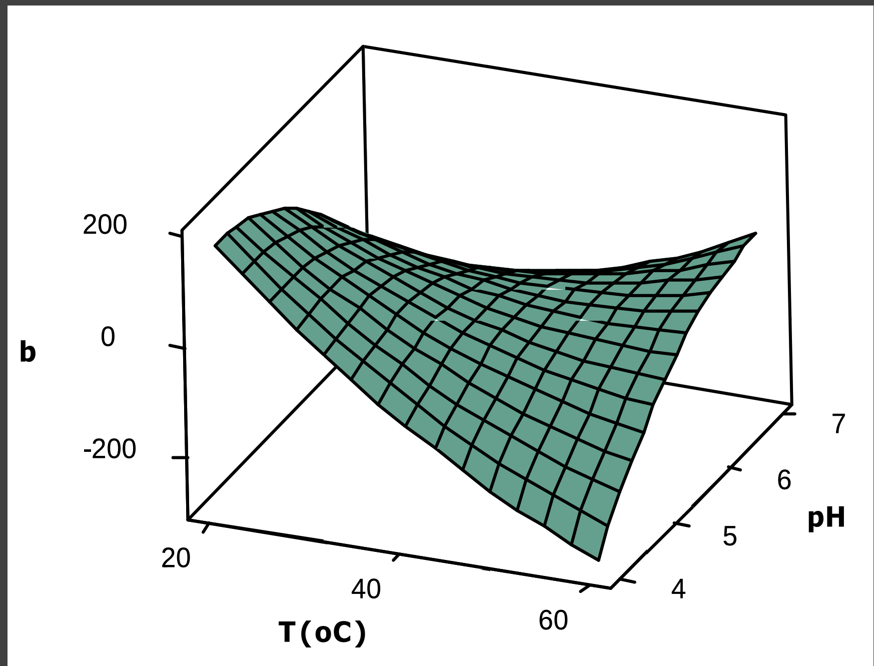
$\boldsymbol{a} = 104 + T - 3365r + 0{,}01\, Co - 97Tr + 0{,}0014 - 0.2927Td + 52d^2$ R^2=32.1%

$\boldsymbol{b} = 1066 - 25\, T + 4\, T\, pH\ - 18\, Tr + 0.0052\, T\, Co - 5pH^2 - 0.18\, pH\, Co - 52\, pH\, d + Co\, d$ R^2=71.8%

