Production of a paper mill sludge-based activated carbon and application in the removal of pharmaceuticals from water

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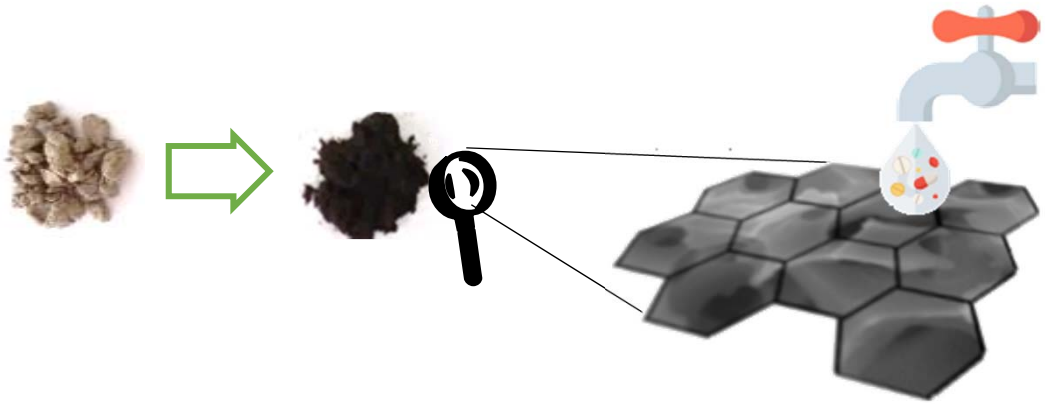

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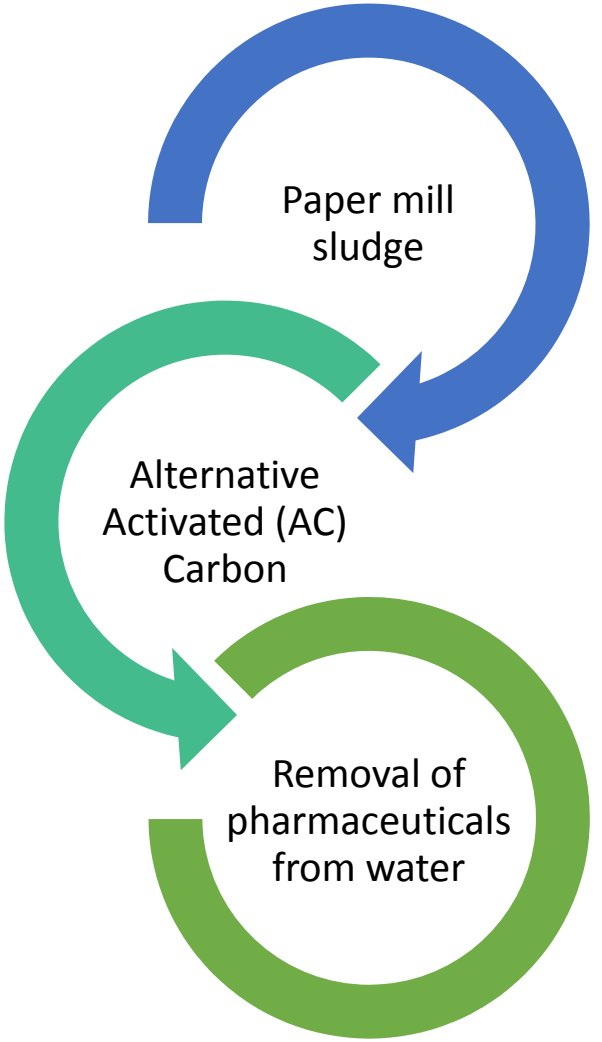
21 – 24 June, ATHENS 2017

