Valorisation of spent tire rubber as carbon adsorbents for Pb(II) and W(VI) recovery in the framework of a circular economy

Maria Bernardo[1], Daniel Dores[1], Nuno Lapa[1], Filomena Pinto[1], Inês Matos[1], Márcia Ventura[1], Isabel Fonseca[1]

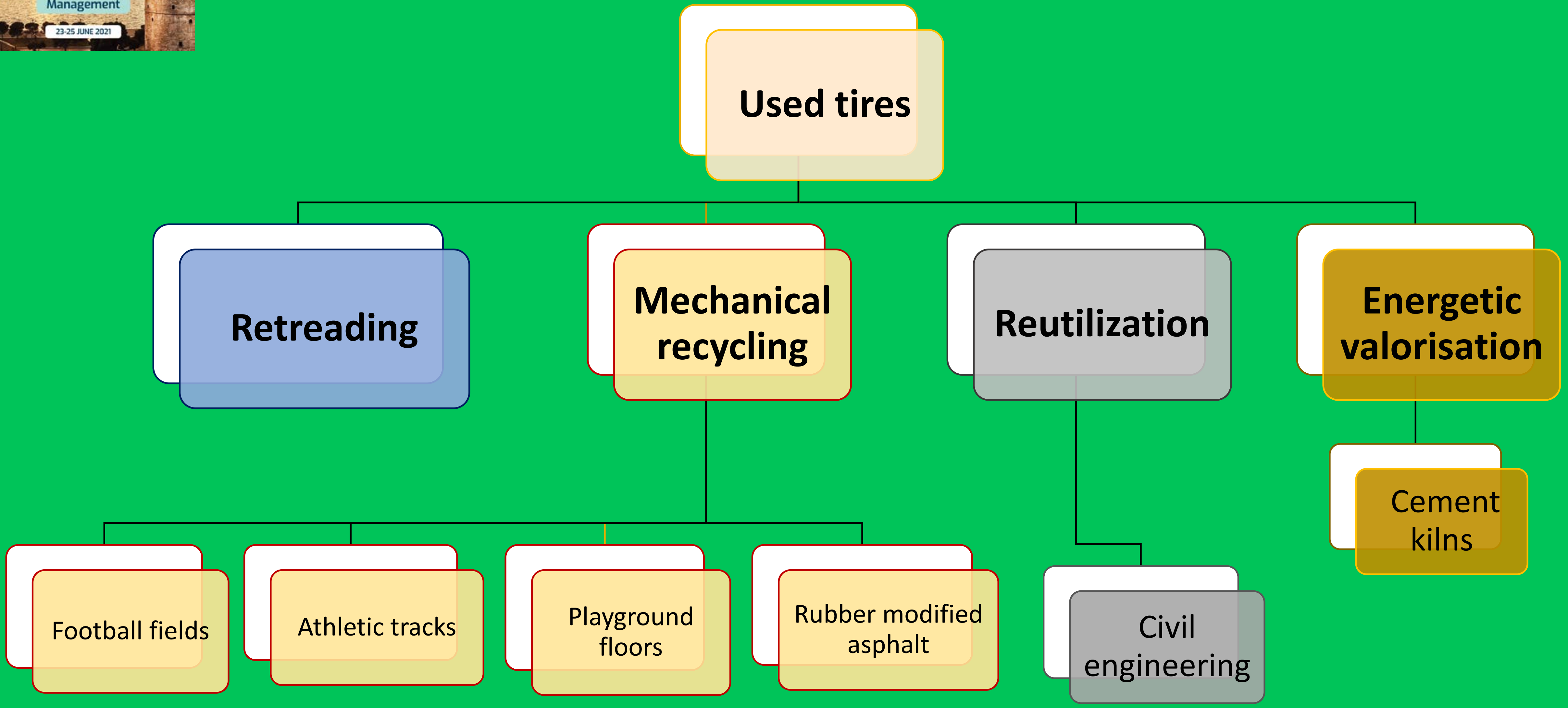
[1]NOVA School of Science and Technology, Caparica, Portugal