Effect of process variables on diffusion model constants

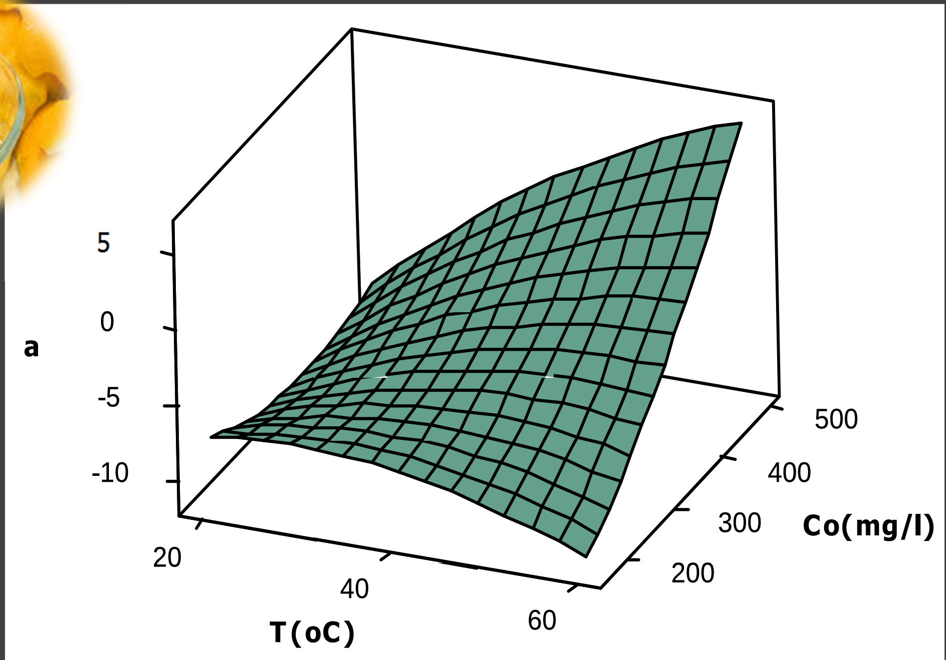
- Adsorption with pomegranate peel

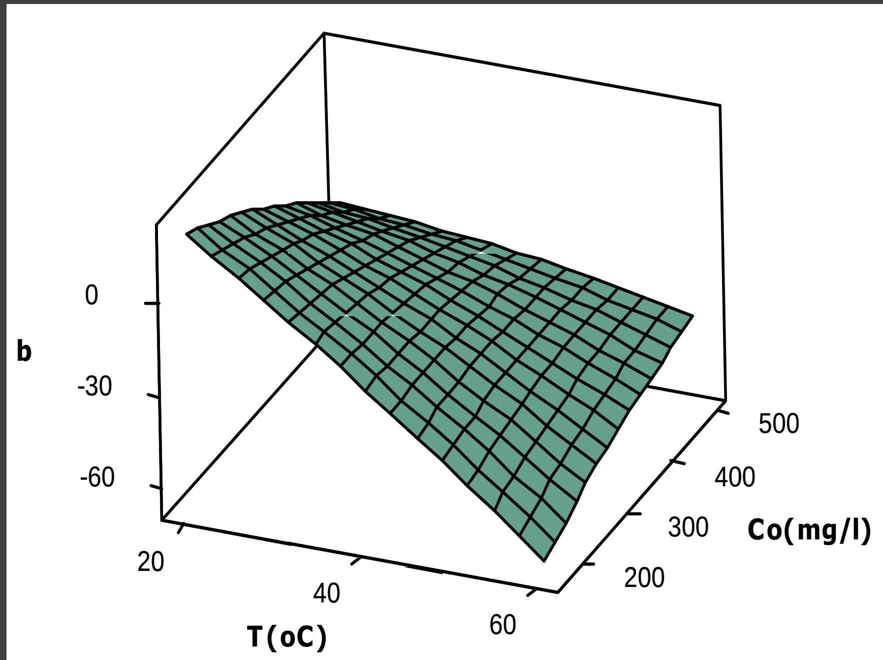




Effect of process variables on diffusion model constants

- Adsorption with orange juice waste





Adsorption Isotherms

Biosorbent	Lagmuir		Freundlich		Temkin	
	Q_m (mg/g)	b (L/mg)	n (-)	K_F ($mg^{1-n}L^n$/ g)	B_T (kJ/mol)	K_T
Pomegranate peel	36.23	69.00	0.13	1096.63	-0.037	6.28
Orange juice waste	4.25	50.09	0.01	$76\ 10^{-10}$	0.018	93.69

Adsorbent	Adsorbate	Q_m (mg/g)	b (L/g)	K_F	n
Activated coal	Phenol	1.84	0.065	0.79	0.79
Resin AP-246		0.071	0.584	0.112	0.35
Resin OC-1074		0.043	0.445	0.0053	0.16
Carbonised beet pulp	Phenol	◊	◊	29.35	5.13
Hydroxyapatite	Phenol	◊	◊	0.37	1.66
Coconut shell	Phenol	205.84	3.91	37.11	3.66
Aged-refuse	Phenol	◊	◊	0.019	1.19
	2-Chlorophenol	◊	◊	0.042	1.22
	4-Chlorophenol	◊	◊	0.195	1.59
	2,4-Dichlorophenol	◊	◊	0.180	1.50
Palm pith carbon	2,4-Dichlorophenol	19.16	0.70	*	*
Paper mill sludge	2,4-Dichlorophenol	4.49	0.003	*	*
Banana peel	Phenolic compounds	688.9	0.24	0.13	1.13

◊ Does not follow Langmuir isotherm/not reported. * Does not follow Freundlich isotherm/not reported.

(Achak et al., 2009)

Conclusions

- Pomegranate peel and orange juice waste have proven to be promising materials for the removal of contaminants from olive mill wastewaters
- **Adsorption mechanism**
  - ✓ pomegranate peel: ion exchange
  - ✓ orange juice waste: chemisorption
- More effective method of **regeneration** for both biosorbents
  - ✓ thermal process, $250^{o}C$ for 2 h
- **Adsorption isotherms** showed that the adsorption with the studied biosorbents is favorable and removal with pomegranate peels is more favorable as compared with orange juice waste.
- **Diffusion model** describes better the adsorption, thus the overall rate of the adsorption appears to be controlled by the diffusion mechanism

Thank you for your attention.