Adsorption of phenolic compounds from olive mill wastewater using a novel low cost biosorbent

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Introduction

Olive oil production

Olive collection and purification

Olive crashing

Mixing

Oil separation

- Traditional pressing
- 2 phase centrifugal extraction system
- 3 phase centrifugal extraction system

(Klen & Vodopivec, 2012)

Olive oil production

<u>Traditional pressing</u>

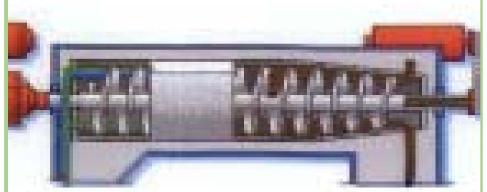
A solid fraction, "olive husk", is obtained as a by-product and an emulsion containing the olive oil.

The olive oil is separated from the remaining olive mill wastewater by decanting

<u>3-phase centrifugal extraction system</u>

Predominant process in modern olive mills

- Two streams of waste
  - i. a wet solid cake (~30% of raw material) called "Olive Cake"
  - ii. a watery liquid (50% of raw material) called **<u>O</u>**live **<u>M</u>**ill **<u>W</u>**astewater (OMW)

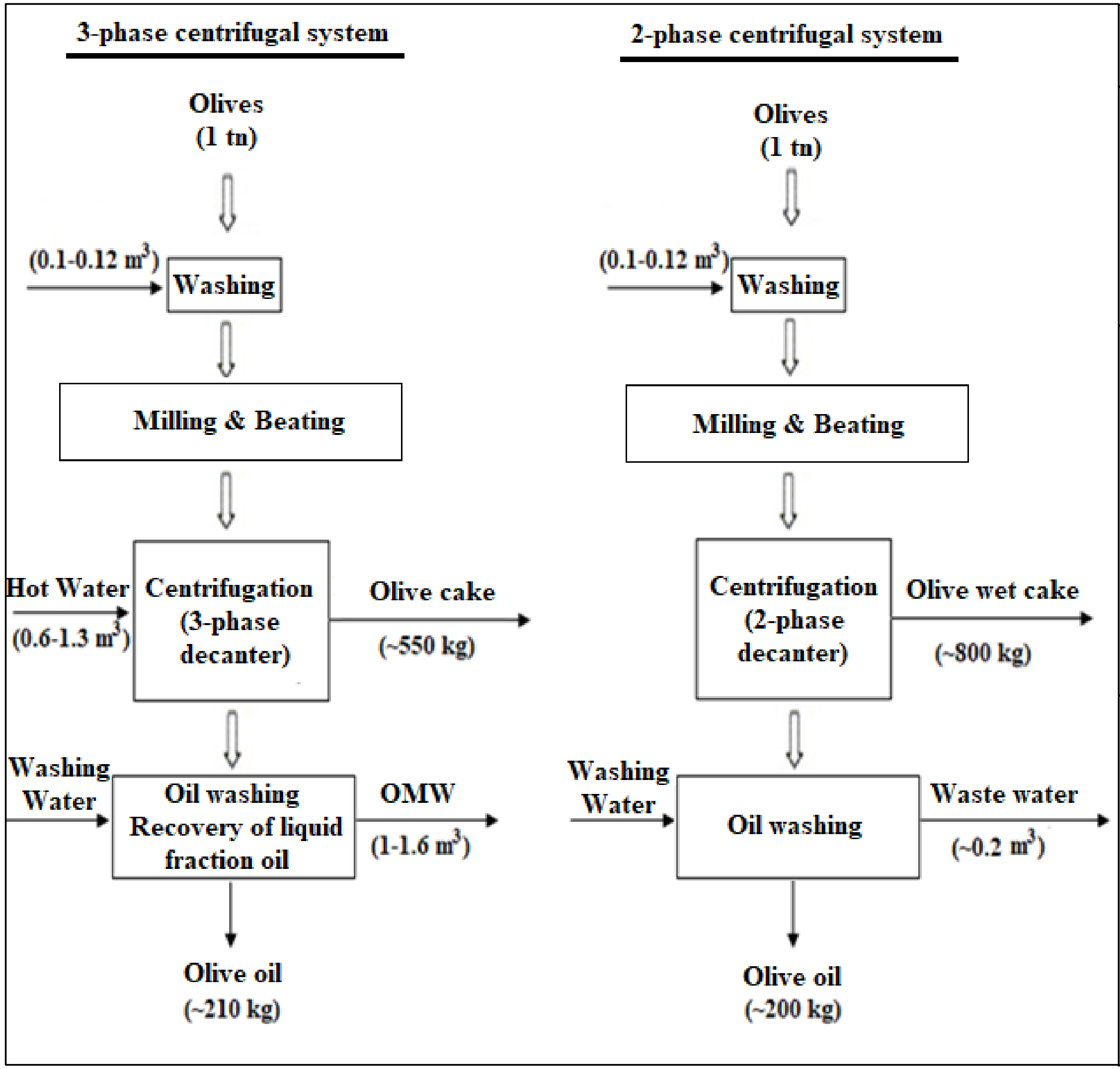


<u>2-phase centrifugal extraction system</u>

"Ecological" method which reduces the olive mill waste by 75%

- Two fractions
  - i. a solid called "Alperujo" or "Olive Wet Husk" or "Wet Pomace" or **<u>T</u>**wo-**<u>P</u>**hase **<u>O</u>**live **<u>M</u>**ill **<u>W</u>**aste (TPOMW)
  - ii. a liquid (Olive Oil)

Olive oil extraction systems



(Alburquerque et al., 2004)

	Input	Output
Traditional pressing	Olives (1 tn) Washing water (0.1-0.12 m^3)	Olive oil (200 kg) Solid waste (400 kg) OMW (400-600 kg)
3-phase Centrifugal system	Olives (1 tn) Washing water (0.1-0.12 m^3) Mixing water (0.5-1 m^3)	Olive oil (200 kg) Solid waste (500-600 kg) OMW (1-1.6 m^3)
2-phase Centrifugal system	Olives (1 tn) Washing water (0.1-0.12 m^3)	Olive oil (200 kg) Solid waste (800-950 kg)

(Caputo et al., 2003)

Olive Mill Waste Management

Solid Waste

Liquid Waste

Physical & physicochemical processes

Biological processes

Physicochemical & biological combination

- 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)

Potential source of phenolic compounds and other natural antioxidants!

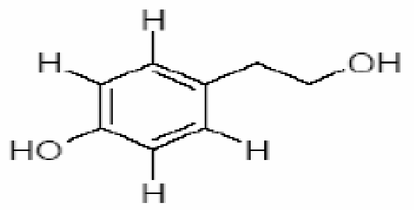
- High **phytotoxicity**
- **Pollution** of natural waters
- Threatening the aquatic life
- Offensive odors

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

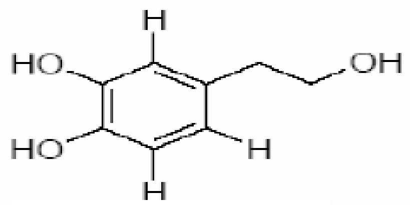
Olive Mill Waste Composition

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

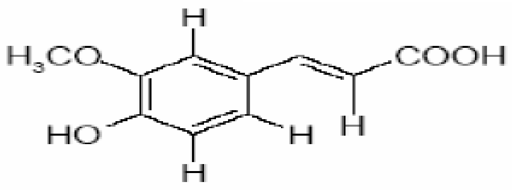
OMW Phenolic Compounds



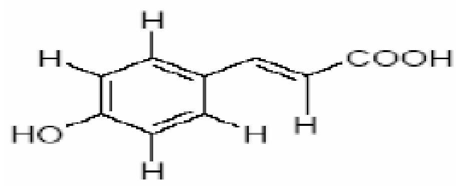
Tyrosol



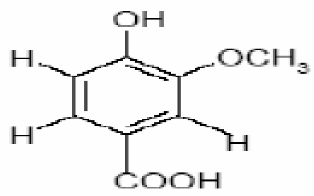
Hydroxotyrosol



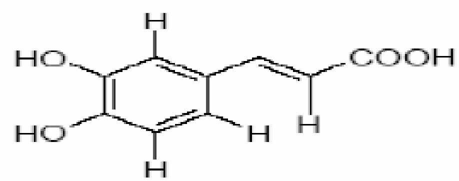
Feroulic acid



p-Coumaric acid



Vanillic acid



Caffeic acid

Phenolic Compound	Content (mg/L)	Reference
Tyrosol	5-1600	Navrozidis, 2008 Kaleh et al., 2010
Hydroxotyrosol	35-550	
Caffeic Acid	4-12	