[2] National Laboratory of Energy and Geology, Lisbon, Portugal

24 June 2021


THESSALONIKI2021
www.thessaloniki2021.uest.gr
8th International Conference
on
Sustainable Solid Waste
Management
23-25 JUNE 2021

FRAMEWORK


Used tires
Retreading
Mechanical recycling
Reutilization
Energetic valorisation
Football fields
Athletic tracks
Playground floors
Rubber modified asphalt
Civil engineering
Cement kilns

FRAMEWORK

European Tyre & Rubber Industry

Spent tires:
3.5 million tons (2018)

Rubber destination

0.35% chemical recycling

57% reuse/recycling

How to manage spent tire rubber products?

35% energy recovery

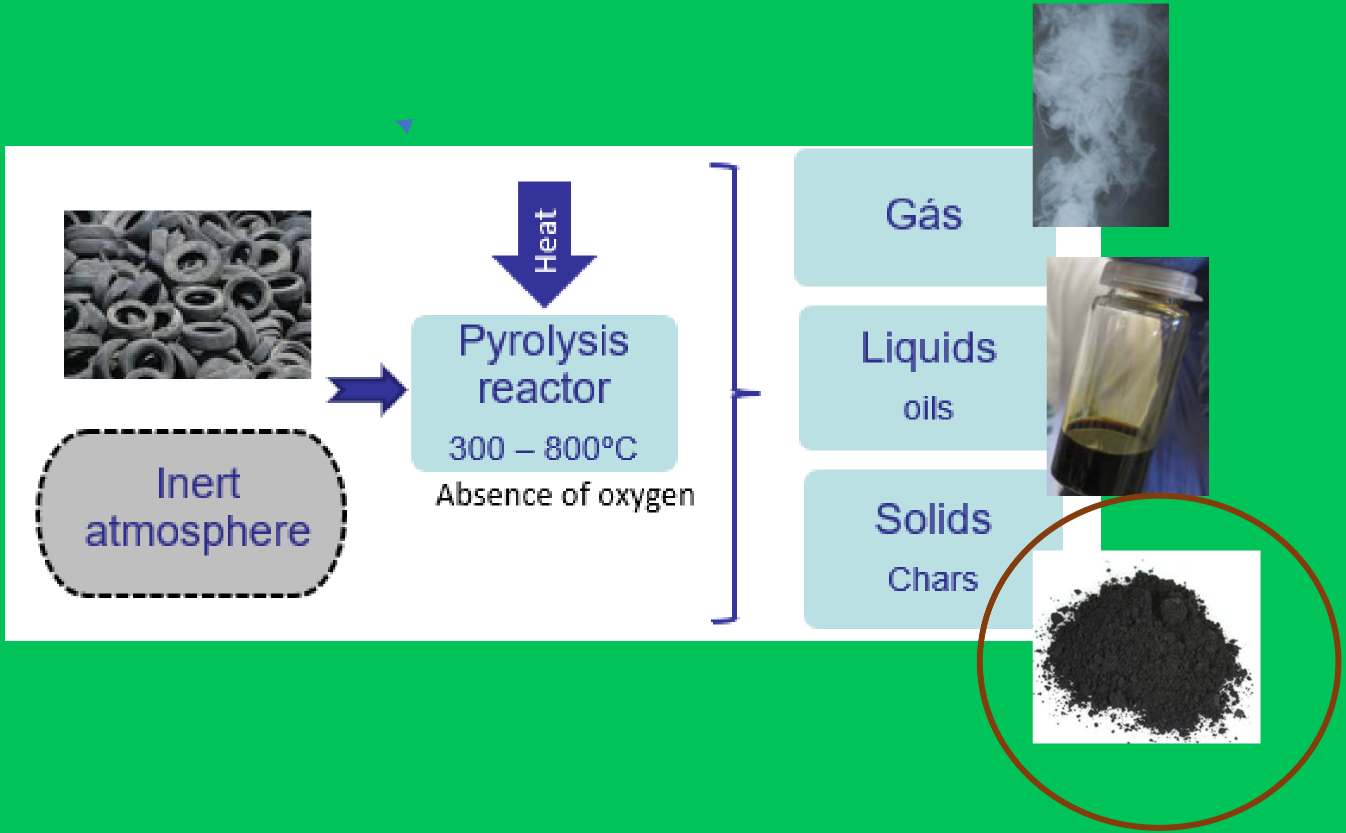
Loss of resources, GHG emissions

8% unknown

Landfill, open dumps,…

FRAMEWORK

Chemical Recycling by Pyrolysis



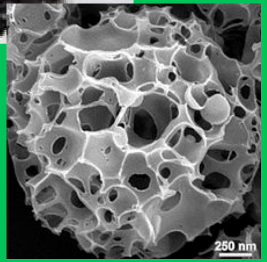
FRAMEWORK

Char upgrading

Pyrolysis char

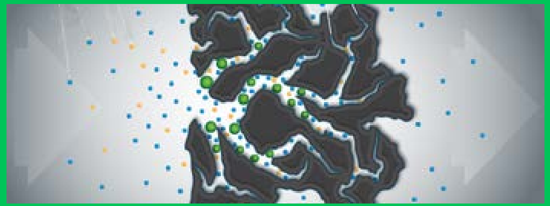
Upgrading/
Activation

Activated carbon



Adsorbent

Water and Flue gases Treatment



FRAMEWORK

Wastes of Electric and Electronic Equipment (WEEE)	Waste Batteries and Accumulators (WBAs)

