Production of biochar and activated biochar from olive mill solid waste for the removal of heavy metals and calcium from water

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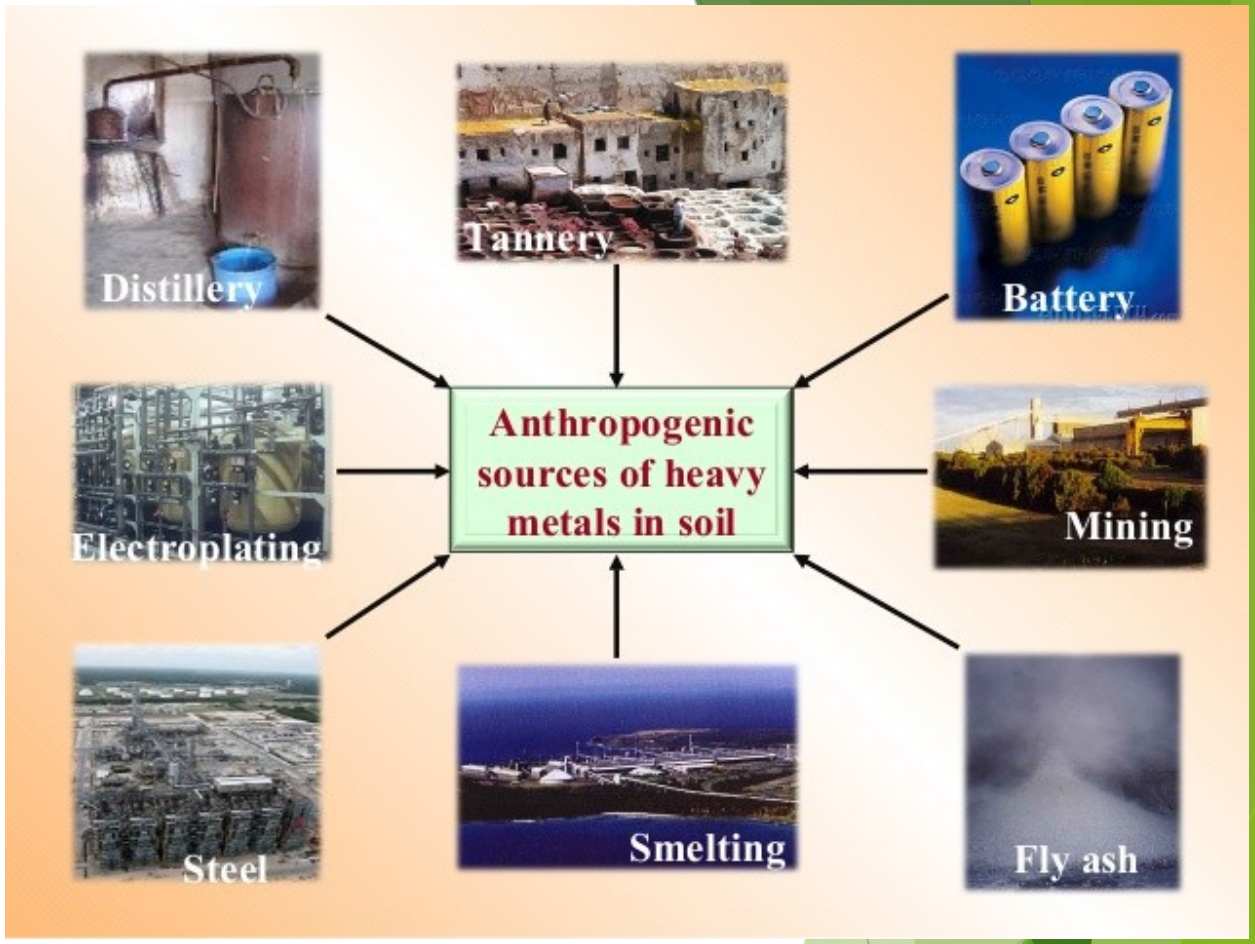
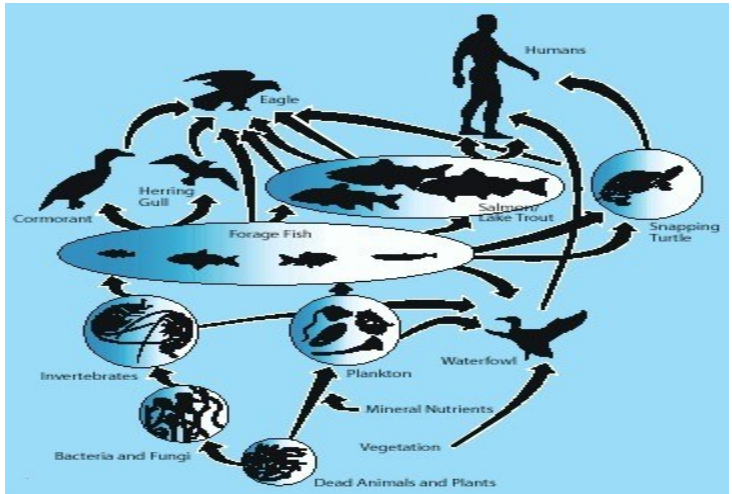
Outlines

- Introduction: Heavy metals contamination
- Olive mill solid wastes (OMSW).
- Objectives
- Results
- Conclusions

Heavy Metals (HM)

- HMs are produced from different sources including mining, industry and even from fertilizers...
- HMs contaminate the Human food chain and the ground water and cause toxic effects.





Physical and Chemical processes have been used for removing HM from water and industrial wastewater

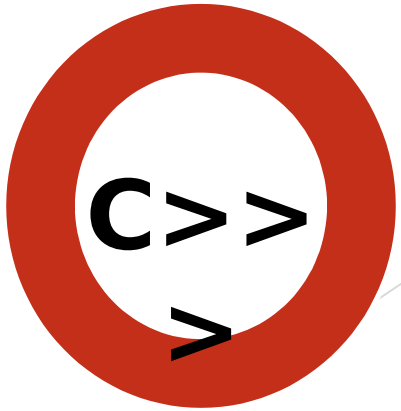
Ion exchange

Precipitation

Reduction

Evaporation

Membrane filtration



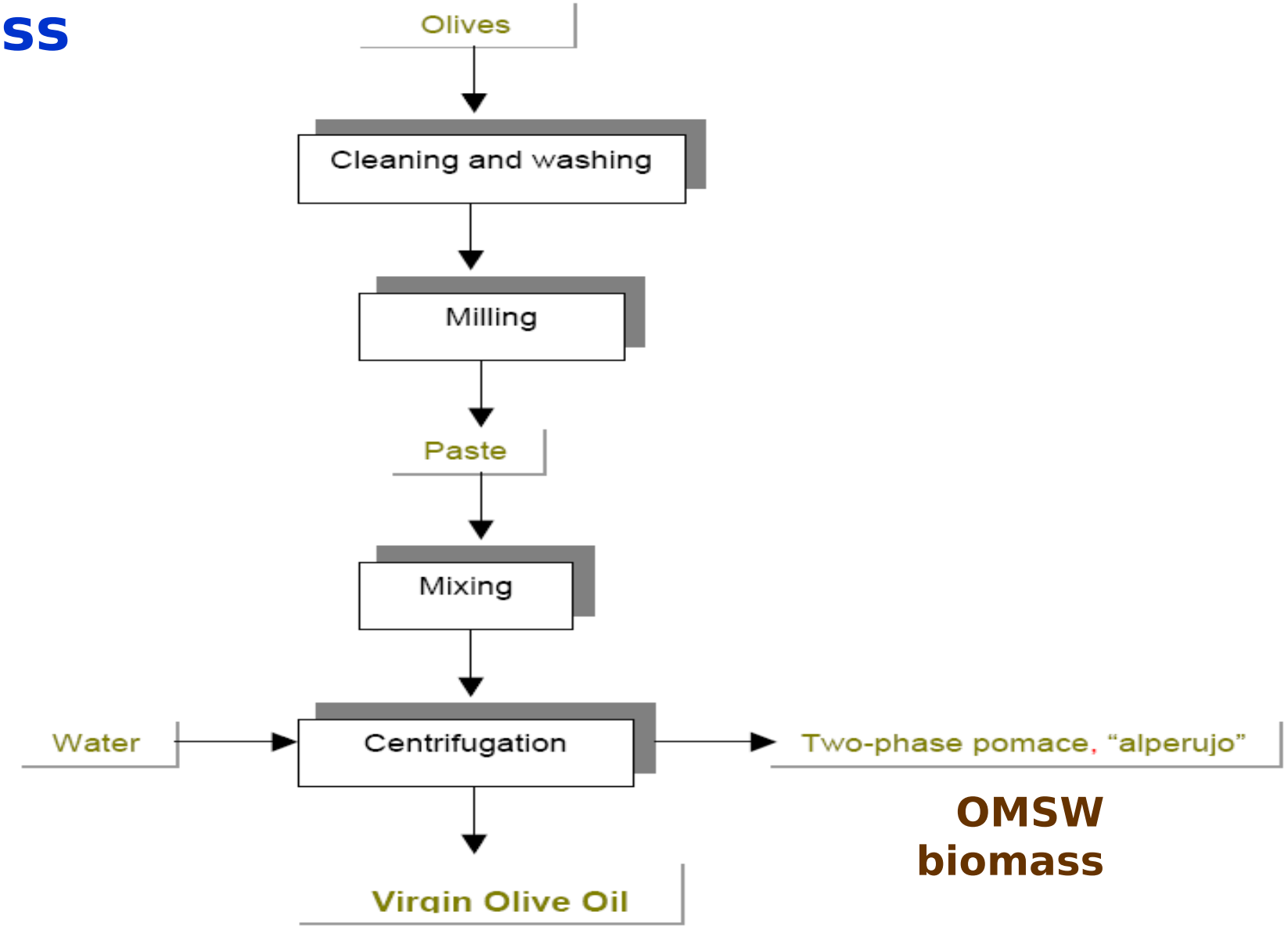
- Activated Carbon (AC) - the most commonly used and th most effective adsorbent
- AC – high cost
- **Alternative:** Low cost waste **biochar**– economical solu