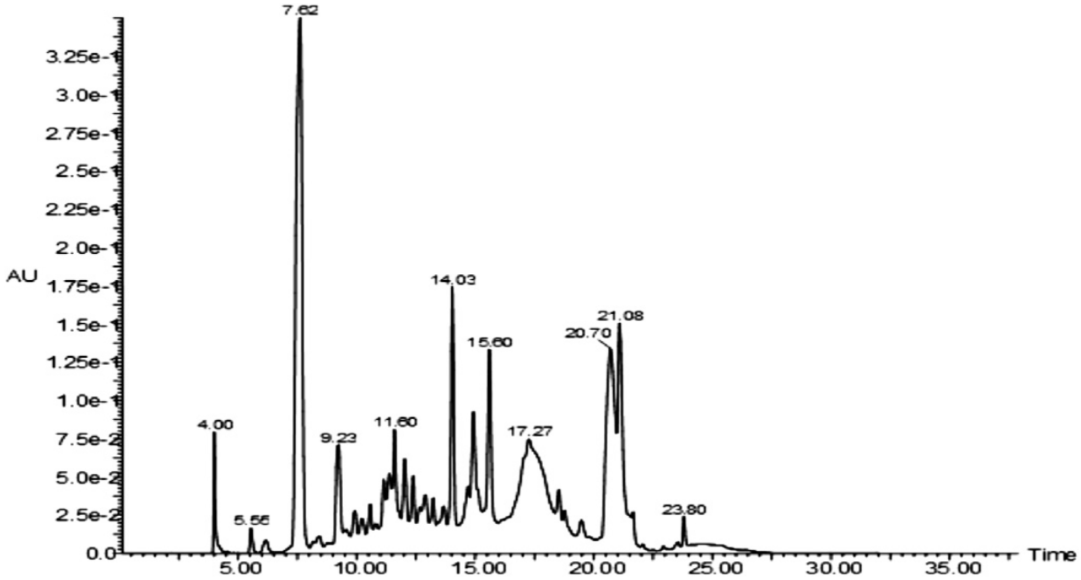
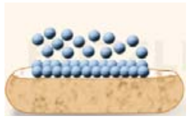
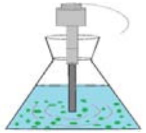
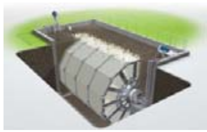


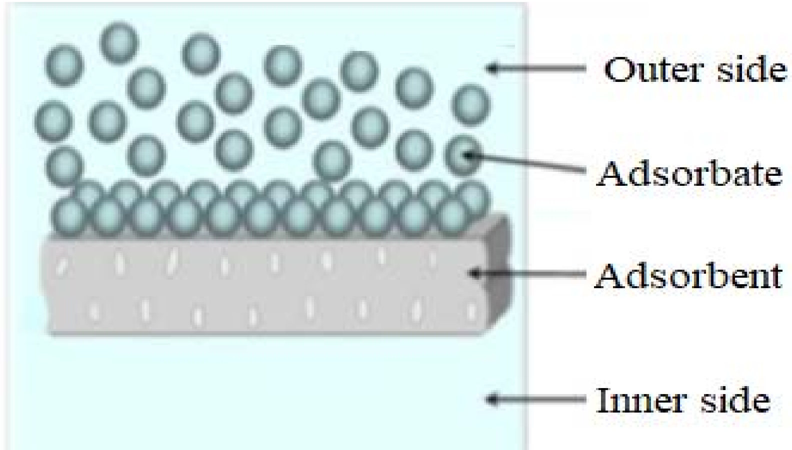
Fig. 1. HPLC chromatograph of polyphenolic fraction after its extraction from real OMW with ethyl acetate solvent. Retention times: gallic acid (5.81 min), hydroxytyrosol (7.62 min), tyrosol (9.23 min), caffeic acid (10.06 min) and oleuropein (14.62 min).

(Kalogerakis et al., 2013)

Recovery of functional components-Adsorption

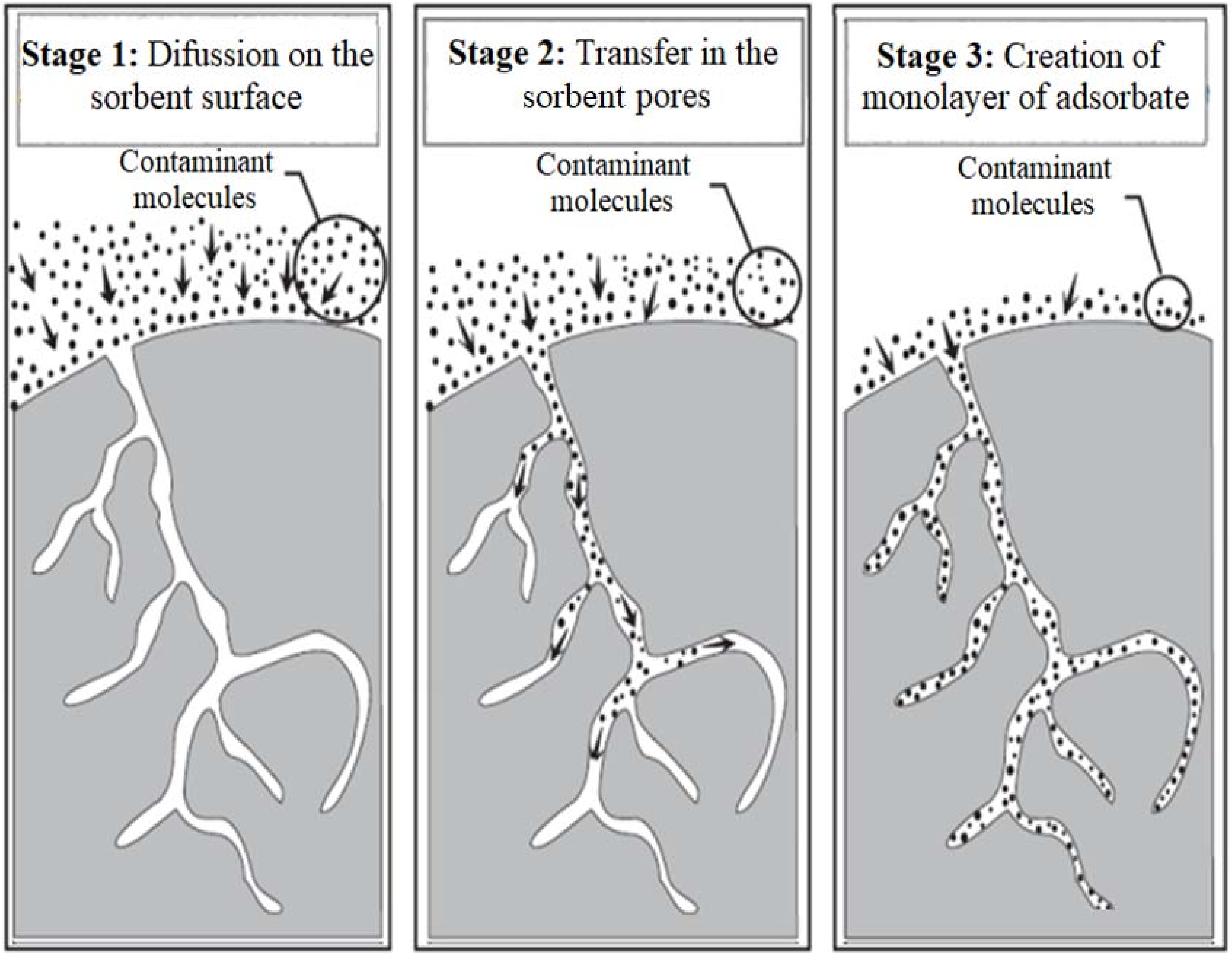
- Adsorption 
- Extraction 
- Chromatographic separation 
- Membrane separation 

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
- ✓ The profitability depends mainly on the <u>adsorption efficiency</u> and on the <u>recovery rates</u> during desorption

Adsorption stages & Mechanisms



Exchange Adsorption (Ion exchange)

Electrostatic due to charged sites on the surface

Physical adsorption

Van der Waals attraction between adsorbate and adsorbent
Reversible process

Chemical adsorption

Chemical bonding between adsorbate and adsorbent
Strong attractiveness
Irreversible process

Adsorbents & Biosorbents

- ✓ **Oxygen Containing** Compounds (Silica gel, zeolites)
- ✓ **Carbon Based** Compounds (Activated carbon, graphite)
- ✓ **Polymer Based** Compounds (Polymers, resins)

Adsorbents used for OMW phenolics recovery

Adsorbent	Yield (%)	Reference
XAD-4	3.5- 97.5	Kaleh et al., 2016
XAD-16	4.5- 99.0	
FPX-66	4.5- 98.0	
PVPP	0.9-100	
AF5	31.7-91.4	
AF6	90- 100	
PAC	93.5- 100	
Zeolite	37- 45	Santi, 2008
Bentonite	29-45	
Banana peel	34 -66	Achak et al., 2009
Wheat Bran	12-63	Achak et al., 2014

Biosorbents used for various compounds' recovery

Biosorbent	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
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