- 10 million tons/year in Europe
- Composed by critical raw materials, such as Tungsten (W)
- And potentially toxic elements, such as Lead (Pb)
- Its recovery from wastewaters/hydrometallurgical effluents is mandatory

OBJECTIVE

PYROLYSIS ASSAYS

CHAR ACTIVATION

RECOVERY ASSAYS

Spent tire rubber

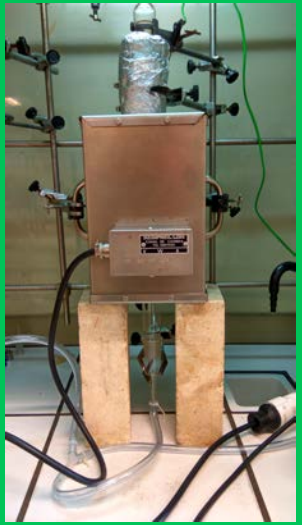
Pyrolysis reactor

Oil

Gas

Char

Activation reactor



Activated Carbon

Aqueous medium with W(VI) and Pb(II)

EXPERIMENTAL

valorpneu

LNEG

NOVA SCHOOL OF SCIENCE & TECHNOLOGY

RUbUST

PYROLYSIS ASSAYS

Spent tire rubber

Sample A
Light vehicles

Sample B
Heavy trucks

- Elemental analysis
- TGA
- Ash content
- Mineral content

Temperature – 405 °C
Reaction time – 30 min
Heating rate - 5°C/min
N_2 atmosphere

Chars

- Sequential extraction: hexane → acetone → water

Char A (CA) and Char B (CB)

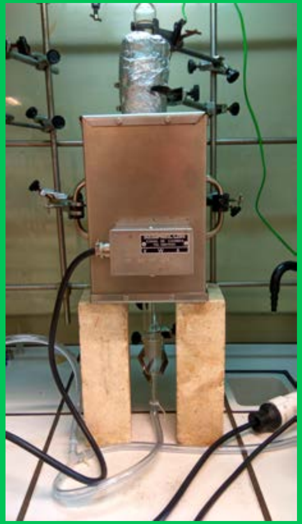
- Elemental analysis
- TGA
- Ash content
- Mineral content
- pH_{PZC}
- XRPD
- FTIR
- N2 adsorption isotherms at 77 K