CONTEXTUALIZATION

ENVIRONMENTAL CHALLENGES

- Industrial waste management

- Contamination of water systems by pharmaceuticals



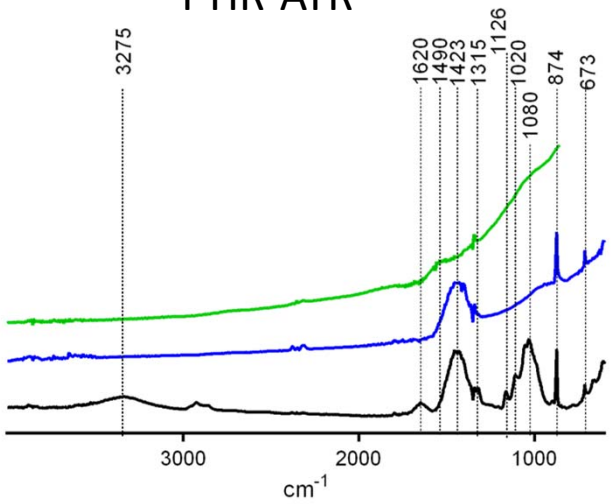
CIRCULAR ECONOMY

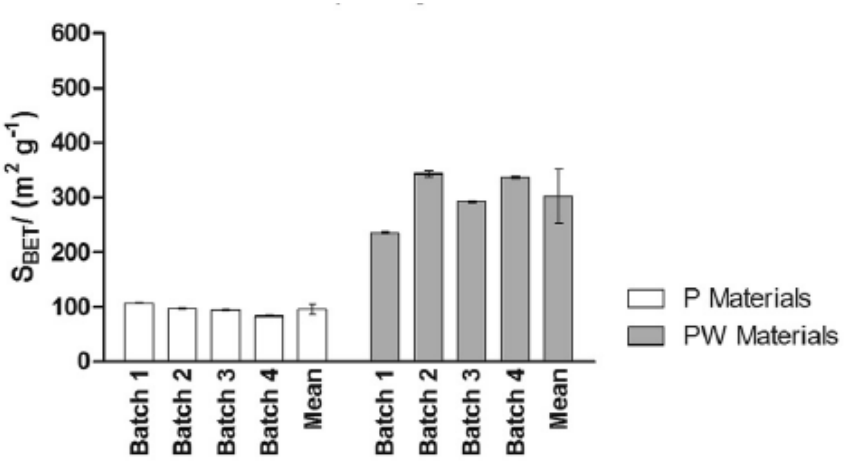
PRODUCTION OF CARBON-BASED ADSORBENTS (ACS)

Primary paper mill sludge

Dried at room temperature
Dried in the oven at 105°C for 24h
Pyrolysis and acid wash

FTIR-ATR





CHEMICAL ACTIVATION

G. Jaria, C. P. Silva, C. I. Ferreira, M. Otero and V. Calisto, *J Environ Manage*, 2017, **188**, 203-211.

V. Calisto, C. I. Ferreira, J. A. Oliveira, M. Otero and V. I. Esteves, *J Environ Manage*, 2015, **152**, 83-90.

PRODUCTION OF ACTIVATED CARBONS (ACs)
Full Factorial Design

Full Factorial Design (FFD) applied to the production of alternative ACs

- Dried at room temperature
- Dried in the oven at 105°C for 24h
- Impregnation with the activating agent
- Pyrolysis and acid wash

→ **CHEMICAL ACTIVATION IN ONE STEP**

Full factorial design with
4 factors at 2 levels (16 experiments):

Variables	Levels	
	-1	+1
U1 – Pyrolysis temperature (°C)	650	800
U2 – Residence time (minutes)	60	150
U3 – Precursor:activating agent ratio	10:1	1:1
U4 – Activating agent	K_2CO_3	KOH

6 responses

- Yield of production (%)
- Carbamazepine (CBZ)
- Sulfamethoxazole (SMX)
- Paroxetine (PAR)

Percentage of Adsorption %

- BET Surface Area (S_{BET}) ($m^2\ g^{-1}$)
- Total Organic Carbon (TOC) (%)