Biosorbents

Banana peel

- ✓ Low cost
- ✓ Environmentally friendly
- ✓ Removal of cadmium and lead from water (Anwar et al., 2010) and phenolic compounds from OMW (Achak et al., 2009)

	Maximum yield conditions		
	Cd (II)	**Pb (II)**	**Phenolic compounds**
Initial concentration	50 µg/mL	50 µg/mL	13.45 g/L
pH	3	5	8-11
Time	20 min	20 min	3 h
Temperature (°C)	25	25	30
Stirring speed (rpm)	100	100	200

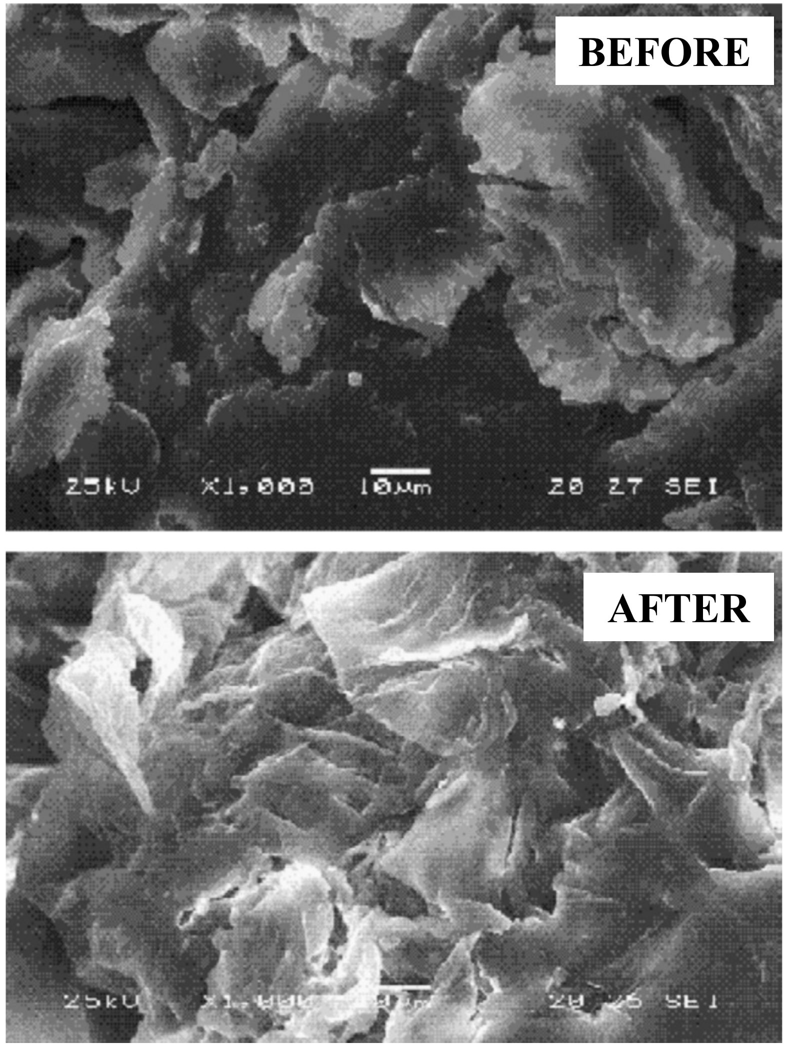
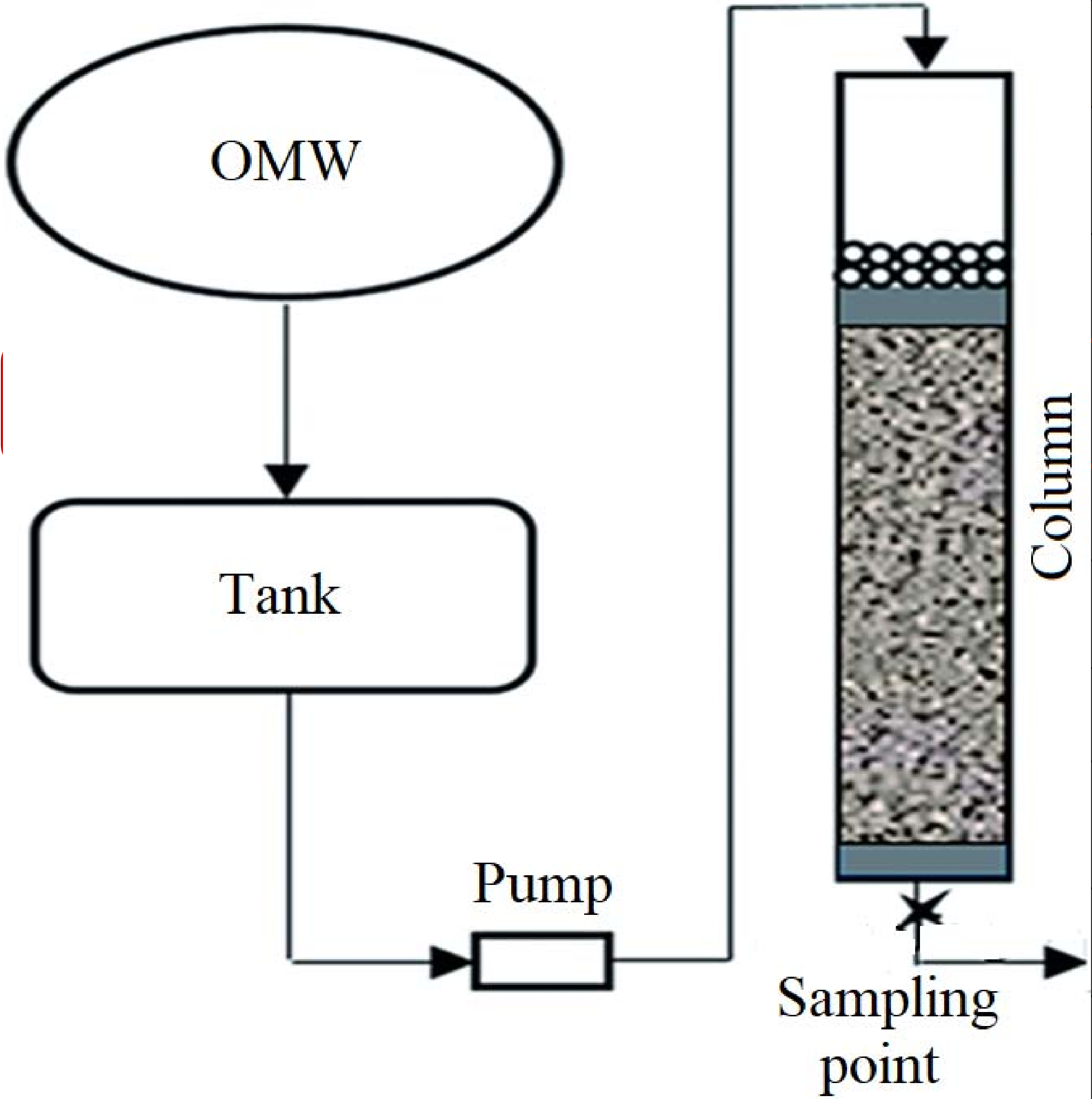


Fig. 2. SEM images for original banana peel and (b) SEM images for banana peel after adsorption.

(Achak et al., 2009)

Fixed Bed Columns Studies



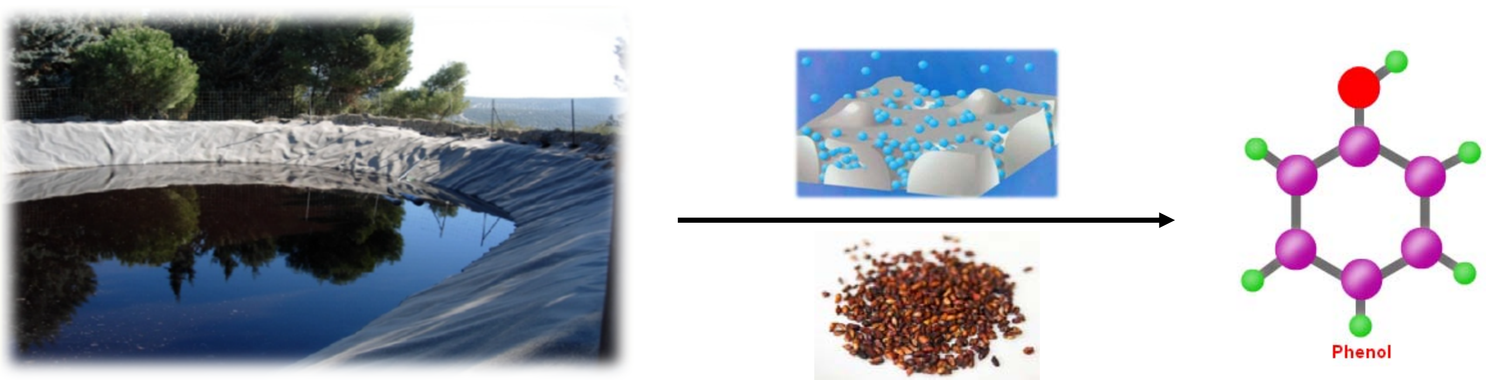
Height (cm)	Diameter (cm)	Flow rate (mL/min)	Reference
20	-	12 - 36	Abdelkreem, 2013
15, 20, 25	2.00	5, 10, 15	Lallan et al., 2017
50	1.05	2.5	Bhatnagara et al., 2010
50	3.20		Chowdhury et al., 2016
34	1.60	11	Fernandez et al., 2014
52.5	2.00	-	Frascari et al., 2016
50	2.44	-	Pinelli et al., 2016
10	2.50	18 – 33	Rocha et al., 2015
15	0.70	1, 3, 9	Stasinakis et al., 2008