- **What about Olive Mill Solid Waste (OMSW)???**

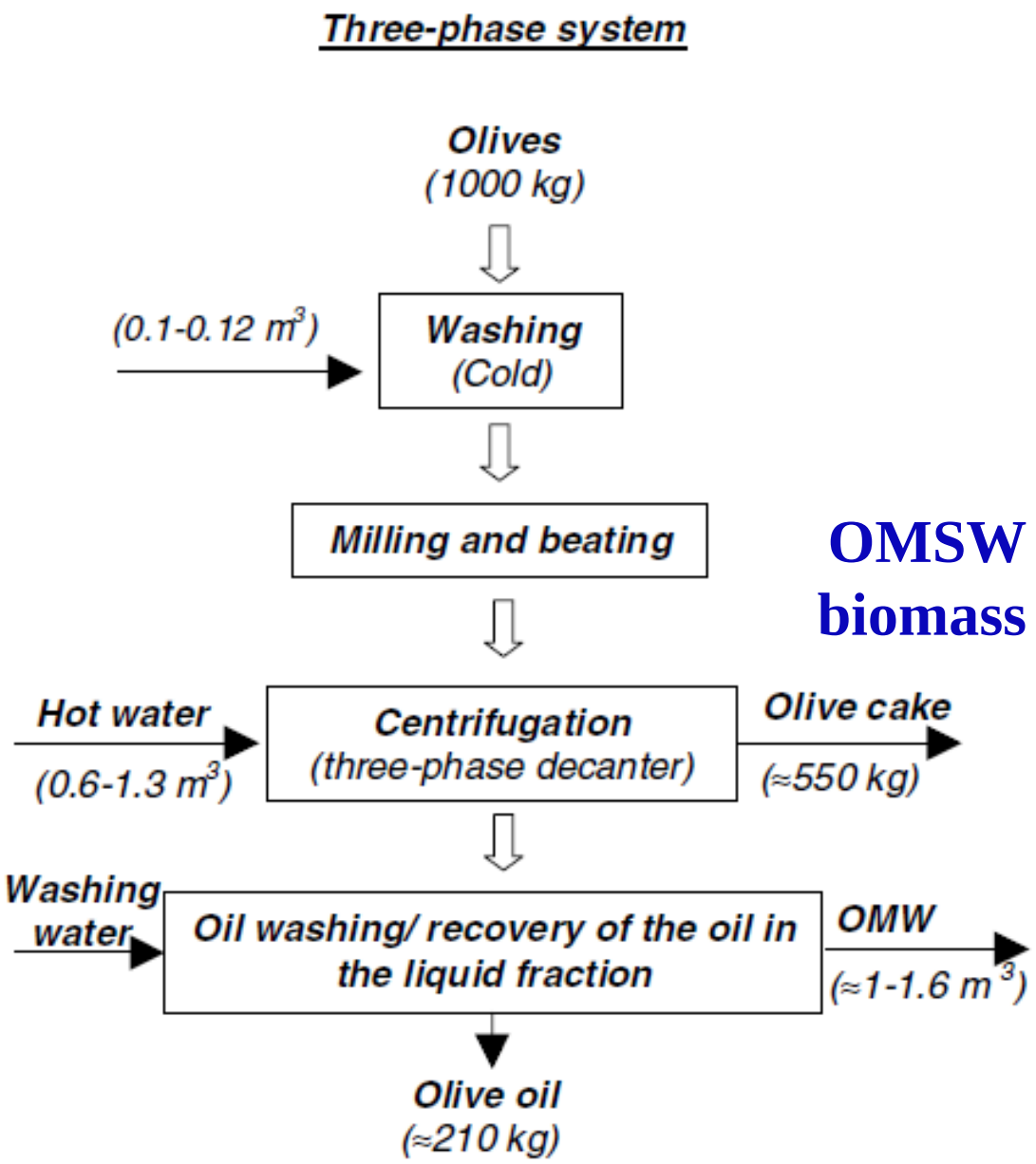
Olive mill products:

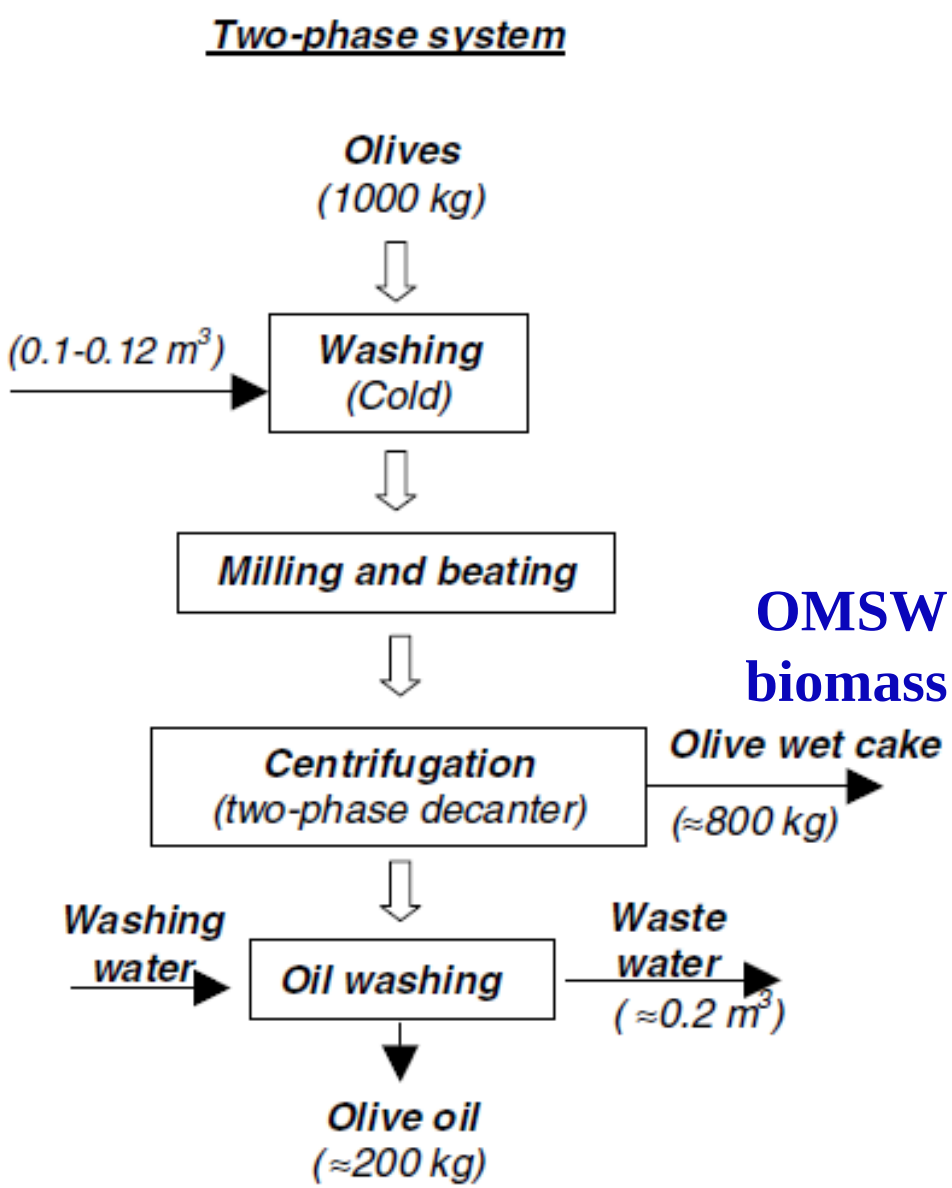
1. Three-phase process

2. Two-phase process



OMSW biomass

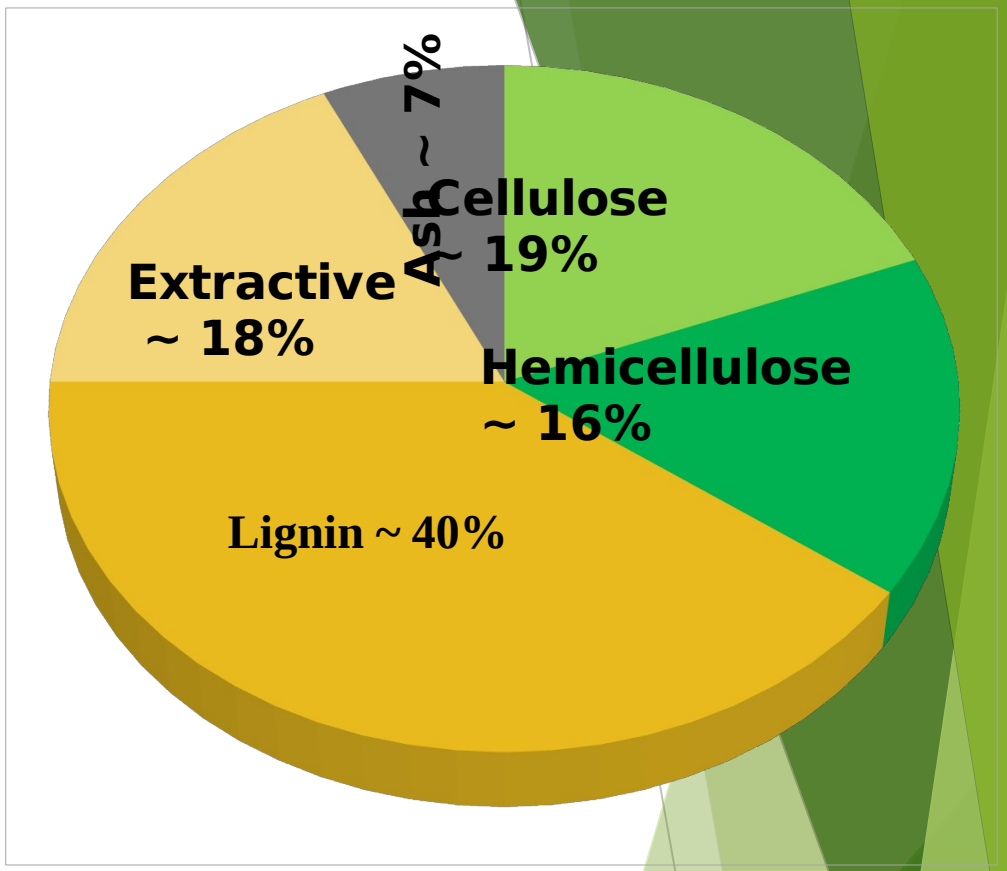




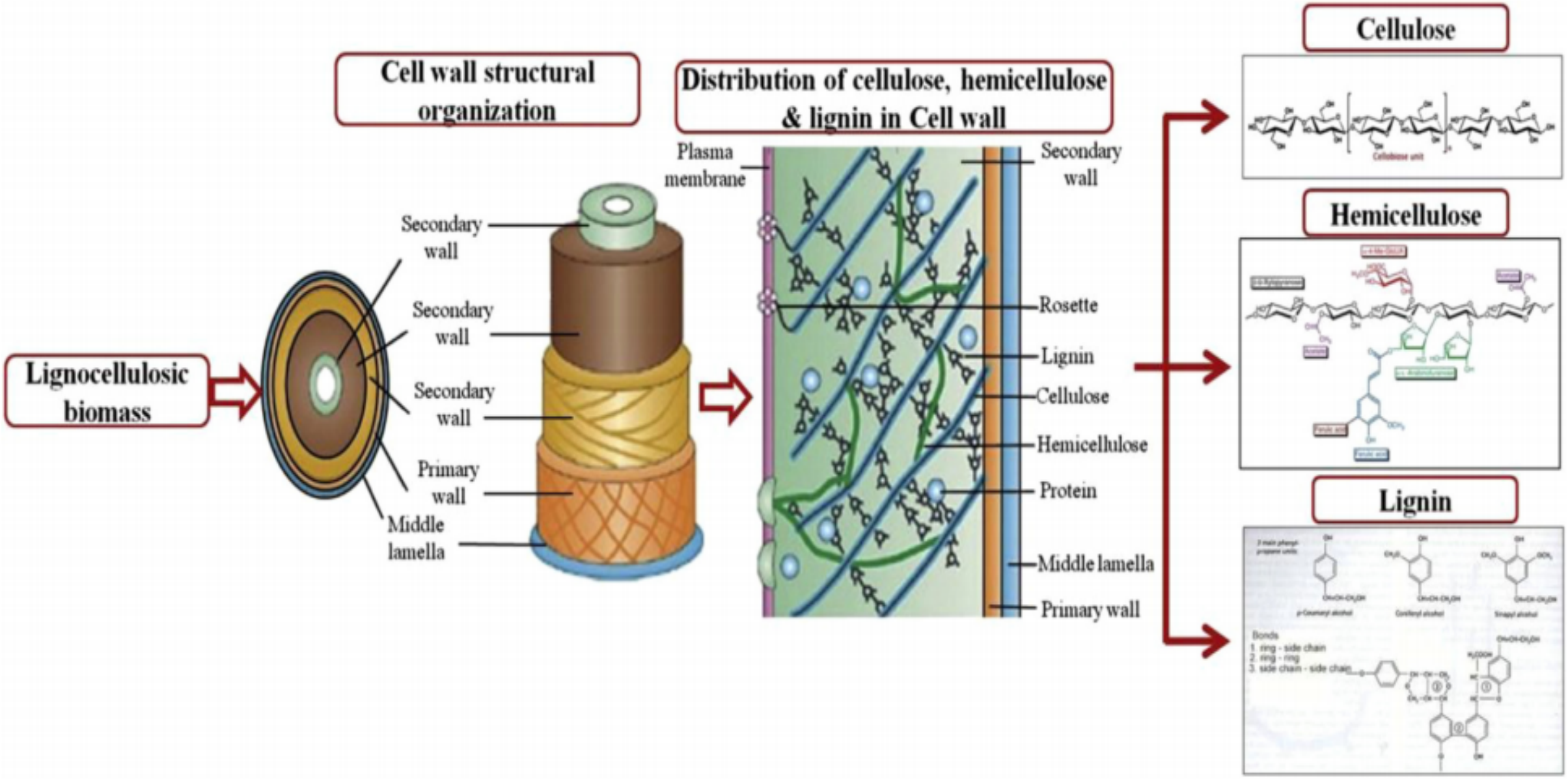
s (Alburquerque et al., 2004).

OMSW biomass

- What it contains?
- Agriculture waste with very low economical value and it is an environmental pollutant.
- Uses: compost, producing animal feed and as energy source to heat houses (burning).