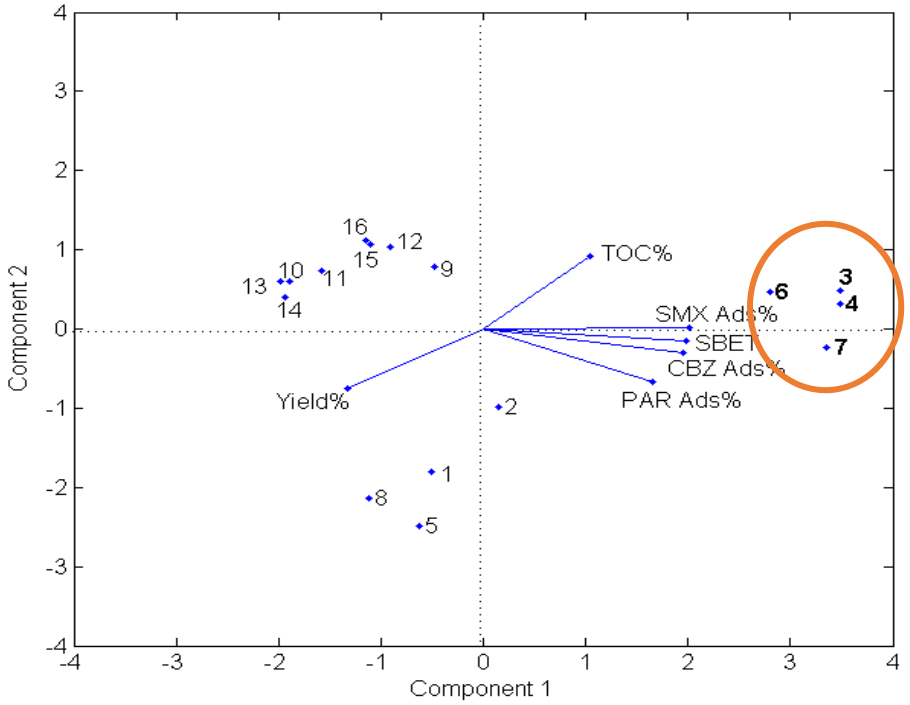
PRODUCTION OF ACTIVATED CARBONS (ACs)
Full Factorial Design

	Variables				Responses					
AC	U1	U2	U3	U4	Yield (%)	Ads (%) SMX (0.015 gL^{-1})	Ads (%) CBZ (0.015 gL^{-1})	Ads (%) PAR (0.015 gL^{-1})	BET surface area ($m^2 g^{-1}$)	TOC %
1	+1	+1	-1	-1	26.42	23.48	31.07	55.03	1017	42.47
2	+1	+1	-1	+1	23.54	31.55	42.09	57.98	923	52.11
3	+1	+1	+1	+1	2.73	70.93	80.50	80.98	1627	66.78
4	+1	-1	+1	+1	2.85	71.41	80.81	89.96	1531	66.16
5	+1	-1	-1	-1	30.88	24.69	32.97	86.23	630	41.31
6	+1	-1	+1	-1	3.68	79.62	58.77	70.49	1389	62.75
7	+1	+1	+1	-1	3.38	74.66	84.68	83.58	1583	59.08
8	+1	-1	-1	+1	29.96	18.57	33.69	54.43	637	39.71
9	-1	+1	+1	-1	5.21	23.28	14.09	20.21	766	53.64
10	-1	-1	-1	+1	23.69	13.17	3.51	9.19	200	58.06
11	-1	+1	-1	+1	21.61	14.20	6.41	9.03	372	59.02
12	-1	+1	+1	+1	5.71	20.94	9.17	15.56	473	54.83
13	-1	+1	-1	-1	22.61	8.30	4.82	4.52	244	56.77
14	-1	-1	-1	-1	27.52	13.08	6.52	7.75	244	58.00
15	-1	-1	+1	-1	7.76	16.10	5.20	7.86	573	55.18
16	-1	-1	+1	+1	6.96	15.59	6.47	6.00	523	54.93
Commercial ACs as reference										
Norit SAE Super (NSS)						55.73	30.21	38.24	996	80.94
Norit Hydrocarbon (HDC)						19.58	13.53	24.12	562	67.42
Chemviron Carbon (PBFG4)						27.46	17.77	37.80	848	77.50

U1 – Pyrolysis temperature (650 ºC (-1) and 800 ºC (+1))
U2 – Residence time (60(-1) or 150 (+1) minutes)
U3 – Precursor:activating agent ratio (10:1 (-1) and 1:1(+1))
U4 – Activating agent (K_2CO_3 (-1) and KOH (+1))

PRODUCTION OF ACTIVATED CARBONS (ACs)
Full Factorial Design

PRINCIPAL COMPONENT ANALYSIS (PCA)



OPTIMIZATION RESULTS

Parameters	Responses					
	Yield (%)	Ads SMX (%)	Ads CBZ (%)	Ads PAR (%)	TOC (%)	BET (m^2 g^{-1})
Max	29.1	75.8	82.7	83.1	64.5	1627.4
U1	800 °C	800 °C	800 °C	800 °C	800 °C	800 °C
U2	60	150	150	150	60	150
U3	10:1	1:1	1:1	1:1	1:1	1:1
U4				KOH		