Objectives

1. Exploitation of pomegranate seed (by-product of juice industry) as a **biosorbent** for the recovery of phenolic compounds from liquid olive mill waste

2. Optimization of batch and continuous adsorption process

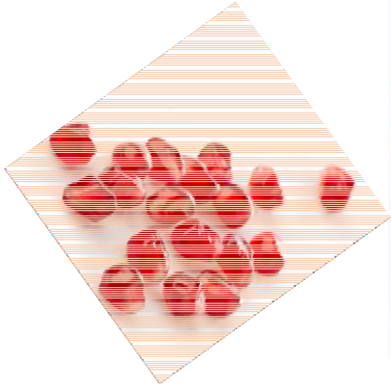
3. Development and proposal of a novel, **low cost** method for the recovery of phenolic compounds and their **exploitation** as **food additives** in food industry



Materials & methods

Pomegranate seed

- 14 % of pomegranate fruit
- Juice industry by-product
- Low cost
- Use as animal feed
- Phenolic content: 0.25%



Chemical composition of pomegranate seed (dry basis with 8.6 % water content)

Component	Value	Component	Value
Fibers (%)	35.3	Potassium (ppm)	45.2
Fat (%)	27.2	Magnesium (ppm)	12.4
Proteins (%)	13.2	Sodium (ppm)	6.0
Pectins (%)	6.0	Ferrum (ppm)	1.3
Sugars (%)	4.7	Copper (ppm)	1.2
Ash (%)	2.0	Zinc (ppm)	1.0

(El-Nemr et al., 1990; Dadashi, Mousazadeh, Emam-Djomeh, & Mousavi, 2013)

Pomegranate seed preparation

Grinding

Drying
(40 ^{o}C, 48 h)

Sieving

Fractions of different size

Extraction/ Removal of phenolic compounds

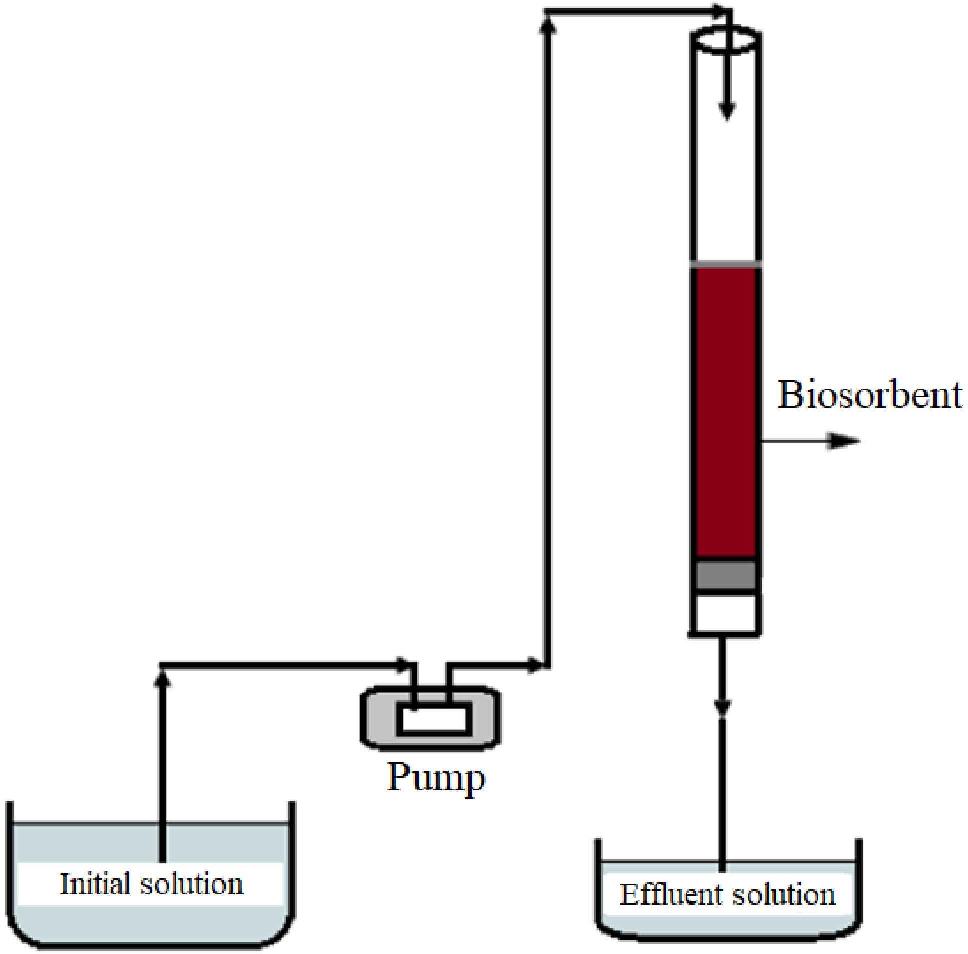
Drying
(40 ^{o}C, 24 h)