Structure of lignocellulose (Anwar et al., 2014)



- **Objectives:**

- **Producing biochar from OMSW of different cultivars (Picual vs Souri) & processes (two- vs three-phases) using pyrolysis process at 350 & 450ºC (5 hours).**

- **Using physical activation to produce Activated Biochar (AB).**

- **Testing the biochar and AB as Adsorbent (biofilter) to HM using Batch experiments.**

- **Looking for functional groups in the using FTIR.**

Methods:

Biochar preparation and pyrolysis

Physical activation

Particles distribution

Surface Area

Langmuir

BET

HMs Removal by ICP

Functional groups by FTIR

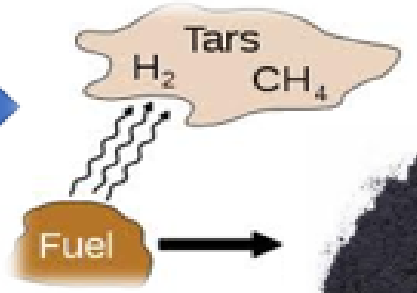
Scheme

OMSW

Char separating: Whole, Cellulose and Kernel

Pyrolysis Process

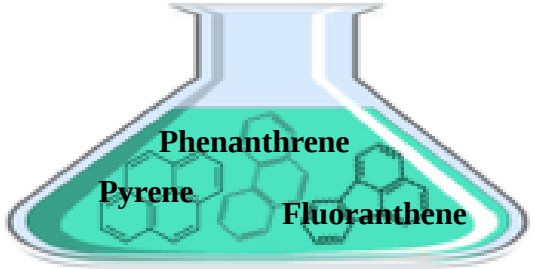
By- Products



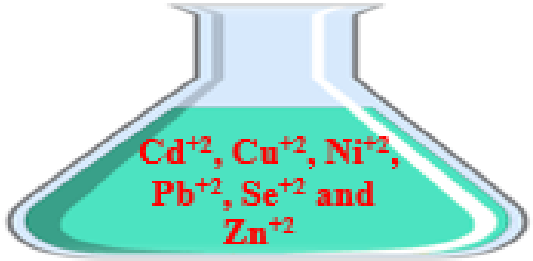
Activated Carbon

Biological Filter

PAH`s Solution (polluted waste water)



Heavy Metals Solution (polluted waste water)



Bach experiment for five time intervals 0,5,15,30 and 60 min.

Results:

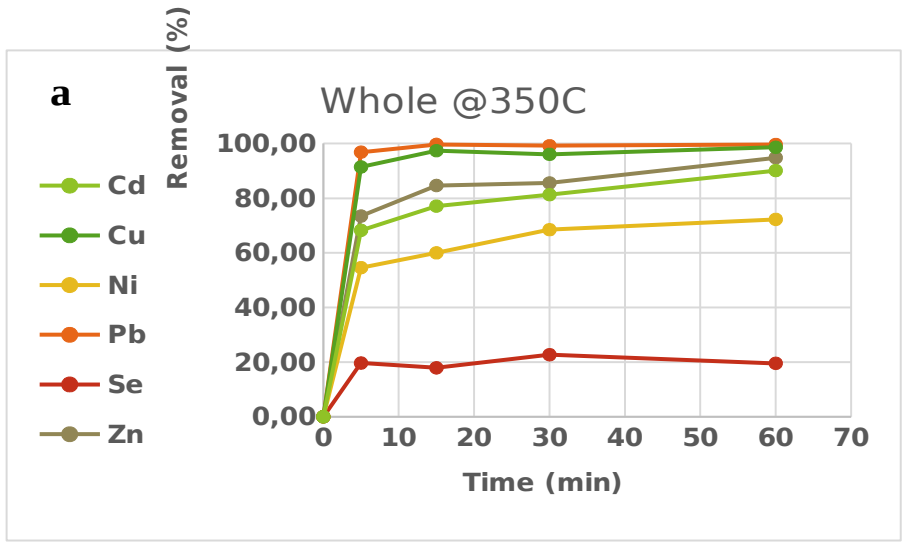
35.6% - 23%

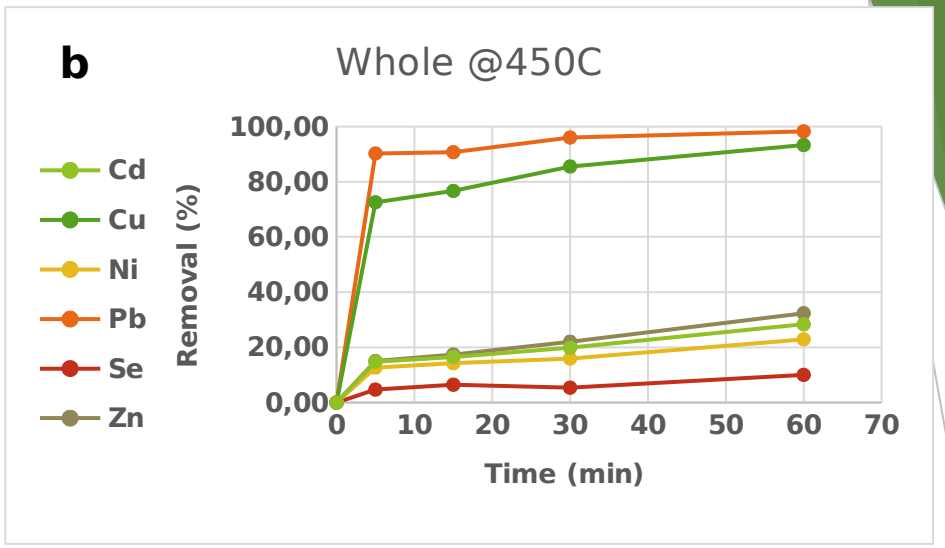
The yield (%) values of the **Picual** two and three phases biochar obtained at **350^{0}C or 450^{0}C** pyrolysis for 5h. Data is mean of 3 replicates ± SD.

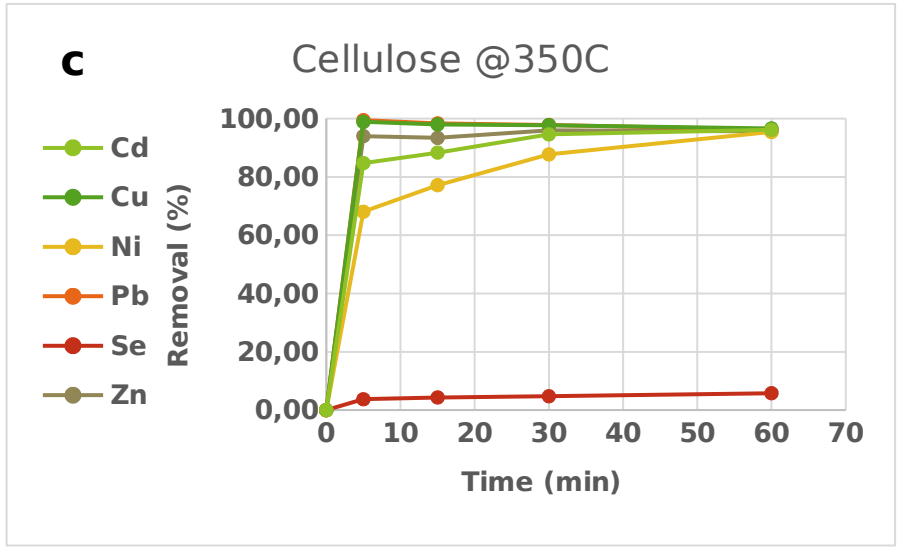
Surface area (Biochar): Langmuir model and BET method

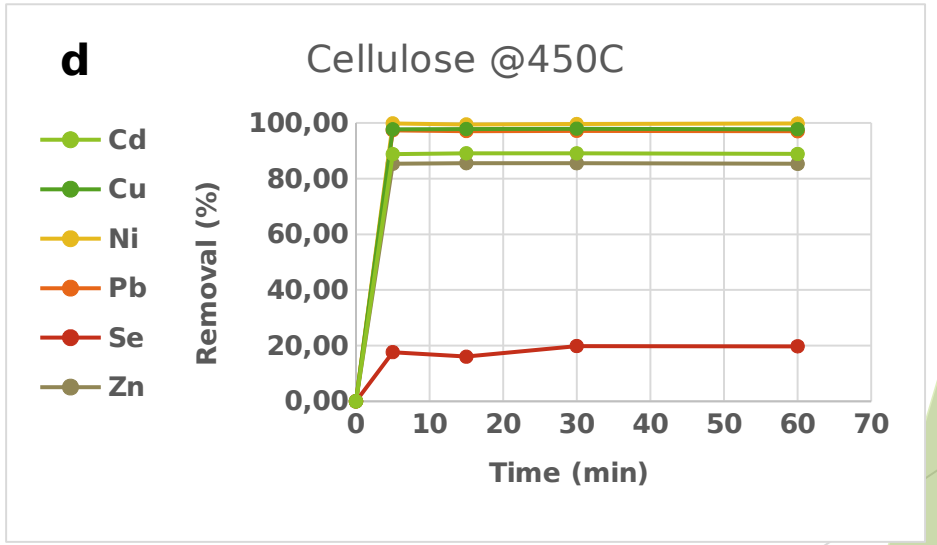
The mean surface area of biochar produced at 450^{0}C of the different OMSW types using Langmuir (MB) and BET method. Data is mean of 3 replicates ± SD.