PHYSICAL AND CHEMICAL CHARACTERIZATION

- BET SURFACE AREA
- TOTAL ORGANIC (TOC) AND INORGANIC CARBON (IC) CONTENT

16 ACs

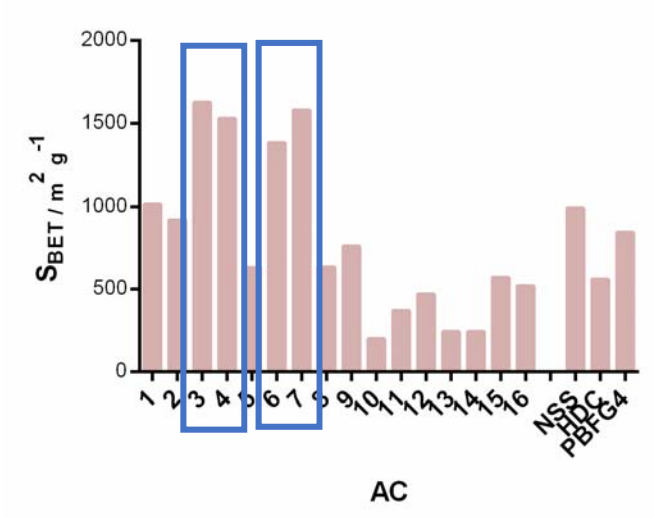
- ULTIMATE AND PROXIMATE ANALYSES
- POINT OF ZERO CHARGE (PZC)
- ACIDIC AND BASIC FUNCTIONAL GROUPS (BOEHM TITRATIONS)
- SCANNING ELECTRON MICROSCOPY (SEM)