Pomegranate seed powder

Experimental set-up for adsorption process

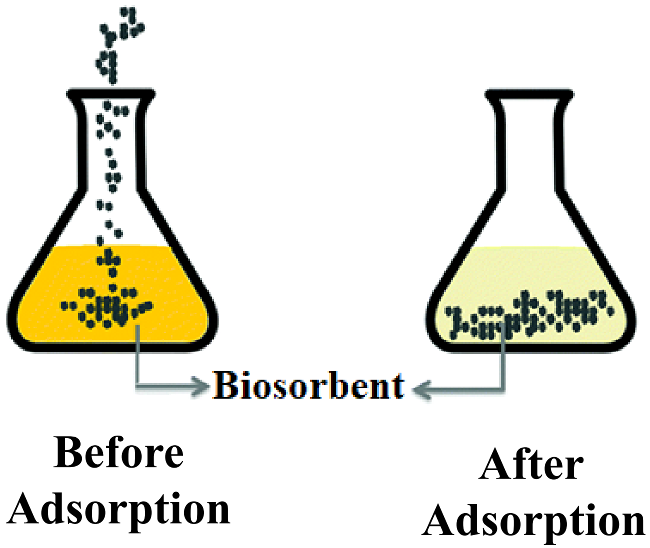
Batch operation

Continuous operation

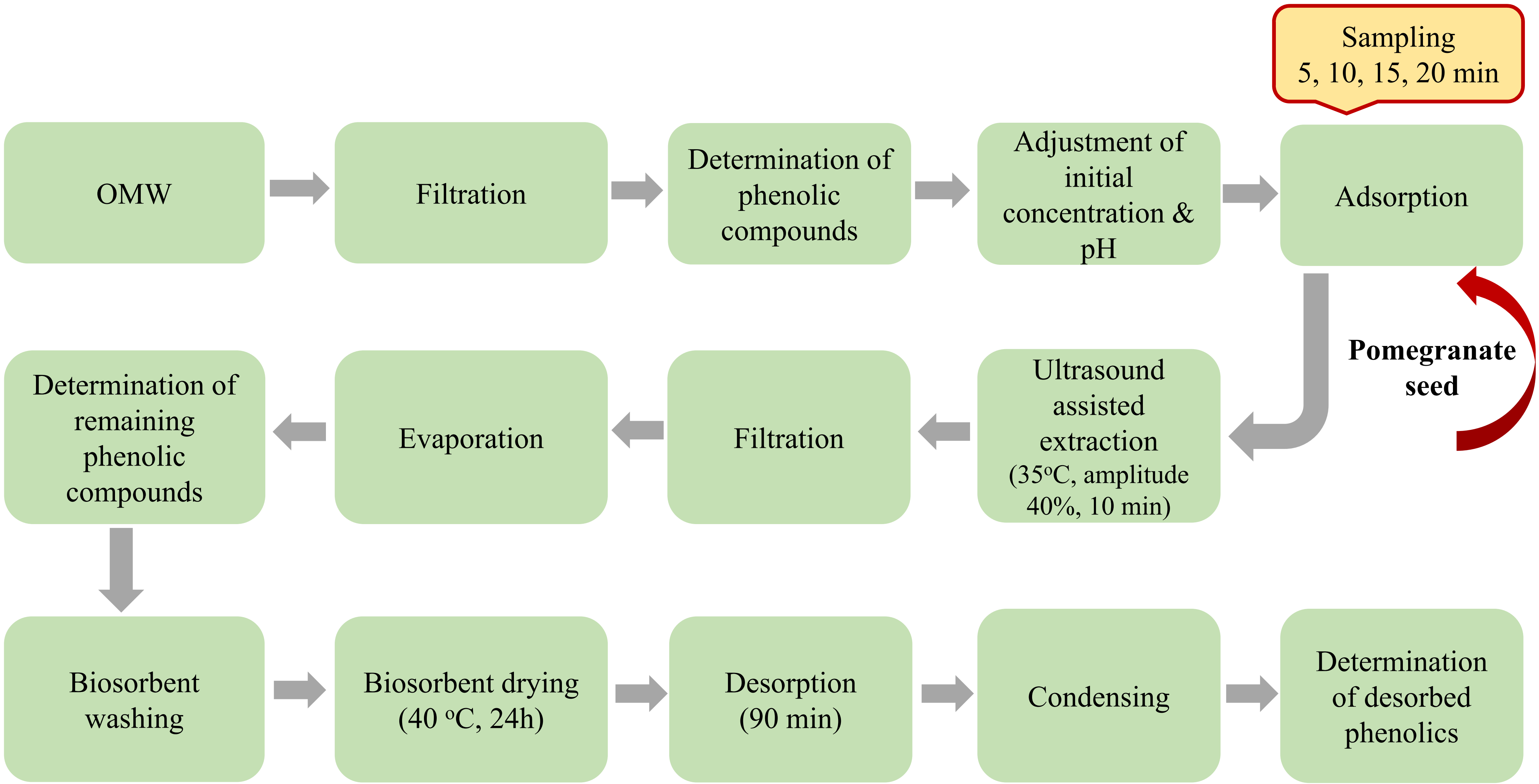


Factors affecting adsorption

- Temperature (T, ^{o}C)
- pH
- Ratio of pomegranate seed to OMW (r, g/mL)
- Initial phenolics concentration in OMW (C_0, mg/L)
- Mean diameter of pomegranate seed particles (d_p, mm)



Integrated process of OMW phenolics' adsorption on pomegranate seed



Experimental design

Statistical program *Minitab* *(Release 13)* → Input of factors to be tested → Experimental design → **32 adsorption experiments**

Parameters Levels (RSM Methodology)				
T (ºC)	**pH**	**Adsorbent/OMW ratio (r, g/mL)**	**Initial phenolics concentration in OMW (C_0, mg/L)**	**Mean diameter of adsorbent particles (d_p, mm)**
20	4.00	0.01	50.0	0.149
30	5.00	0.02	162.5	0.410
40	6.00	0.03	275.0	0.664
50	7.00	0.04	387.5	0.922
60	8.00	0.05	500.0	1.180

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

C_0 : Initial phenolics concentration in OMW

C : Remaining phenolics concentration in OMW after adsorption

Adsorption kinetics

❖ **Pseudo-first order**

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

❖ **Pseudo-second order**

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

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

❖ **Difussion model**

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

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

(Achak et al., 2009)

Adsorption isotherms

❖ **Langmuir Isotherm**

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

❖ **Freundlich Isotherm**

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

❖ **Temkin Isotherm**

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

- **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)

Activation of biosorbent

1. Chemical activation

NaOH 2M

Stirring (2 g/33 mL, 24 h, room temperature) → Stirring 45 ^{o}C 2 h → Washing & Filtration → Drying 80 ^{o}C 4 h

99% MeOH

Stirring (9 g/633 mL, 24 h, 60 ^{o}C) → Washing & Filtration → Drying 40 ^{o}C, 24 h

2. **Thermal activatin** (Drying of biosorbent for 2-3 h)

100 ^{o}C

150 ^{o}C

200 ^{o}C

250 ^{o}C

Desorption of phenolic compounds from the biosorbent

Biosorbent separation & washing with distilled water → Drying (40 °C, 24 h) → Stirring with different solvents (90 min, room temperature) → Determination of desorption yield and adsorption mechanism

Ratio
1 g / 100 mL

$$\textbf{Desorption yield} = \frac{C_1}{C_0 - C}$$

C_1 : Phenolics concentration in the solvent after desorption

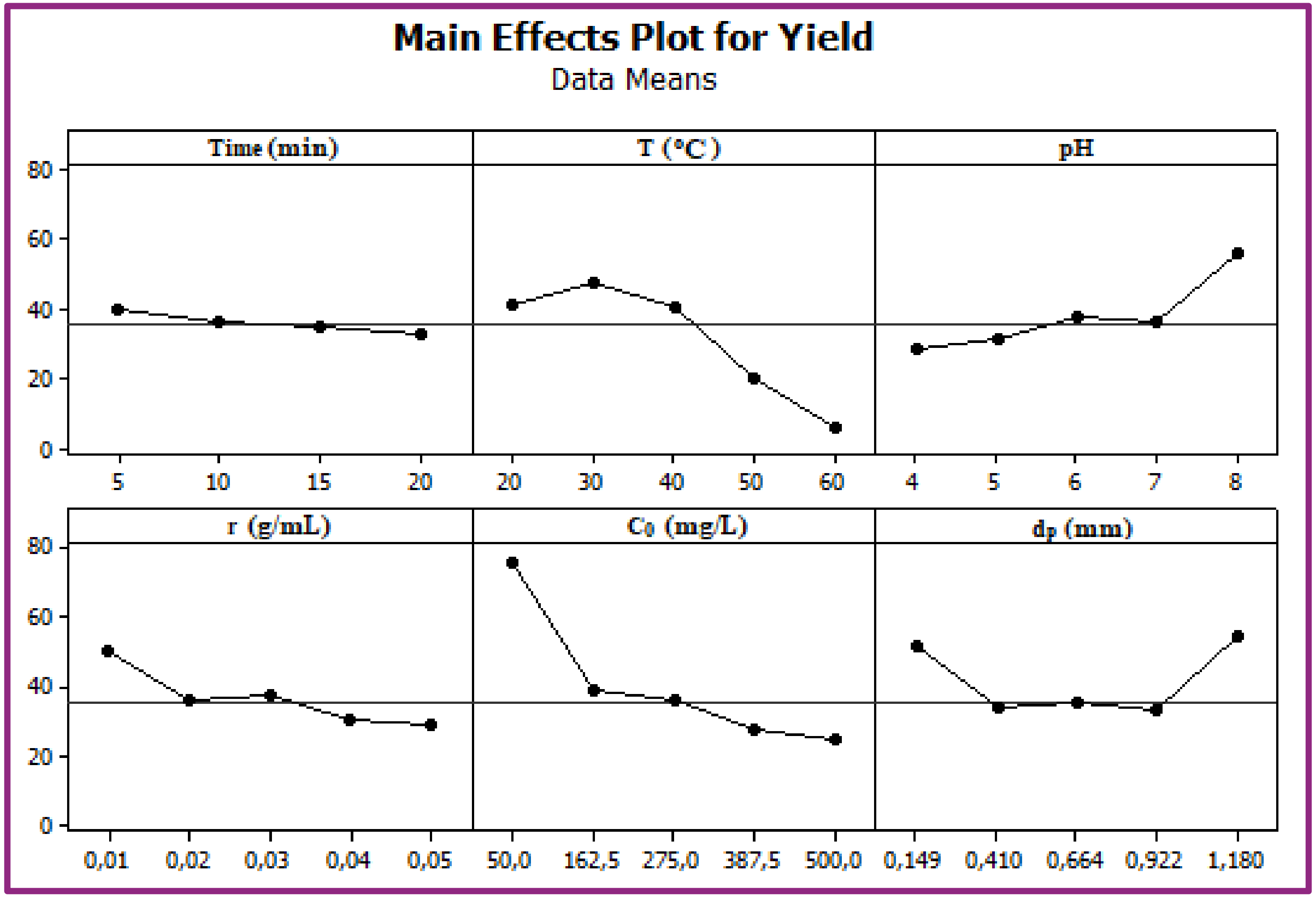
C_0 : Phenolics concentration in OMW before adsorption

C : Phenolics concentration in OMW after adsorption

Neutral water, pH 7	Alkaline water, pH 12	Acetic acid 50%, pH 1.2
Adsorption mechanism Physical adsorption	**Adsorption mechanism** Ion exchange	**Adsorption mechanism** Chemical adsorption