SA_{BET} (m^2/g)	SA_{MB} (m^2/g)	Type @450^{0}C
1.0 + 0.005	1.65 ± 0.14	Picual Two-phase
3.5 + 0.0175	8.12 ± 0.85	Picual Three-phase
1.2 + 0.006	3.48 ± 0.01	Souri Two-phase
5.3 + 0.0265	4.30 ± 1.22	Souri Three-phase
1100 + 5.5	-	Commercial Activated Carbon

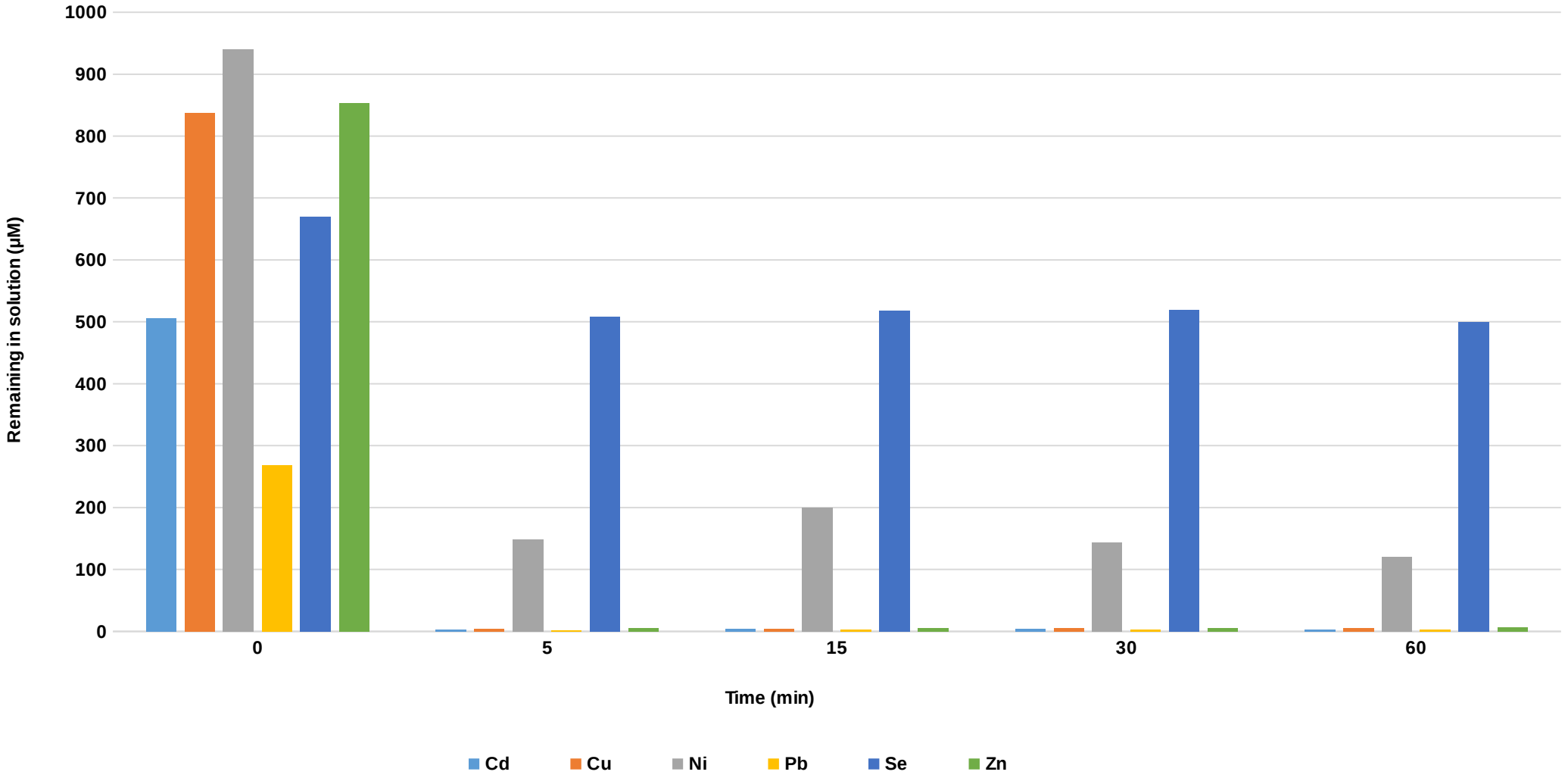




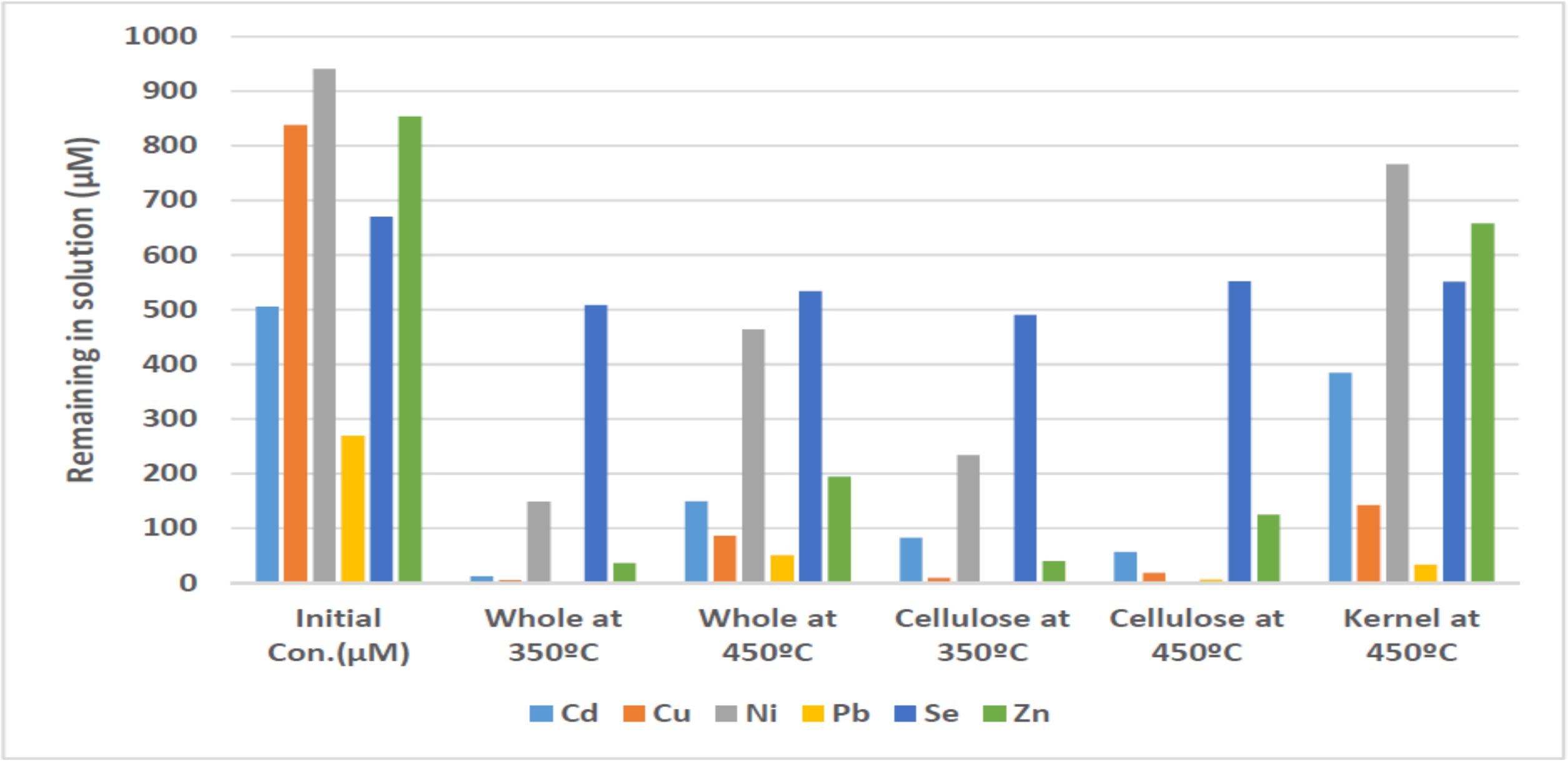




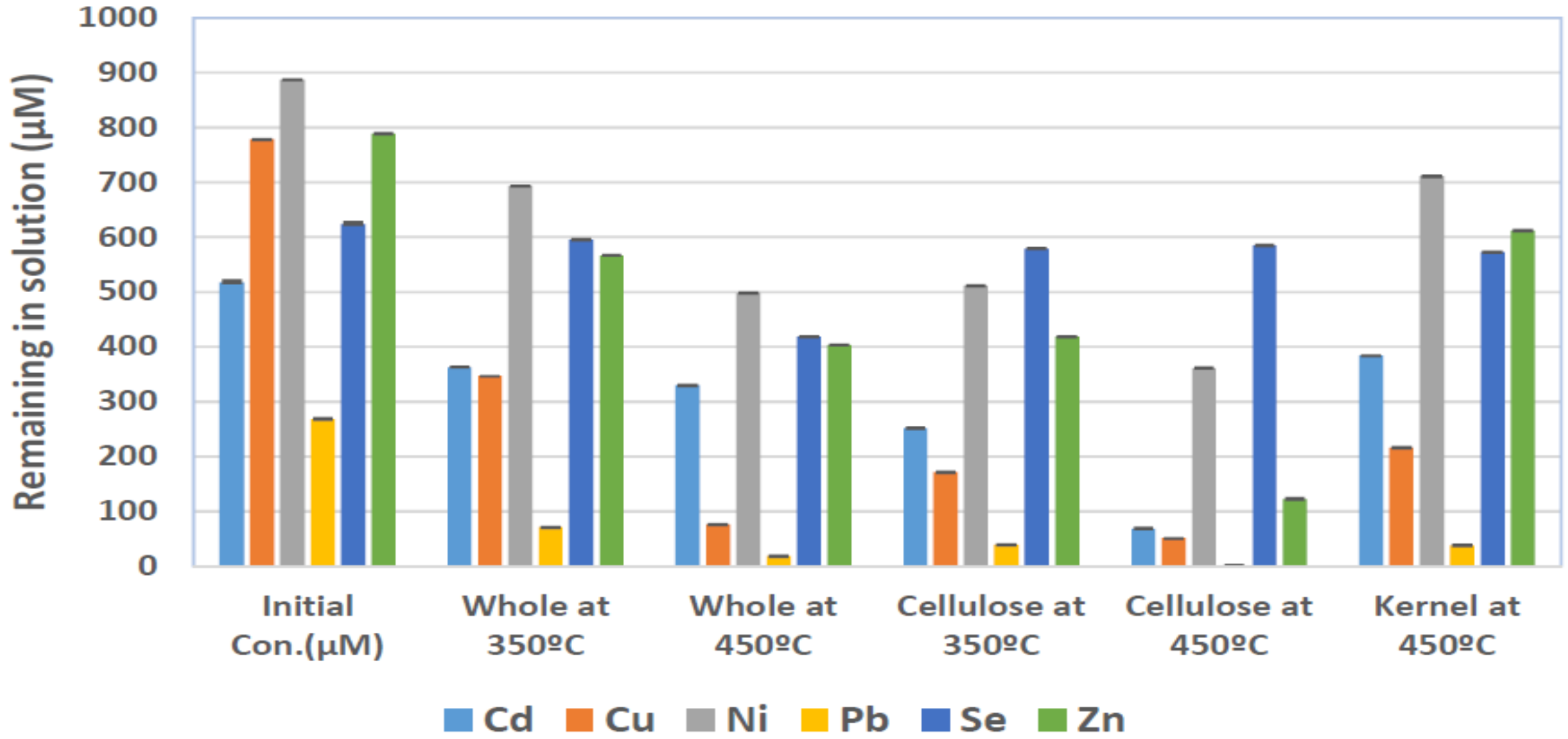