ACs 3, 4, 6 and 7

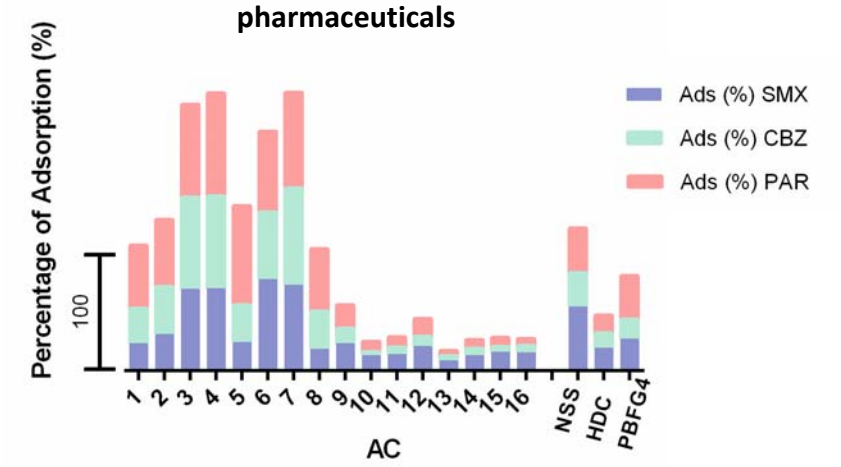
PHYSICAL AND CHEMICAL CHARACTERIZATION

BET SURFACE AREA (S_{BET}), TOTAL ORGANIC (TOC) AND INORGANIC (IC) CARBON

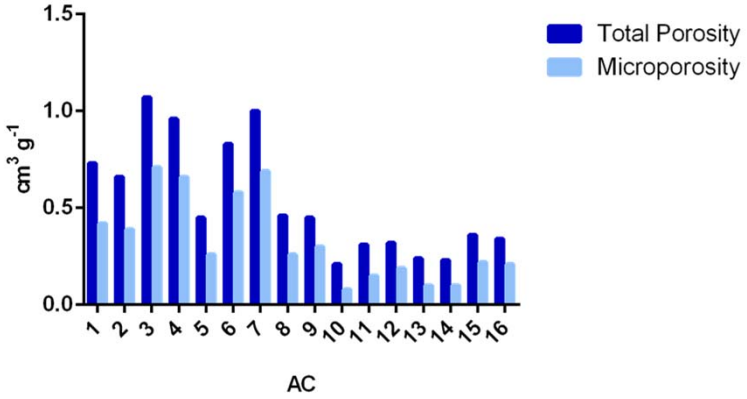
BET surface areas



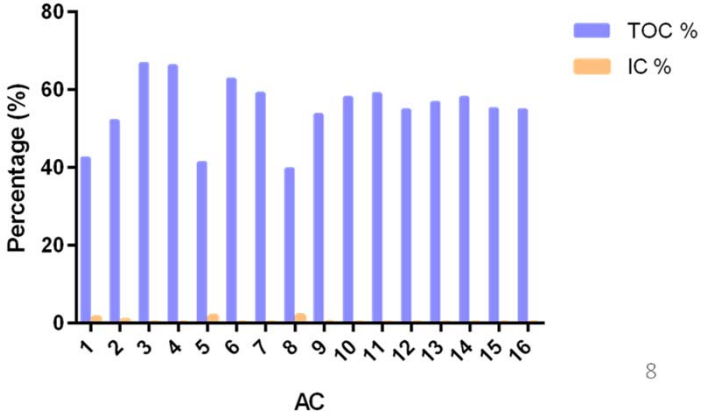
Percentages of adsorption for the 3 pharmaceuticals



Porosity

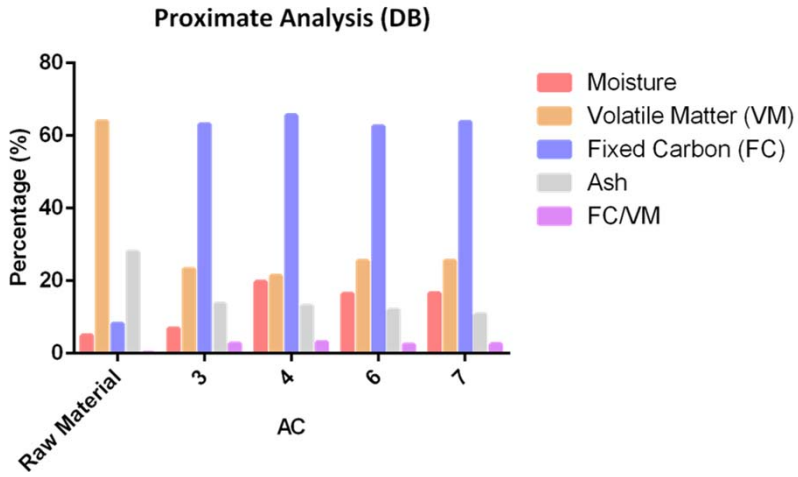


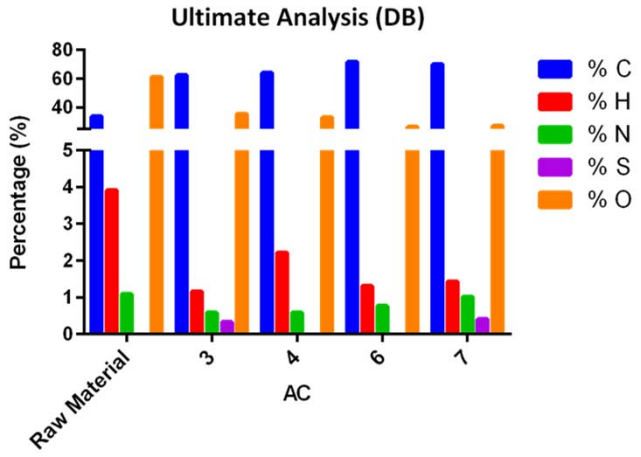
Total organic (TOC) and inorganic (IC)carbon