EXPERIMENTAL

CHAR ACTIVATION

CA and CB

Activation reactor



Physical activation with CO_2
Temperature – 800 °C
Reaction time – 6 h
CO_2 flow – 100 ml/min

Activated Carbons
CA - CO2
CB - CO2

Chemical activation with H_3PO_4
Impregnation mass ratio - 1:1
Temperature – 500 °C
Reaction time – 2 h
N_2 flow – 150 ml/min

Activated Carbons
CA - H3PO4
CB - H3PO4

EXPERIMENTAL

RECOVERY ASSAYS of W(VI) and Pb(II)

Ammonium Tungstate solution
$(NH_4)_2WO_4$

Lead nitrate salt
$Pb(NO_3)_2$

Activated Carbons

CA - CO2

CB - CO2

CA - H3PO4

CB - H3PO4

$$R\ (\%) = \frac{(C_0 - C_f) \times 100}{C_0}$$

$$q_t = \frac{(C_0 - C_f) \times V}{m}$$

Influence of initial pH

- Adsorbent mass = 30 mg
- pH = 2 - 7
- t = 24 h
- Solution volume = 10 ml
- Metal concentration = 100 mg/L

Kinetic study

- Adsorbent mass = 10 mg
- pH = 5 (Pb) and 2 (W)
- t = 5 min - 72 h
- Solution volume = 10 ml
- Metal concentration = 100 mg/L

Results adjusted to pseudo-first and pseudo-second order non-linear kinetic models

Adsorption isotherms

- Adsorbent mass = 10 mg
- pH = 5 (Pb) and 2 (W)
- Solution volume = 10 ml
- Equilibrium time = 48 h
- Metal concentration = 20 - 200 mg/L

Results adjusted to Langmuir's and Freundlich's non-linear equations

RESULTS

Samples characterization

Elemental analysis, ash content and pH_{PZC} of rubber and carbon samples

	C (%)	H (%)	N (%)	S (%)	Ashes (%)	pH_{PZC}
Rubber A	79.20	7.07	0.40	1.64	9.16	n.d.
Rubber B	83.39	7.60	0.40	2.04	3.92	n.d.
CA	71.33	0.71	0.28	2.51	21.4	7.4
CB	79.06	0.86	0.33	3.94	13.9	6.7
CA-H3PO4	69.00	0.52	0.20	0.42	23.8	3.0
CB-H3PO4	70.16	0.48	0.24	0.44	21.3	2.8
CA-CO2	70.26	0.16	0.23	2.90	27.3	8.5
CB-CO2	76.26	0.14	0.29	3.70	17.5	7.8

RESULTS

Samples characterization

Textural properties

	A_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
CA	73	0.13	0.01	0.12
CB	90	0.13	0.02	0.11
CA-H3PO4	48	0.11	0.004	0.11
CB-H3PO4	42	0.09	0.004	0.09
CA-CO2	95	0.14	0.02	0.12
CB-CO2	104	0.12	0.03	0.09