The removal (%) values of the six heavy metals using the **Picual two-phase (a) Whole @350⁰C, (b) Whole @450⁰C, (c) Cellulose @350⁰C, and (d) Cellulose @450⁰C** biochar after incubation for 0, 5, 15, 30, 60 min. Data is mean of 3 replicates ± SD.



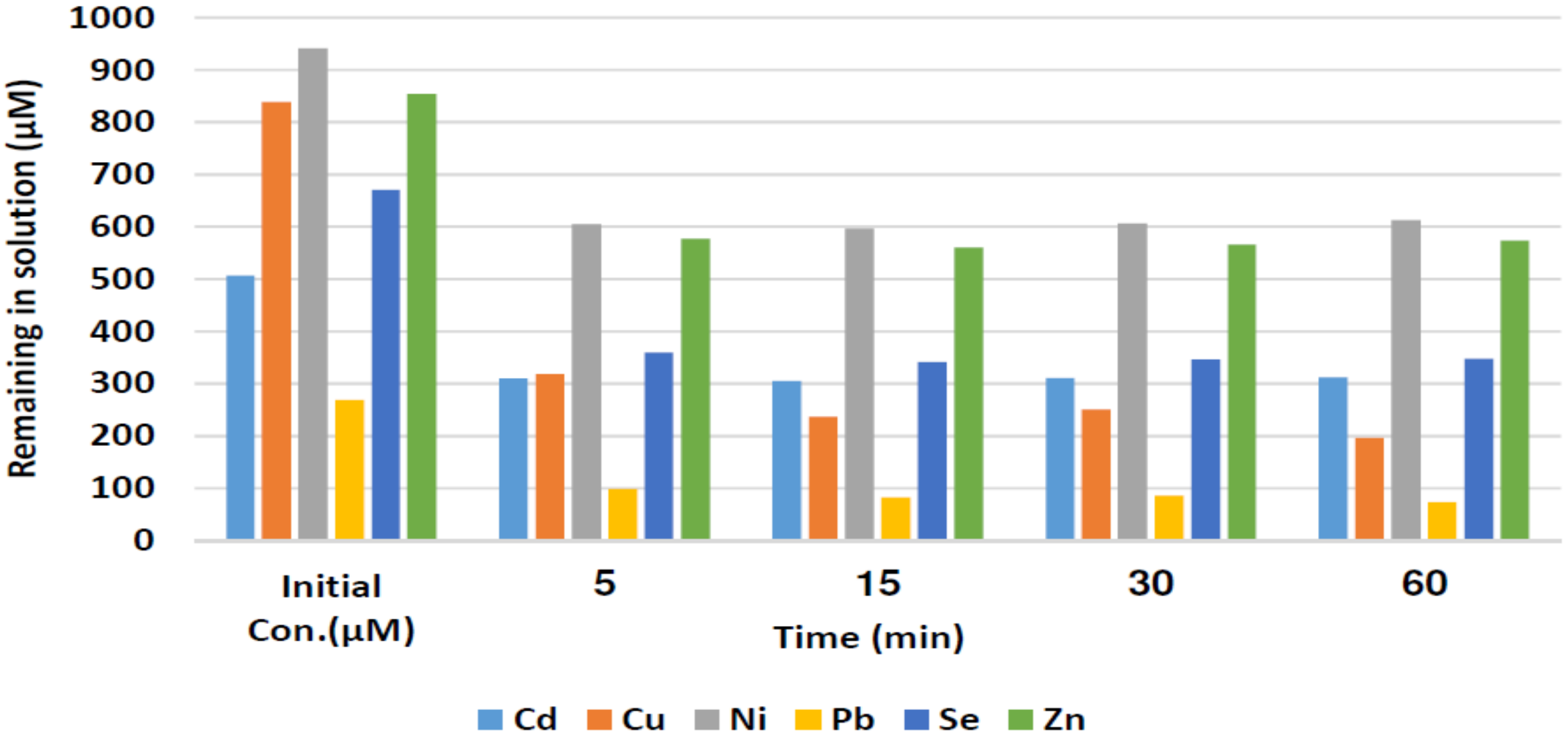
The remaining concentration (µM) of the six heavy metals using the **Cellulose of Picual of two phases** biochar at 350^{0}C after incubation for **0, 5, 15, 30, 60 min**. Data is mean of 3 replicates ± SD.