Results

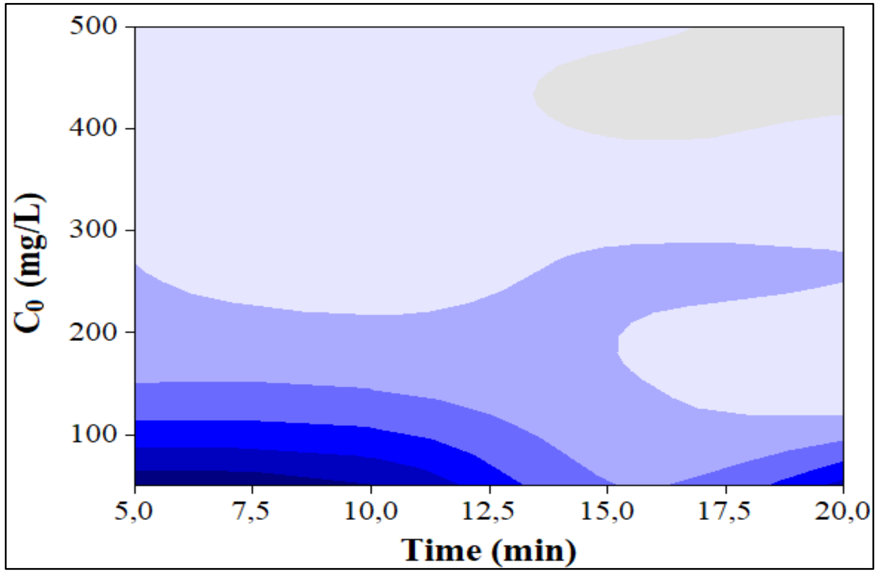
Factors Affecting Adsorption Process

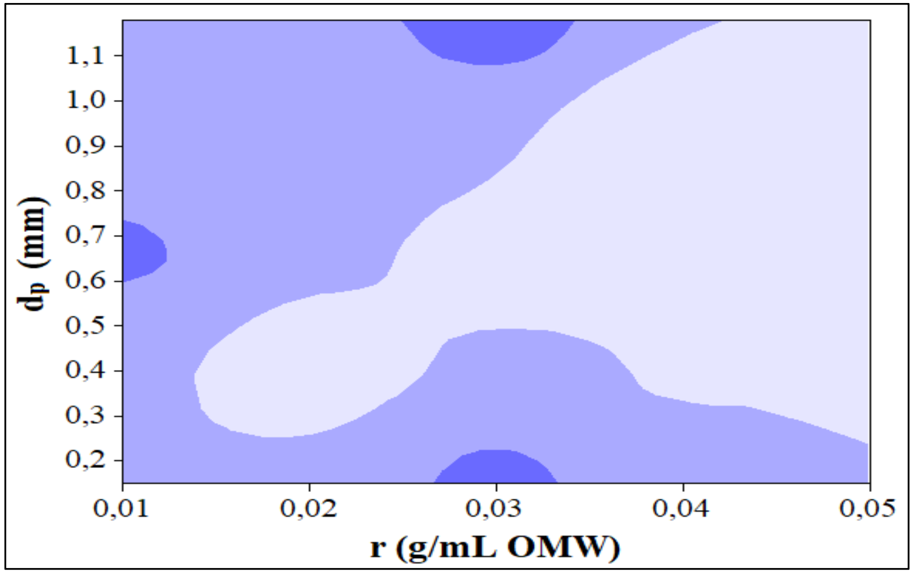


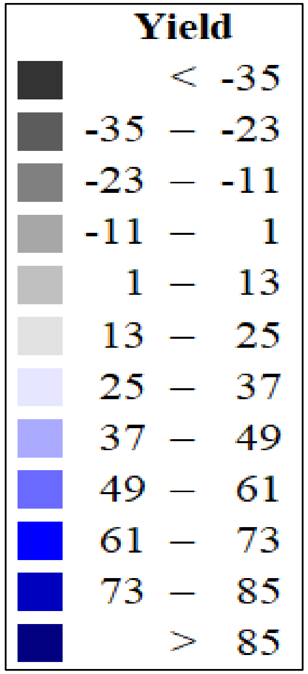
Maximum adsorption yield

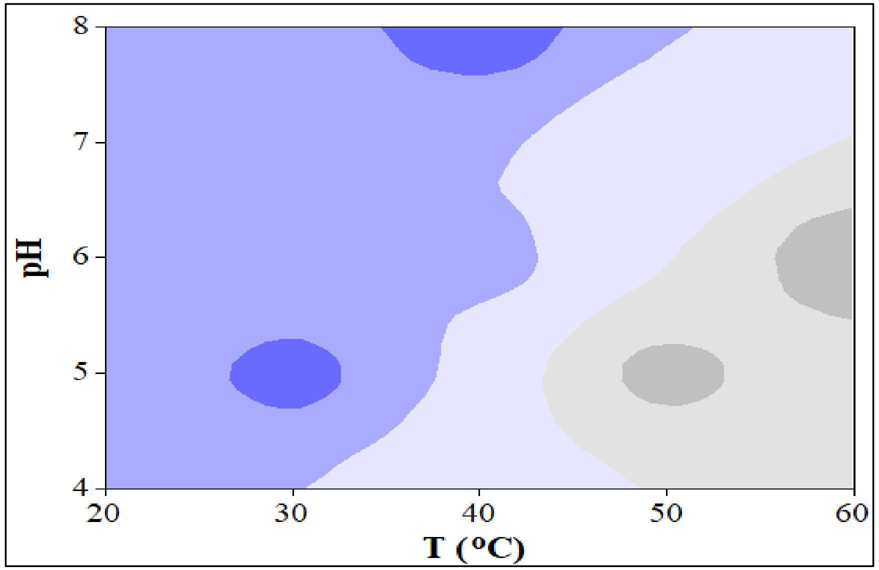
Time , t (min)	10
Temperature, T (°C)	30
pH	5
Biosorbent/OMW, r (g/ml)	0.02
Initial phenolic concentration, C_0 (mg/L)	162.5
Mean diameter of biosorbent particles, d_p (mm)	0.922
Yield (%)	**92.8**

Factors Affecting Adsorption Process









Statistically significant parameters ($p \leq 0.05$)

r : ($p = 0.023$)

C_0 : ($p = 0.027$)

T^2 : ($p = 0.033$)

d_p^2 : ($p = 0.050$)

T x pH : ($p = 0.002$)

T x r : ($p = 0.002$)

r x d_p : ($p = 0.026$)

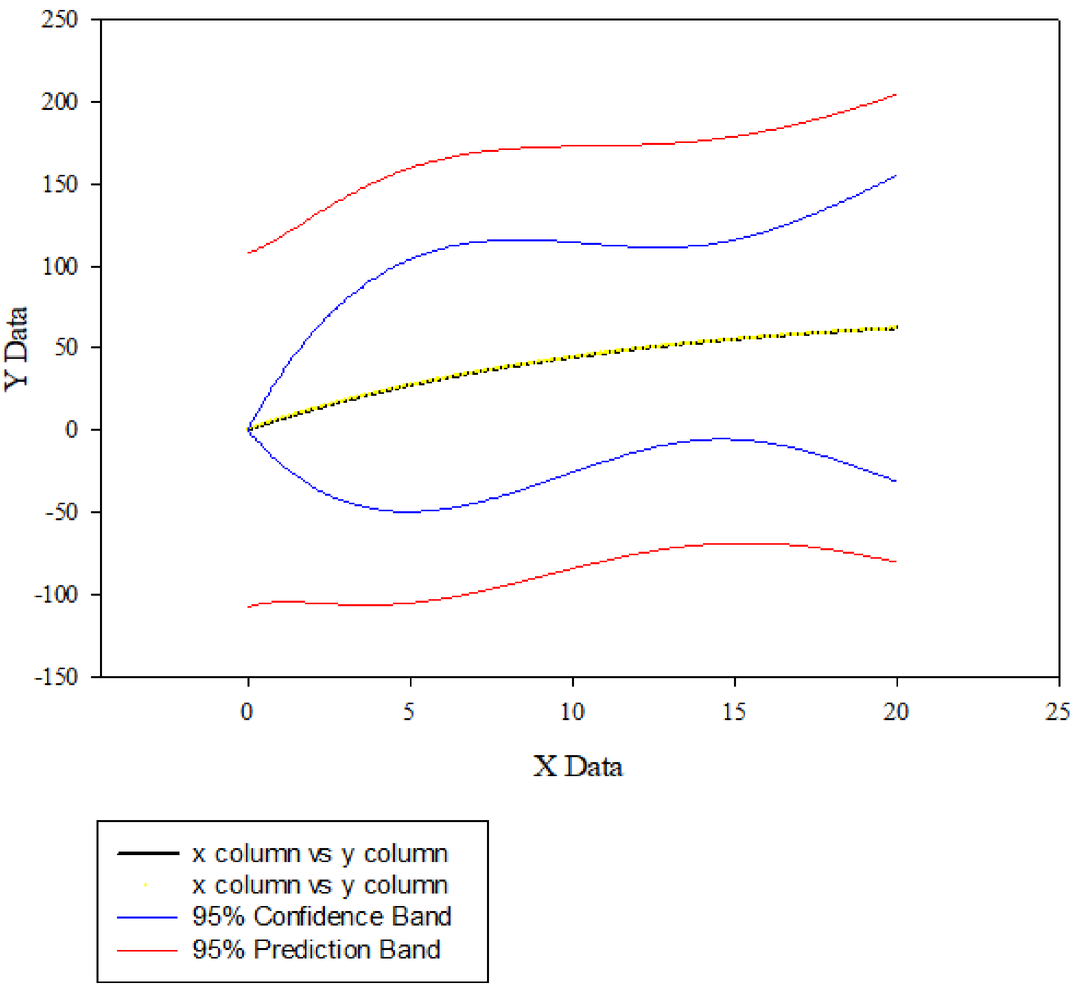
Kinetics of Adsorption

Kinetic model	R^2	R_{adj}^2	SSE
Pseudo- first order	0.698	0.598	18.0013
Pseudo- second order	0.653	0.537	19.8738
Diffusion model	0.497	0.328	27.5700