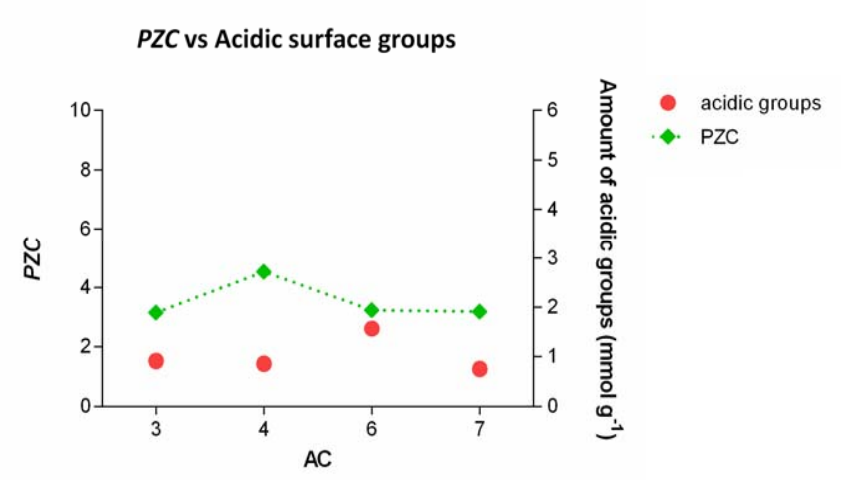
PHYSICAL AND CHEMICAL CHARACTERIZATION

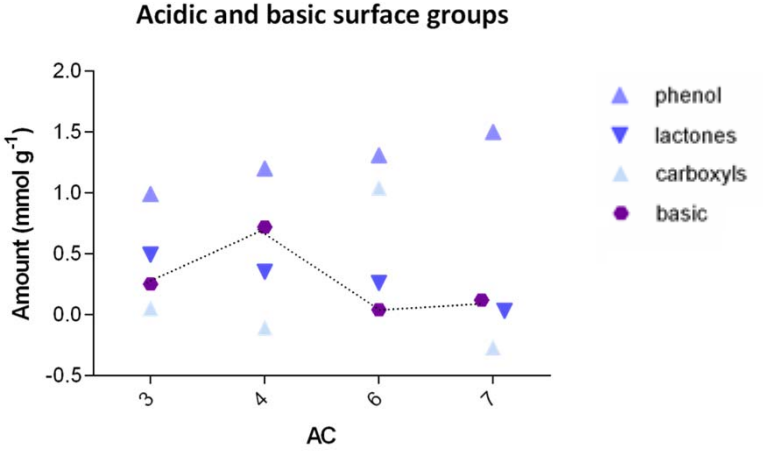
PROXIMATE AND ULTIMATE ANALYSES





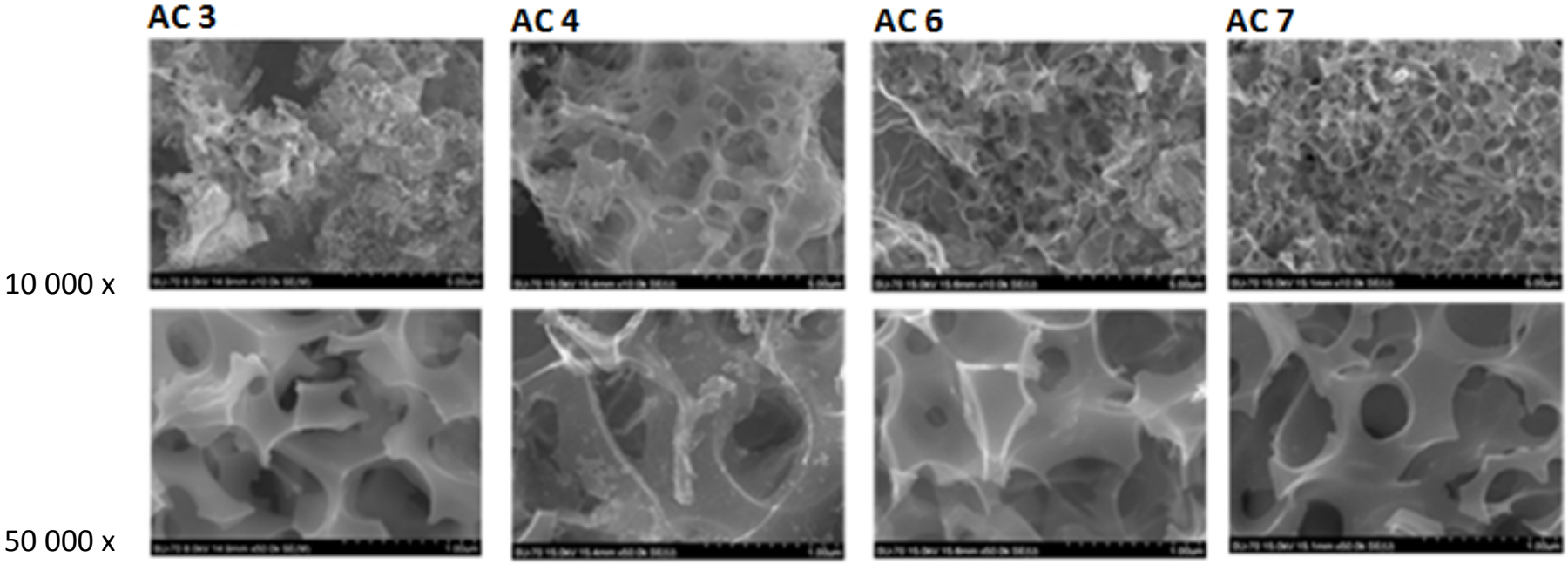