The remaining concentration (µM) of the six heavy metals using the **Picual two phases biochar** obtained at 350ºC or 450ºC separated to Cellulose and Kernel compared to whole after incubation **for 5 min.** Data is mean of 3 replicates ± SD.



The remaining concentration (µM) of the six heavy metals using the **Souri two phases biochar** obtained at 350^{0}C or 450^{0}C separated to Cellulose and Kernel compared to whole after incubation **for 5 min.** Data is mean of 3 replicates $\pm$ SD.



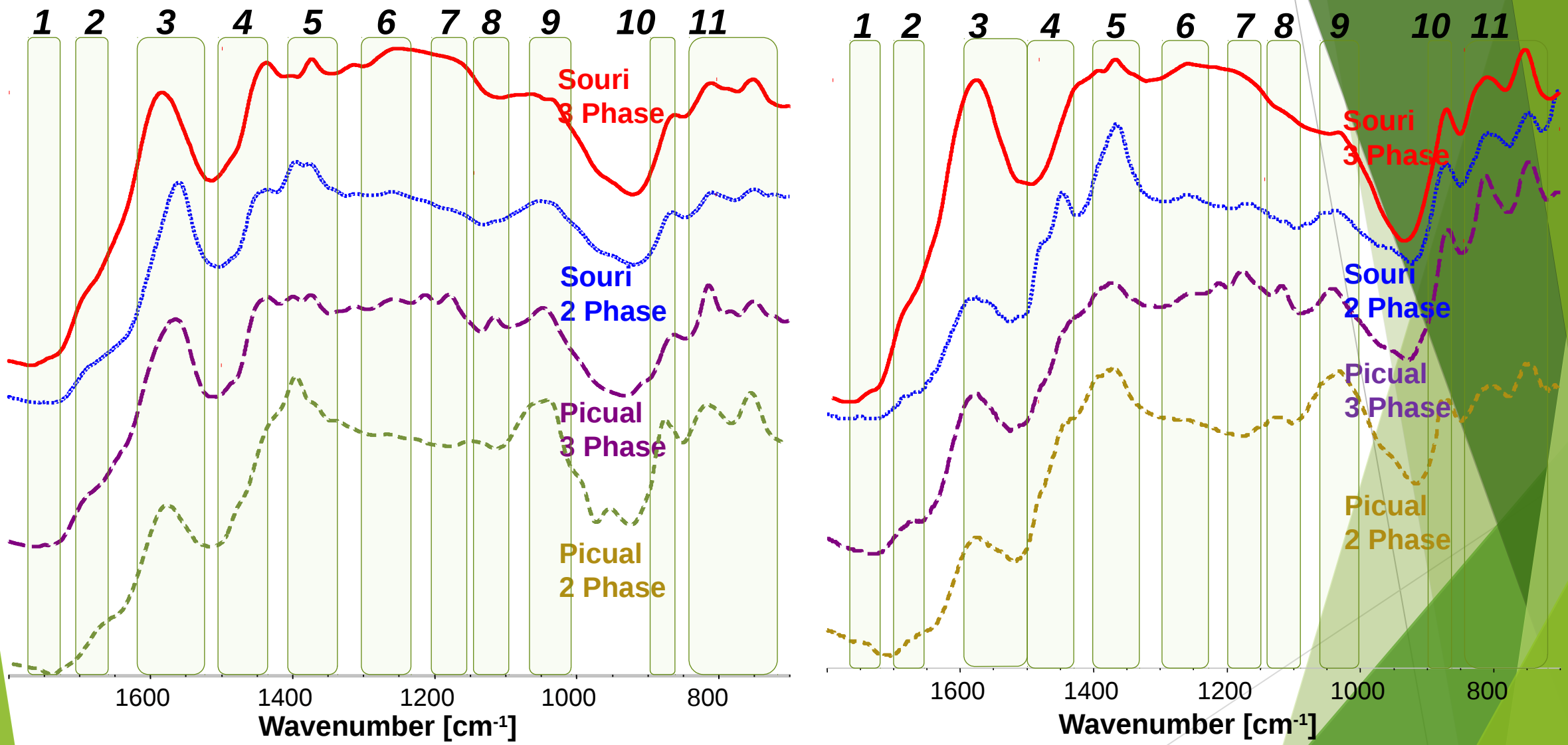
The remaining concentration (µM) of the six heavy metals using the **Commercial Activated Carbon** (**CAC)** after incubation for 5, 15, 30, 60 min. Data is mean of 3 replicates $\pm$ SD.

Why Se was not removed from solution??

Zeta potential of biochar is negative

- $CuCl_2 \rightarrow Cu^{+2} + 2Cl^{-1}$ (1)
- $Pb(NO_3)_2 \rightarrow Pb^{+2} + 2NO_3^{-1}$ (2)
- $NiNO_3 \rightarrow Ni^{+2} + 2NO_3^{-1}$ (3)
- $ZnSO_4 \rightarrow Zn^{+2} + SO_4^{-2}$ (4)
- $CdSO_4 \rightarrow Cd^{+2} + SO_4^{-2}$ (5)
- $Na_2SeO_4 \rightarrow 2Na^{+1} + \boldsymbol{SeO_4^{-2}}$ (6)