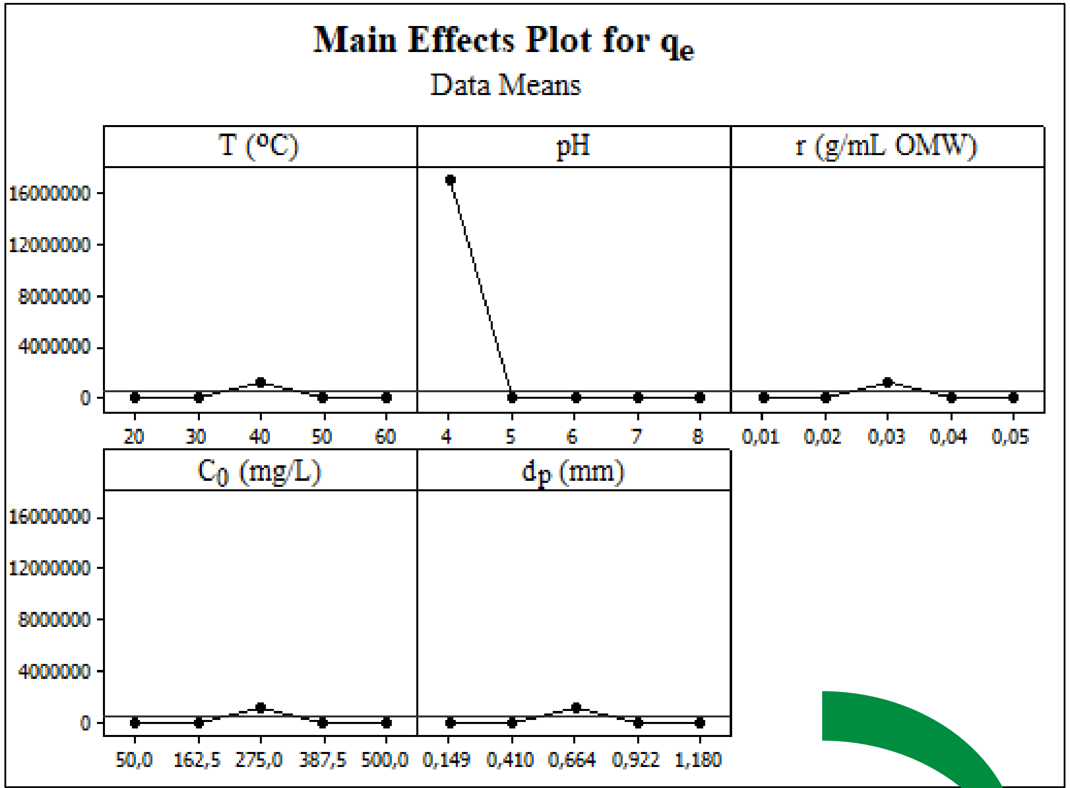
$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$

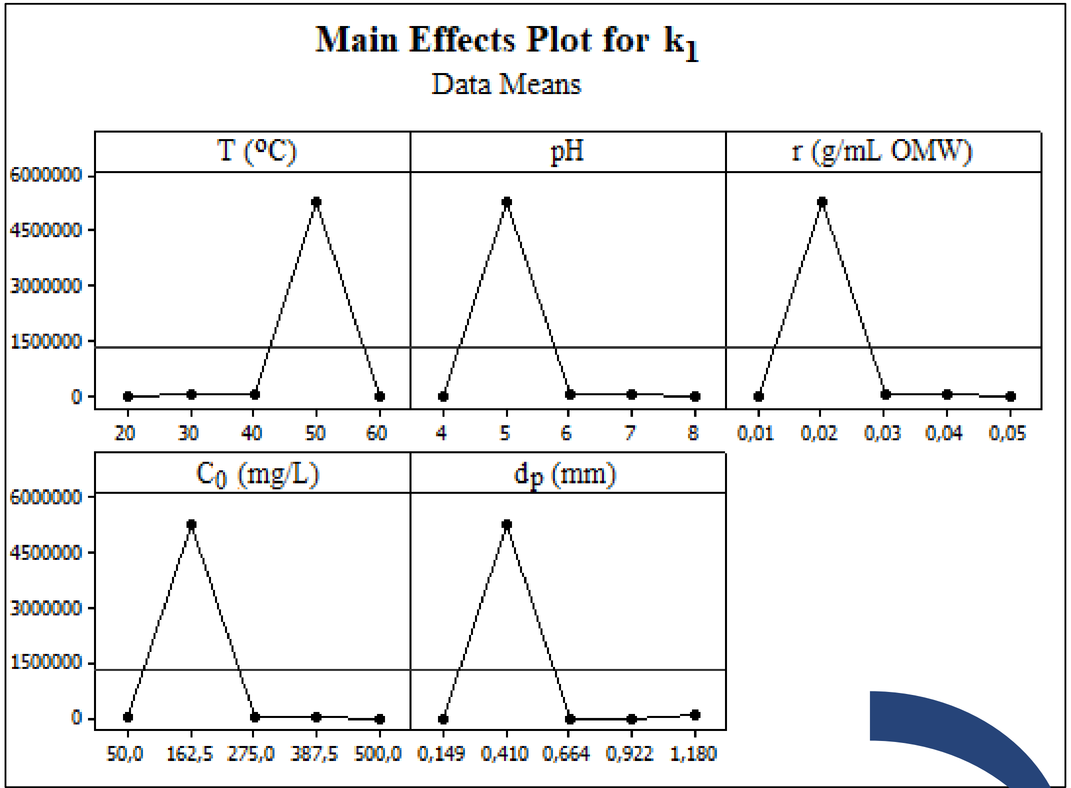
$$q_t = q_e - q_e(e^{-k_1 t})$$

Pseudo first order model



Kinetics of Adsorption





The q_e parameter is related to the system equilibrium

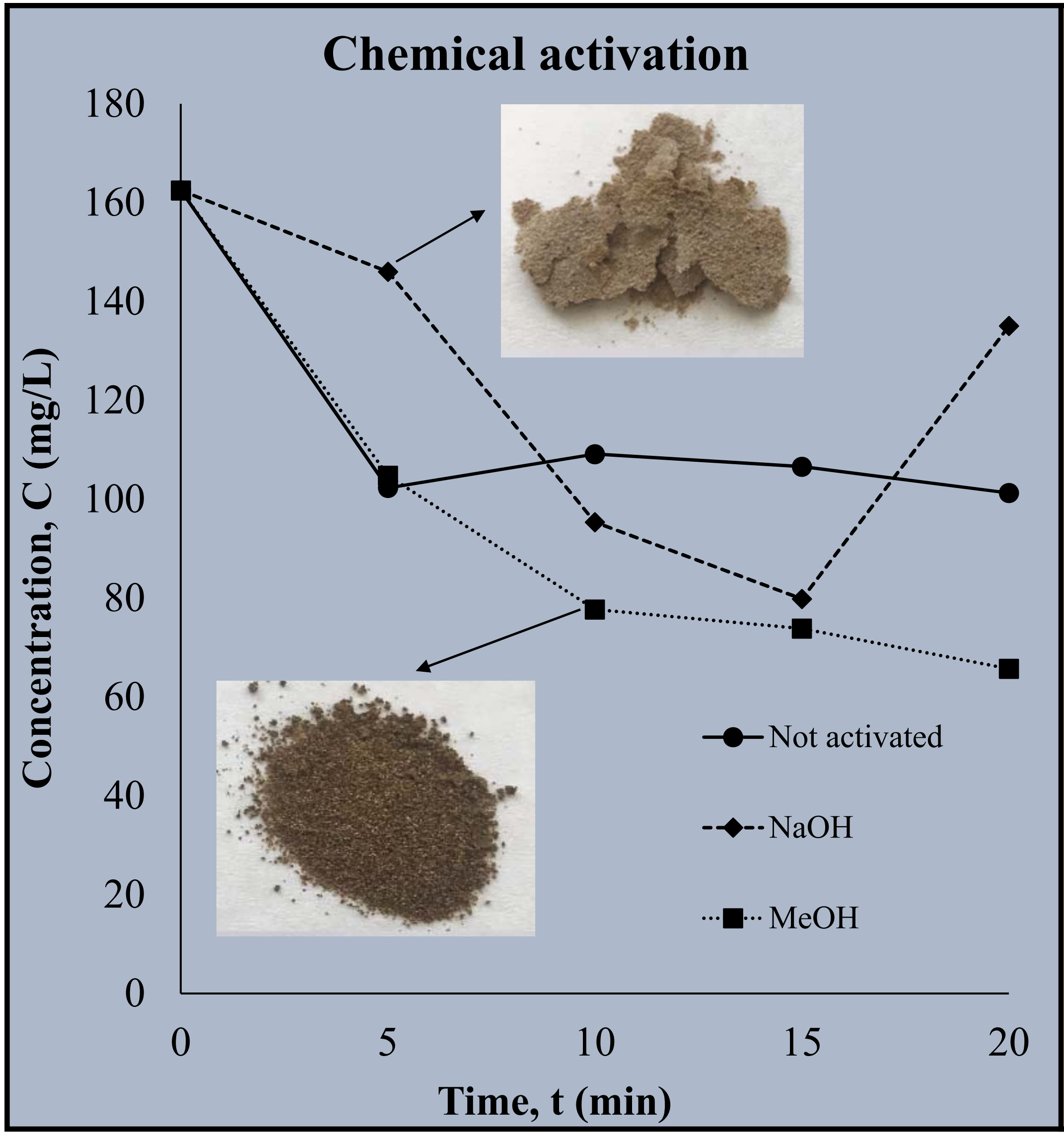
The k_1 parameter is related to the rate of changes that take place during the process