PZC AND BOEHM TITRATIONS





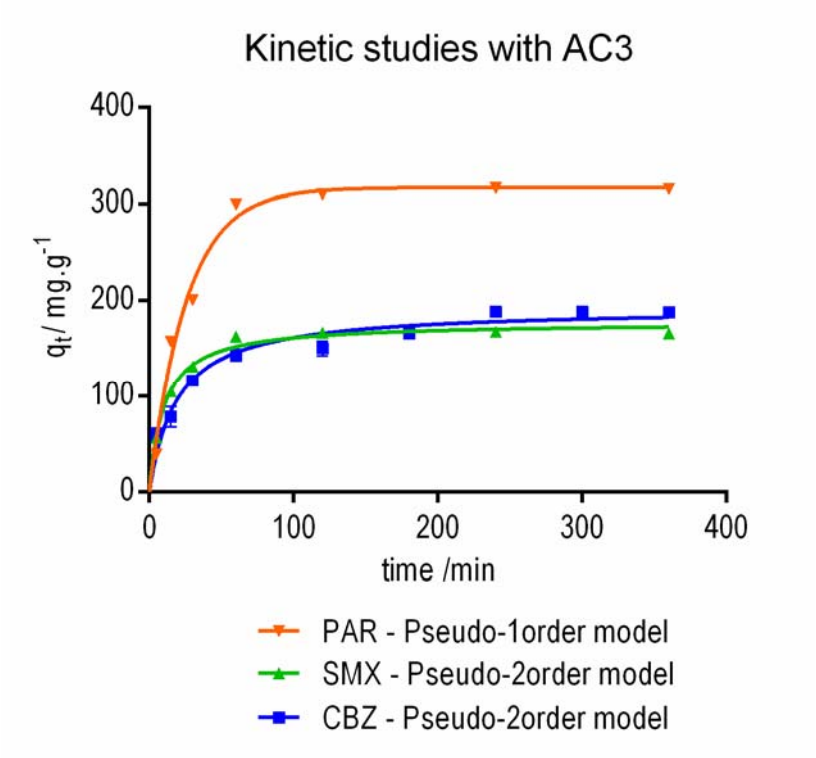
PHYSICAL AND CHEMICAL CHARACTERIZATION

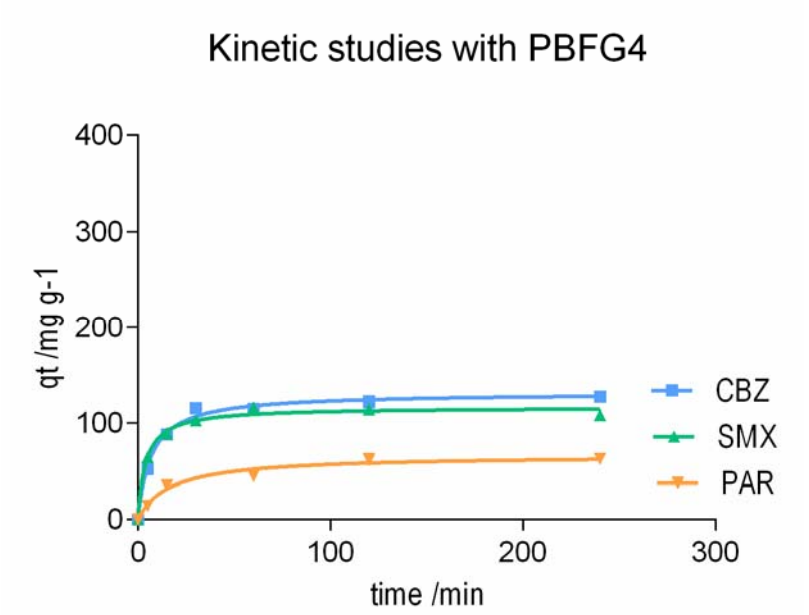
SCANNING ELECTRON MICROSCOPY (SEM)



