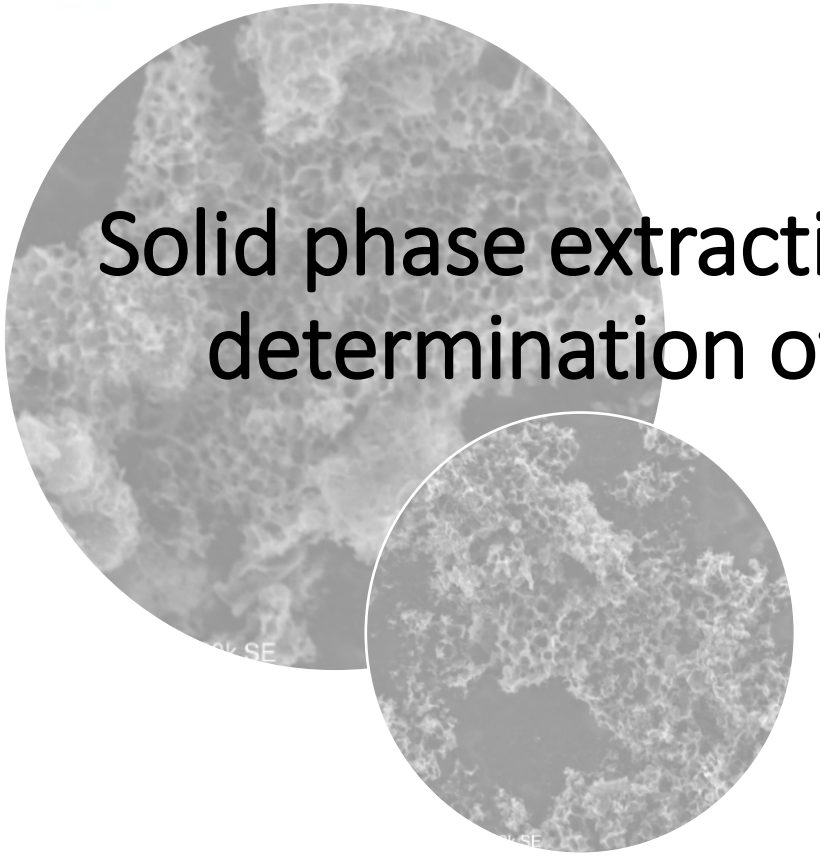
4th INTERNATIONAL CONFERENCE ON RISK ASSESSMENT OF PHARMACEUTICALS IN THE ENVIRONMENT

Barcelona, 9 - 10 October 2023



Solid phase extraction using waste-based sorbents for the determination of pharmaceuticals in water matrices

Diana Lima, Alexandr Stratulat, Érika Sousa, Vânia Calisto

diana.lima@ua.pt;
diana.lima@estesc.ipc.pt

CESAM CENTRE FOR ENVIRONMENTAL AND MARINE STUDIES

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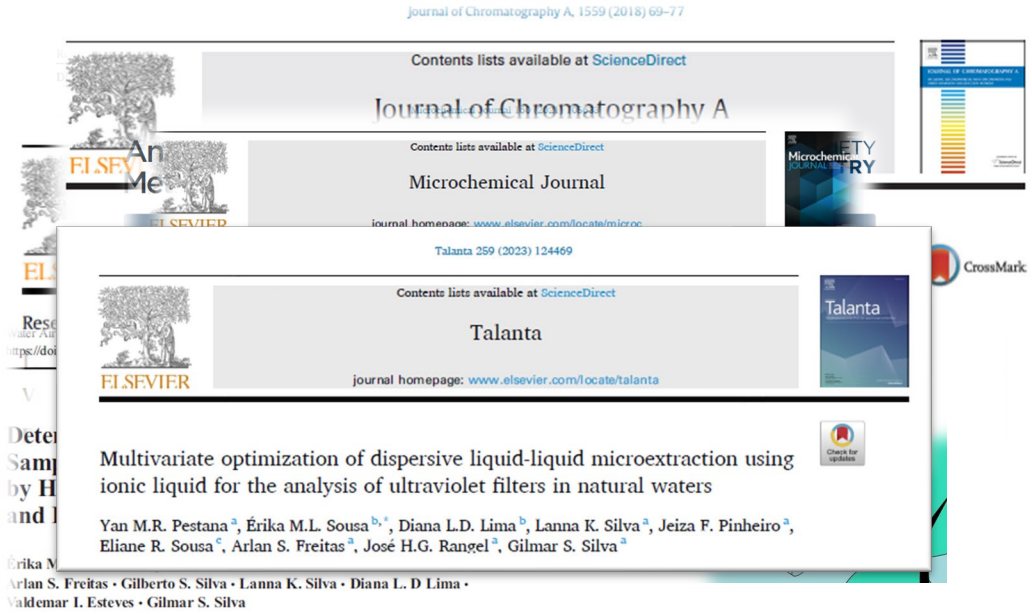
Research area 1