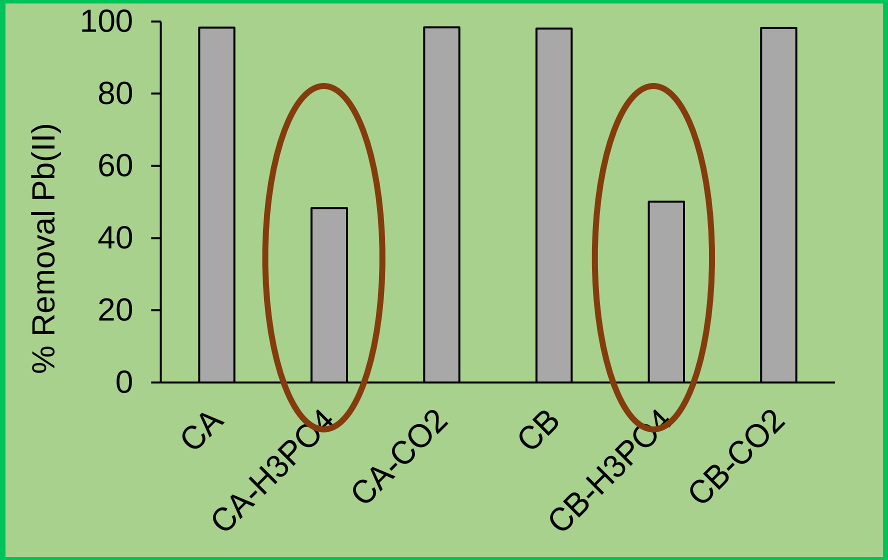
Mineral content

Concentration (mg/g)	Rubber A	Rubber B	CA	CB
Zn	29.2	38.6	69.6	93.5
Ca	13.0	6.38	21.9	11.9
Fe	2.18	4.25	4.96	8.75
Mg	0.815	0.870	1.79	1.74
Cu	0.473	1.02	0.318	1.63
Pb	0.081	0.043	0.118	0.112
Ti	0.067	<0.004	<0.004	<0.004
Mn	0.029	0.025	0.052	0.059
Ba	0.202	$<4x10^{-5}$	$<4x10^{-5}$	$<4x10^{-5}$
Cr	0.002	0.006	0.008	0.010
Ni	0.004	0.004	0.012	0.016
Mo	$<4x10^{-4}$	$<4x10^{-4}$	0.036	0.120