ADSORPTION STUDIES – BATCH EXPERIMENTS

ADSORPTION OF CARBAMAZEPINE (CBZ), SULFAMETHOXAZOLE (SMX) AND PAROXETINE (PAR) BY AC3

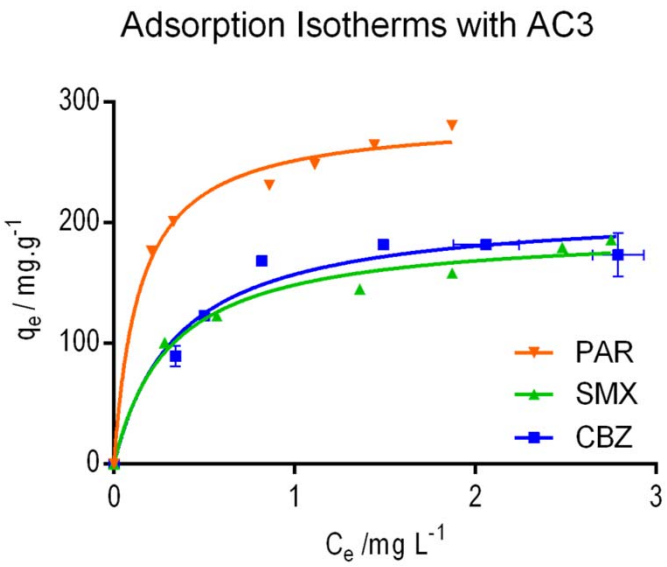


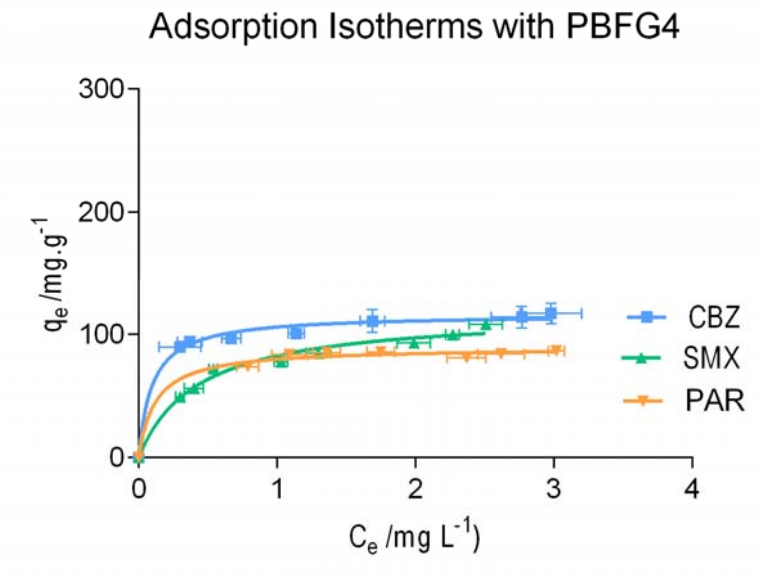


Pseudo-second order model

V. Calisto, C. I. Ferreira, J. A. Oliveira, M. Otero and V. I. Esteves, *J Environ Manage*, 2015, **152**, 83-90.

ADSORPTION STUDIES – BATCH EXPERIMENTS





Langmuir isotherm fitting – AC3			
Parameter	**CBZ**	**SMX**	**PAR**
q_m (mg g^{-1})	**212.4**	**194.5**	**287.3**
k_L (L mg^{-1})	2.854	3.277	7.032
R^2	0.9655	0.9794	0.9909

Langmuir isotherm fitting – PBFG4			
Parameter	**CBZ**	**SMX**	**PAR**
q_m (mg g^{-1})	**116.4**	**118.1**	**89.50**
k_L (L mg^{-1})	2.786	2.339	8.288
R^2	0.9906	0.9819	0.9907

V. Calisto, C. I. Ferreira, J. A. Oliveira, M. Otero and V. I. Esteves, *J Environ Manage*, 2015, **152**, 83-90.

CONCLUSIONS AND FUTURE WORK

Conclusions:

- Best conditions obtained by FFD: 800 ^{o}C/150 min/1:1/KOH (AC3)
- The best activated carbons presented a high BET surface area with values around 1500 m^2 g^{-1} (ACs 3, 4, 6 and 7)
- ACs 3, 4, 6, and 7 presented very good adsorption percentages and AC3 high adsorption capacities for CBZ, SMX, and PAR
- The low yield in the production of these ACs may be a practical limitation

Future work:

- Use microwave heating to enhance the production yield
- Production of a granular AC (GAC) for fixed-bed utilization (scale-up)

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