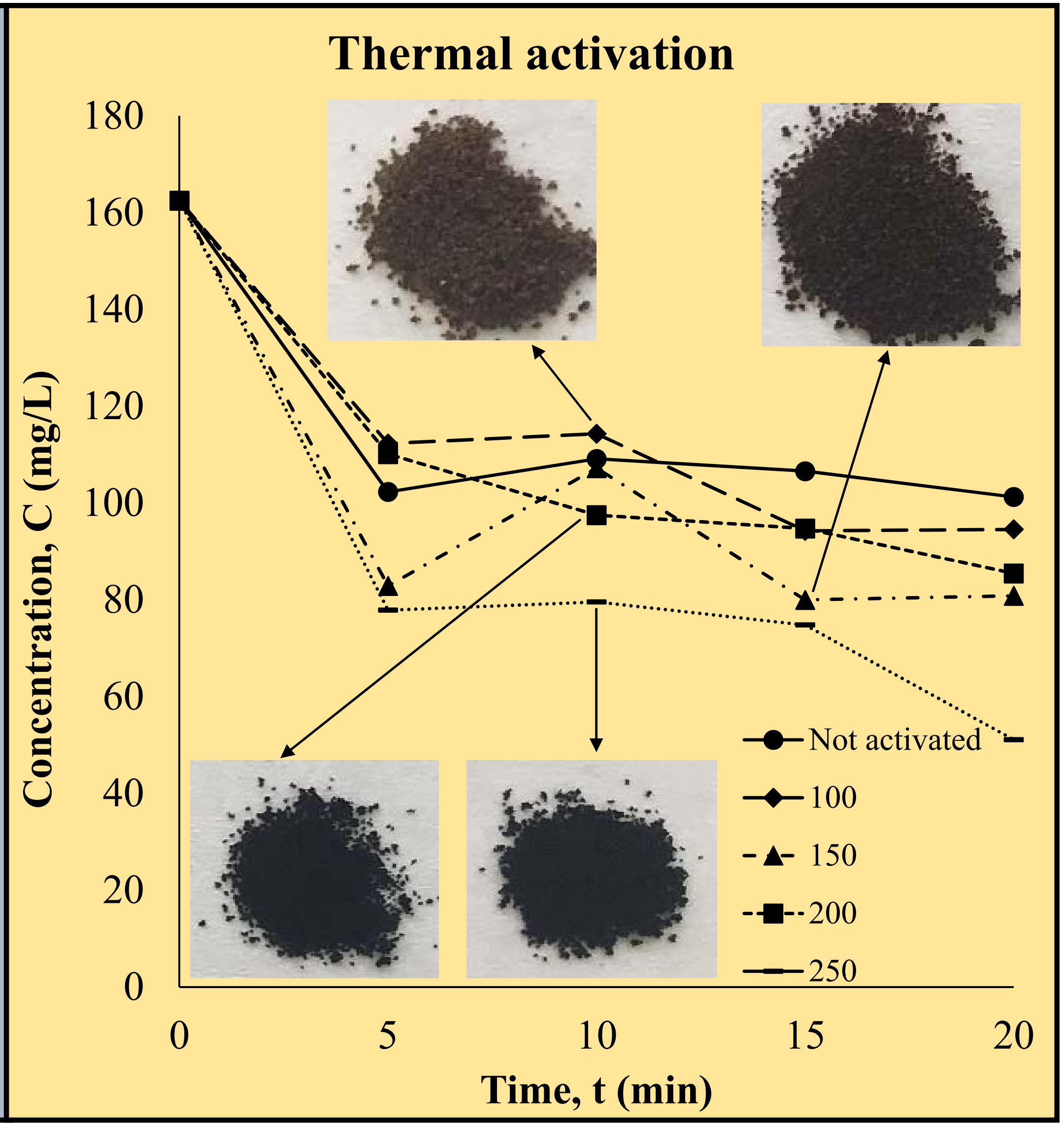
Adsorbent	Adsorbate	Q_m (mg/g)	b (L/g)	K_F	n
Activated coal	Phenol	1.84	0.065	0.79	0.79
Resin AP-246		0.071	0.584	0.112	0.35
Resin OC-1074		0.043	0.445	0.0053	0.16
Carbonised beet pulp	Phenol	◊	◊	29.35	5.13
Hydroxyapatite	Phenol	◊	◊	0.37	1.66
Coconut shell	Phenol	205.84	3.91	37.11	3.66
Aged-refuse	Phenol	◊	◊	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)

Biosorbent Activation





Desorption of phenolics from the biosorbent

- ✓ Selection of maximum yield experiment

Conditions: *10 min*

30 °C

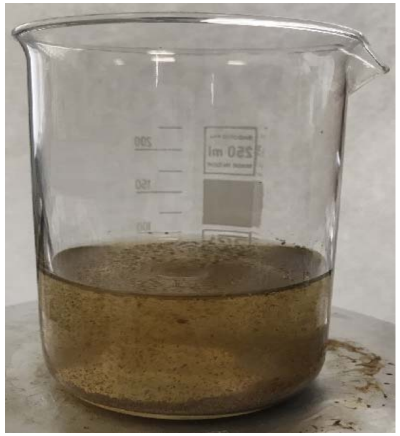
pH 5

r = 0.02 g/mL OMW

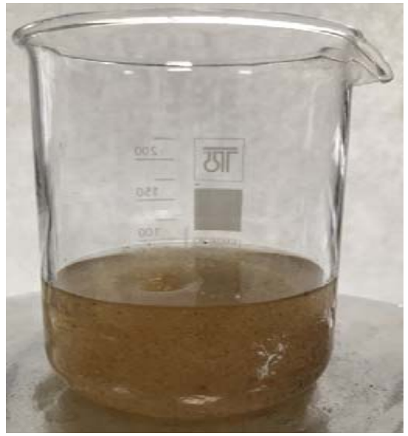
$C_0 = 162.5$ *mg/L*

$d_p = 0.922$ *mm*

Water
pH 7



Alkaline water
pH 12



Acetic acid 50%
pH 1.2

	Desorption percentage			**Adsorption Mechanism**
	Water pH 7	***Alkaline water pH 12***	***Acetic acid 50% pH 1.2***	
Not activated biosorbent	-	42.0%	73.2%	**Chemical adsorptiom**
Chemical activated biosorbent	-	39.3%	45.9%	**Chemical adsorptiom**
Thermal activated biosorbent	-	-	8.1%	**Chemical adsorptiom**

Conclusions

- **Pomegranate seed** by product has proven to be a promising material for the recovery of phenolic compounds from olive mill wastewater (OMW).
- The **maximum** yield of the batch adsorption process was **92.8%**, achieved in 10 min, at 30 ^{o}C, pH 5, r = 0.02 g/mL OMW, C_0 = 162.5 mg/L and d_p = 0.922 mm.
- The most likely **adsorption mechanism** for the adsorption process seemed to be **chemical sorption**.
- The most effective **activation** method of the pomegranate seed was the thermal activation (250 ^{o}C for 2-3 h).
- **Pseudo-first order** kinetic model described better the adsorption process.
- **Adsorption isotherms** studies showed that the adsorption isotherm that described the adsorption process better was the **Langmuir** isotherm.

Thank you
for your attention