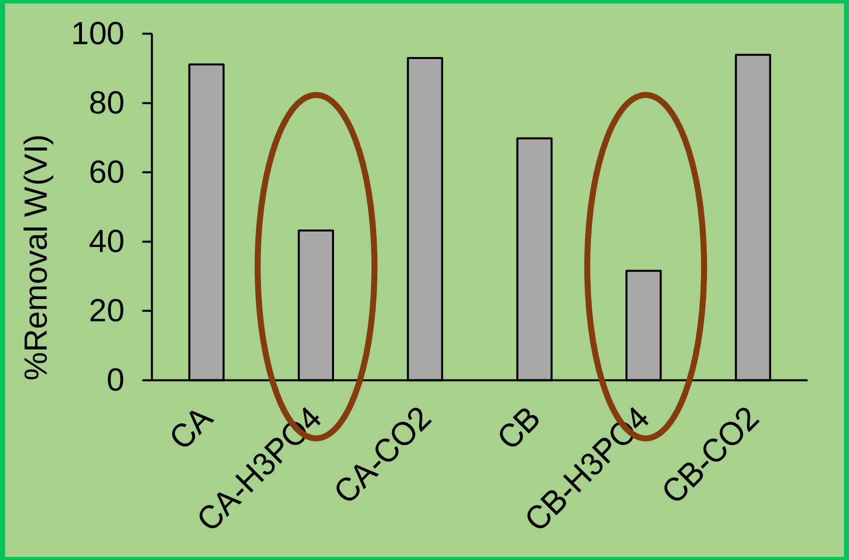
RESULTS

Adsorption assays

Removal of Pb(II) at pH of 5



Removal of W(VI) at pH of 2

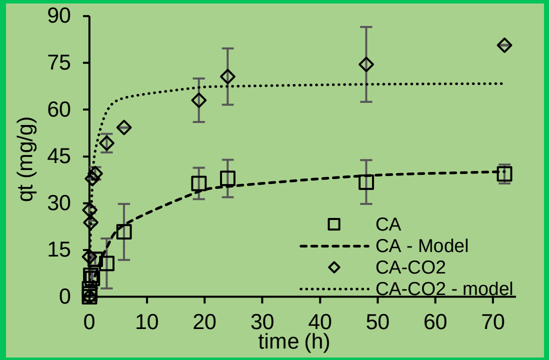


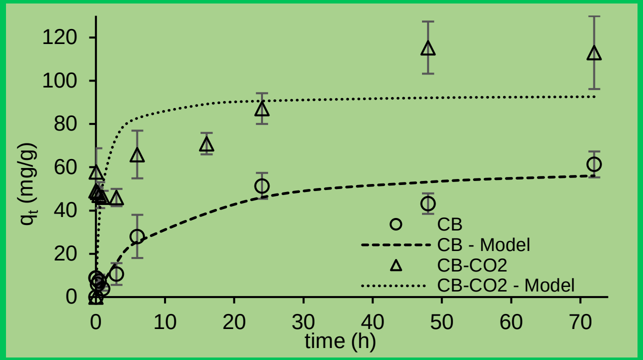
- Higher removals of Pb(II) and W(VI) ions were obtained for initial pH values of 5 and 2, respectively
- Cation exchange – presumable mechanism of Pb(II) ion removal
- Electrostatic attraction – W (VI) oxyanions removal

RESULTS

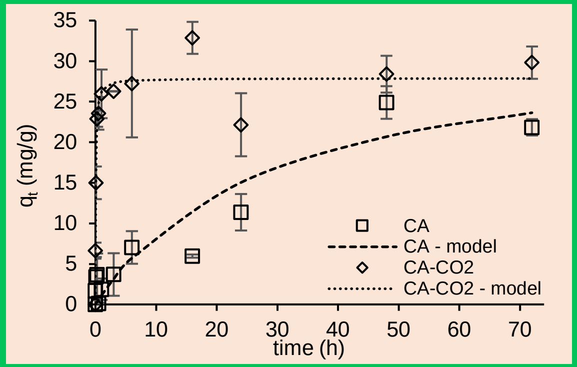
Kinetic assays

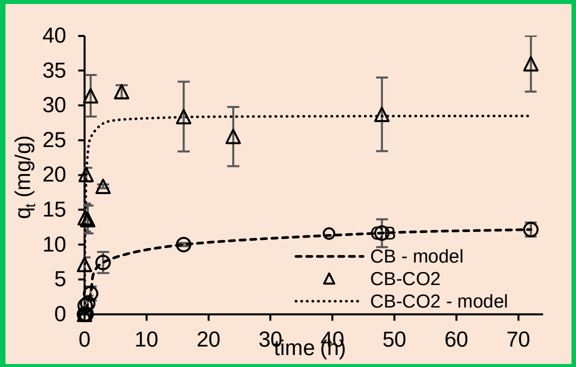
Kinetic data of Pb(II) ions adsorption adjusted to pseudo 2nd order kinetic model





Kinetic data of W(VI) ions adsorption adjusted to pseudo 2nd order kinetic model





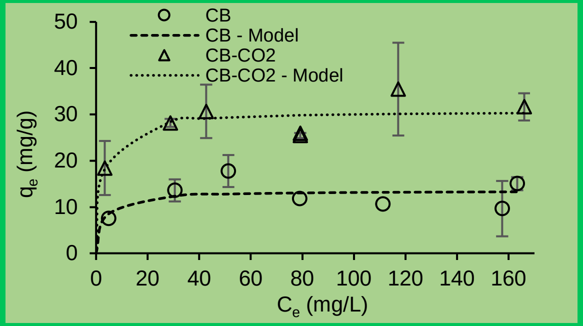
	Pb(II)			W(VI)		
	q_e (mg/g)	k_2 (g/mg.min)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2
CA	43.0	0.004	0.967	33.1	0.001	0.932
CA-CO2	68.8	0.031	0.897	27.9	0.548	0.937
CB	62.9	0.002	0.934	12.4	0.03	0.986
CB-CO2	93.6	0.013	0.603	28.6	0.286	0.776