Functional groups

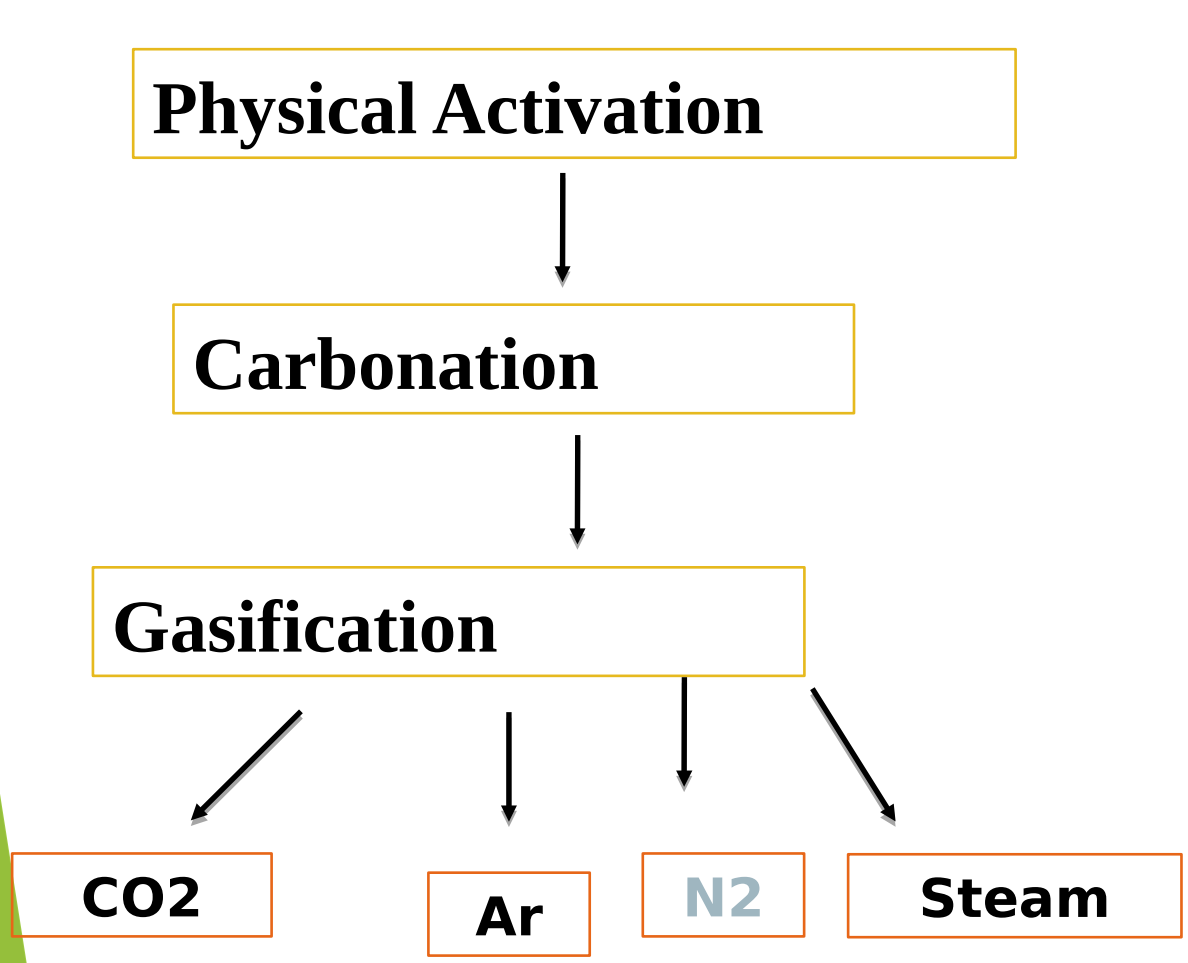


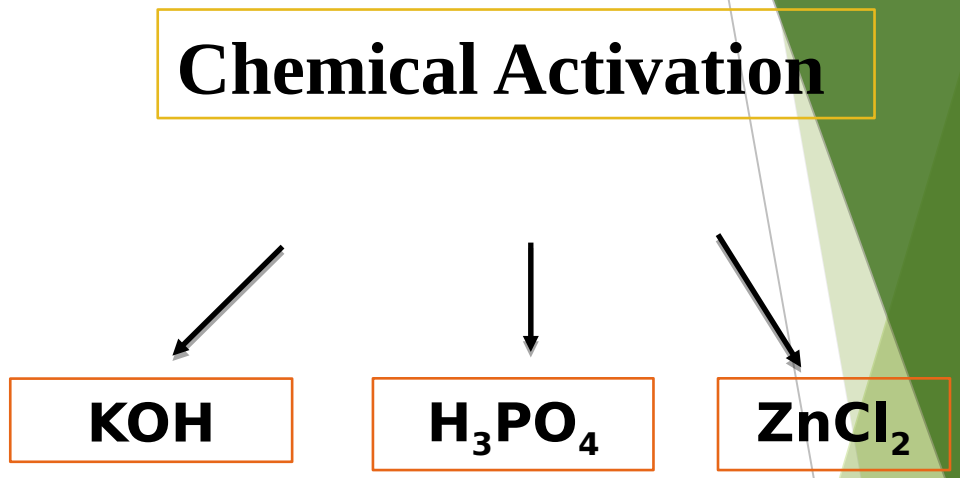
Summary of the **FTIR** analysis for functional groups associated with the different wavelength ranges between 800-1800 cm^{-1} obtained for the different biochar samples produced at 350°C (left) or at 450 °C (right).

Summary of the functional groups of the different OMSW types associated with the different wavelength ranges between 800-1800 cm^{-1} based on FTIR analysis

#	Wavenumber (cm^{-1})	Assignment (Functional groups)	Reference
1	~1740	Unconjugated C = O in hemicellulose	(Pandey and Pitman, 2003; Naumann et al., 2007)
2	~1670	Conjugated C = O	
3	~1580	Aromatic skeletal vibration in lignin	
4	~1440	C–H deformation in lignin and carbohydrates	
5	**~1370**	**C–H deformation in cellulose and hemicellulose**	
6	~1250	Syringyl/guiacyl ring breathing and C–O stretch in lignin and xylan	
7	~1170	C–O–C vibration in cellulose and hemicellulose	
8	~1120	Aromatic skeletal and C–O stretch	(Pandey and Pitman, 2003)
9	**~1040**	**C–O stretch in cellulose and hemicellulose**	
10	~890	C–H deformation in cellulose	
11	~830, ~760	Aryl C–H and/or aryl C–O groups	(Baldock and Smernik, 2002)

OMSW Activation





(Physically Activated Biochar):

The Yield (%) and the mean surface area of biochar produced at 350⁰C of different whole OMSW types and the porosity using BET model after physical activation. Data is mean of 3 replicates ± SD.

Porosity (%)	SA_{BET}(m^2/g) after activation	Yield (%)	Type: pyrolyzed at 350⁰C for 5h
87.4	501.5 ± 2.50*	59.7	Picual Two-phases
91.53	304.46 ± 1.52*	58.6	Picual Three-phases
88.34	213.27 ± 1.06*,**	70.4	Souri Two-phases
91.05	172.6 ± 0.86*	63.3	Souri Three-phases

Conclusions

- The yield of the produced biochar was dependent on pyrolysis temperature.
- **The removal capacity for HMs dependent on the cultivar and processing type.**
- The best HM removal was by using Picual-cellulose of the two-phase obtained at 350^{0}C.
- **There was no correlation between surface area and the removal capacity of the different biochar types.**
- Using physical activation caused hundreds of times increase in surface area but the HM removal capacity was not affected.

Conclusions

- The FTIR analysis indicated that more significant absorption bands for the two-phase samples, that are considerably smaller in the three-phase. Peaks 5 (C–H) and 9 (C–O).
- **The main functional groups in metals removal are related to remains of cellulose in the produced biochar.**
- Zeta potential explains why the produced biochar and AB didn’t remove Se from the solution.

Thank you for your attention

Olives

Pressing ~~Process~~

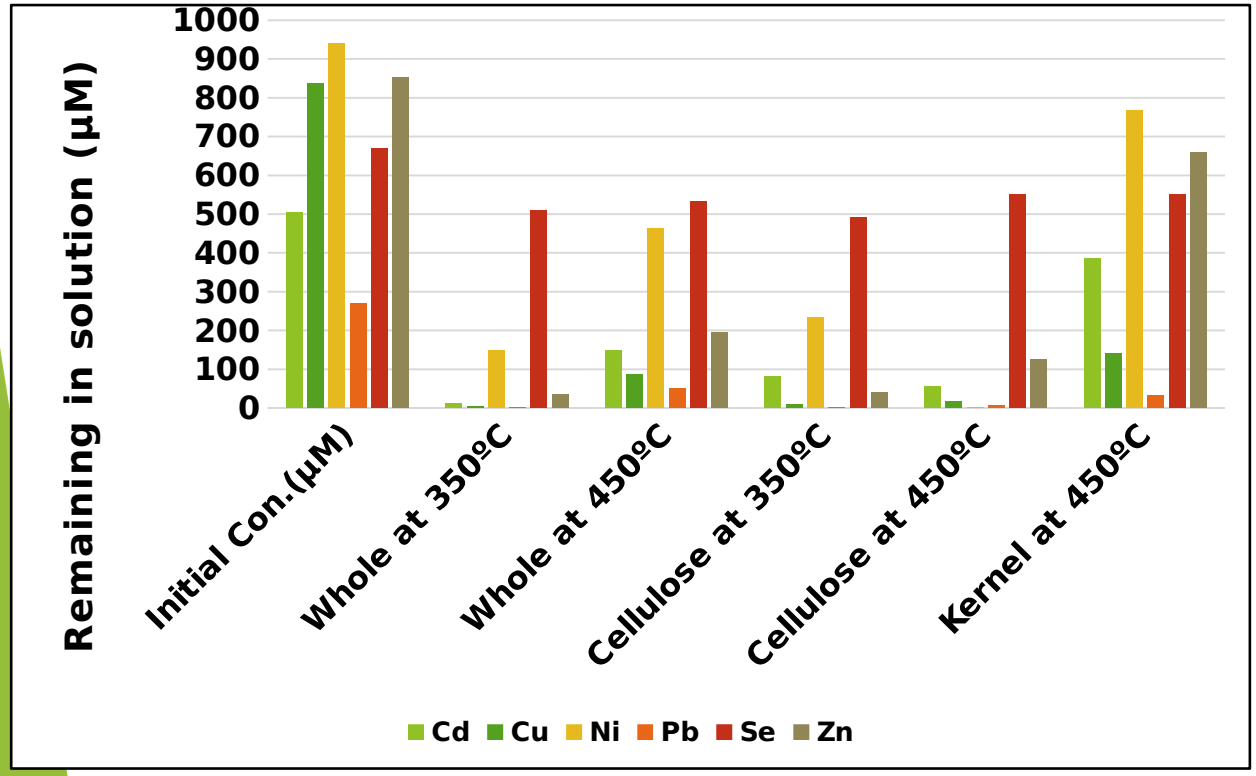
OMSW separation: Whole, Cellulose and Kernel

Pyrolysis Process at 350ºC, 450ºC

Biochar

Physical Activation

Activated Carbon



Biological Filter

Organic and Inorganic Pollutants

Zn^{+2}

Cd^{+2}

Se^{+2}

Ni^{+2}

Cu^{+2}

Pb^{+2}