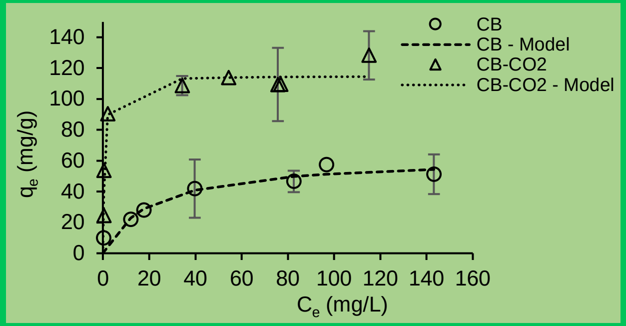
- Equilibrium time – 48 h
- Samples from CO_2 activation – higher uptake capacities and kinetic constants
- CO_2 activated carbon richer in exchangeable cations

RESULTS

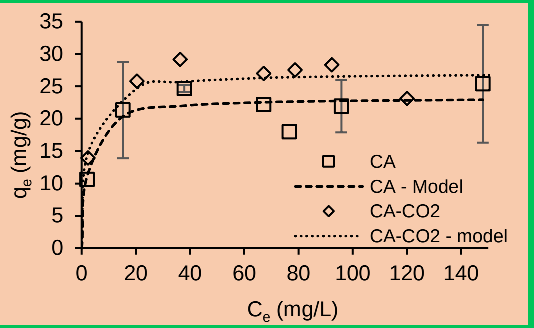
Equilibrium assays – adsorption isotherms

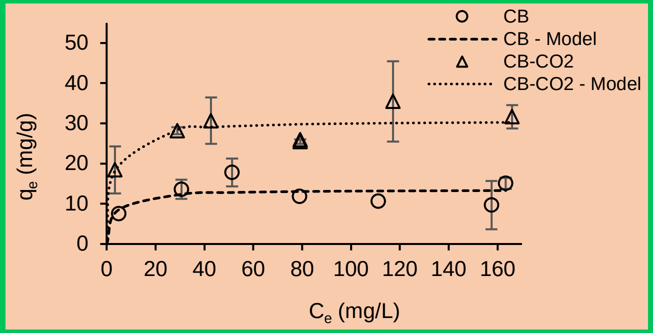
Pb(II) adsorption isotherms adjusted to Langmuir model





W(VI) adsorption isotherms adjusted to Langmuir model





		Pb(II)				W(VI)			
		CA	CA-CO2	CB	CB-CO2	CA	CA-CO2	CB	CB-CO2
Langmuir	q_m (mg/g)	39.1	103	62.1	116	23.3	27.1	13.5	30.7
	K_L (L/mg)	1.31	2.06	0.049	1.77	0.461	0.508	0.346	0.430
	R^2	0.978	0.899	0.961	0.955	0.930	0.936	0.749	0.921
Freundlich	K_F (mg/g)(mg/L)^n	21.3	52.8	12.4	60.5	12.4	16.7	9.10	16.9
	n (dimensionless)	7.46	5.71	3.26	6.41	7.35	9.26	13.3	7.81
	R^2	0.911	0.821	0.959	0.915	0.884	0.855	0.689	0.921

- Best fitting model – Langmuir – monolayer adsorption
- Samples from CO_2 activation – higher maximum uptake capacities and Langmuir constants

CONCLUSIONS

H_3PO_4 activated chars:

- Lower surface areas than the raw chars
- Acidic surface chemistry affected their performance
- Low content of exchangeable cations

- **CO_2 activated chars:**
- Increased surface areas
- Increased mineral content
- High content of exchangeable cations
- Higher uptake capacities for both Pb(II) and W(VI) ions

Valorisation of spent tire rubber through pyrolysis and activation of the obtained chars - viable alternative to obtain efficient adsorbents of critical metallic elements.

Valorisation of spent tire rubber as carbon adsorbents for Pb(II) and W(VI) recovery in the framework of a circular economy

THANK YOU

24 June 2021