Development **of alternative and low-cost methodologies for pharmaceuticals determination in aquatic environment**



Research area 2

Development of **waste-based carbon materials** to be applied as advanced wastewater treatments, for the removal of pharmaceuticals from wastewater

Solid phase extraction using waste-based sorbents for the determination of pharmaceuticals in water matrices

*Stratulat, A.; Sousa, E.M.L.; Calisto; V.; Lima, D.L.D.; Microchemical Journal 188 (2023)108465

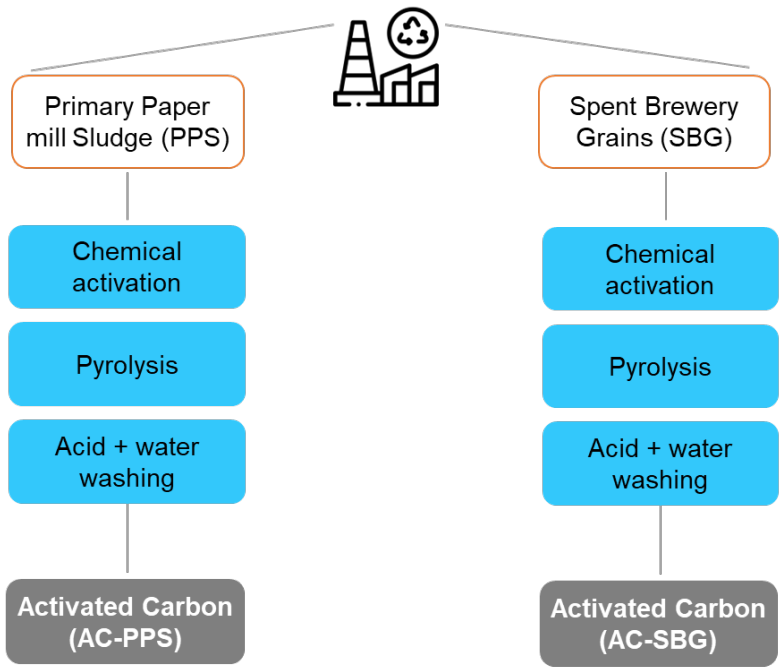
Aims of this Work

- Applying waste-based sorbents developed in our laboratory as an alternative to commercially available and costly sorbents.
- Evaluating their extraction capacity for two highly used pharmaceuticals, carbamazepine (CBZ) and sulfamethoxazole SMX.
- Evaluating several factors that affect the extraction capacity: type and amount of sorbent, elution conditions, sample volume.
- Evaluate water sample matrix effects on the extraction procedure.

METHODOLOGY:

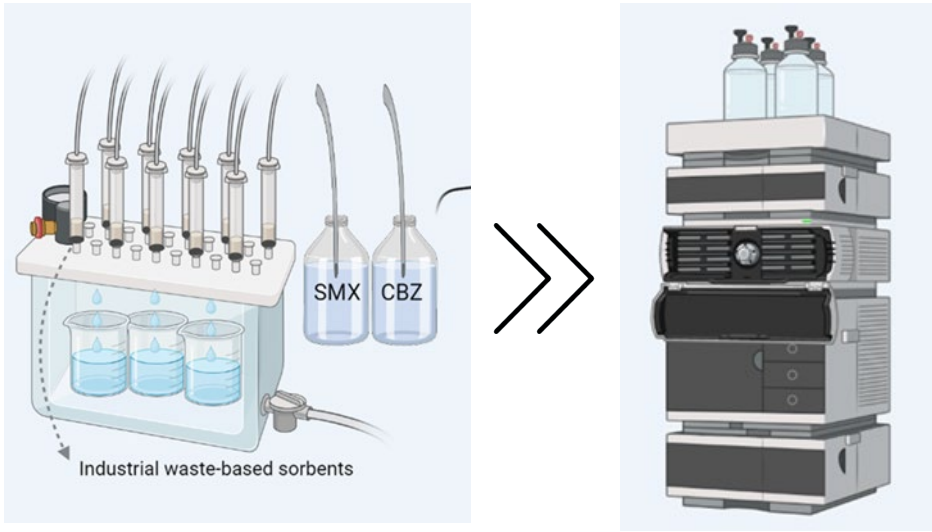
1. Waste-based sorbents production

Two agro-industrial residues



Scheme 1. Production of waste-based sorbents

2. Solid phase extraction (SPE) and chromatographic analysis



Scheme 2. Solid phase extraction and chromatographic analysis

Evaluation of several factors:

- type and amount of sorbent
- elution conditions
- sample volume

RESULTS:

1. Chemical and textural characterization of the sorbents

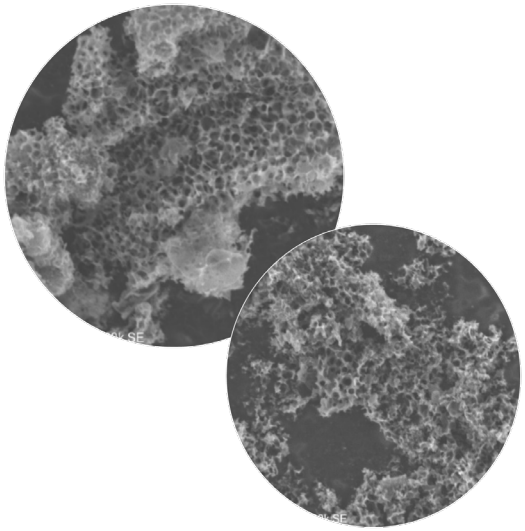


Figure 1. Scanning electron microscopy images of waste-based sorbents produced and used as sorbents in solid phase extraction at magnifications of 3000 x

Table 1. Specific surface area and pore morphology for AC-PPS and AC-SBG

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	DR W_0 (cm^3/g)	DR L (nm)	D (nm)
AC-PPS	1363	0.93	0.54	1.95	1.36
AC-SBG	1274	0.73	0.51	1.79	1.14

S_{BET}: Specific surface area; V_p: Total pore volume; DR: Dubinin-Radushkevich; D: Average pore diameter; W_0: Total micropore volume; L: Average micropore width; AC-PPS: Primary papermill sludge derived activated carbon; AC-SBG: Spent brewery grains derived activated carbon.

Two microporous materials were obtained with remarkably **similar properties** in what concerns average pore diameter (D), average micropore width (L) and total pore volume (V_p)

The point of zero charge (PZC)

AC-PPS ~ 6.1

AC-SBG ~ 5.4

RESULTS:

2. Evaluation of the pre-concentration procedure

2.1. Type and amount of sorbent

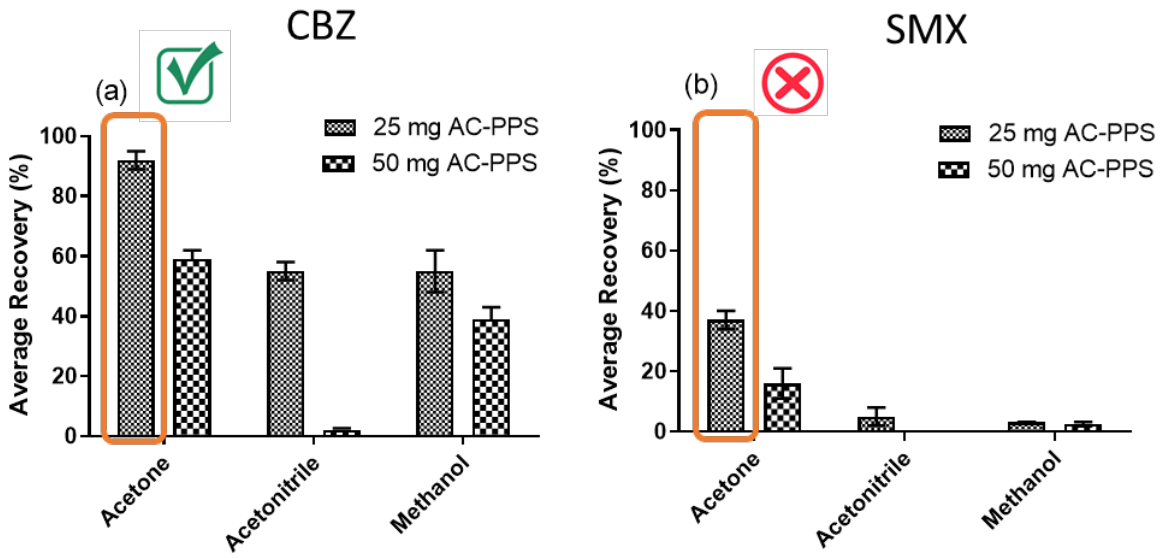


Figure 2. Extraction recovery for (a) carbamazepine (1000 µg/L) and (b) sulfamethoxazole (100 µg/L), using different mass of AC-PPS and different eluents (n=3). Volume of eluent used: 5 + 5 mL and 10 min of contact time. Volume of standards loaded: 100 mL.

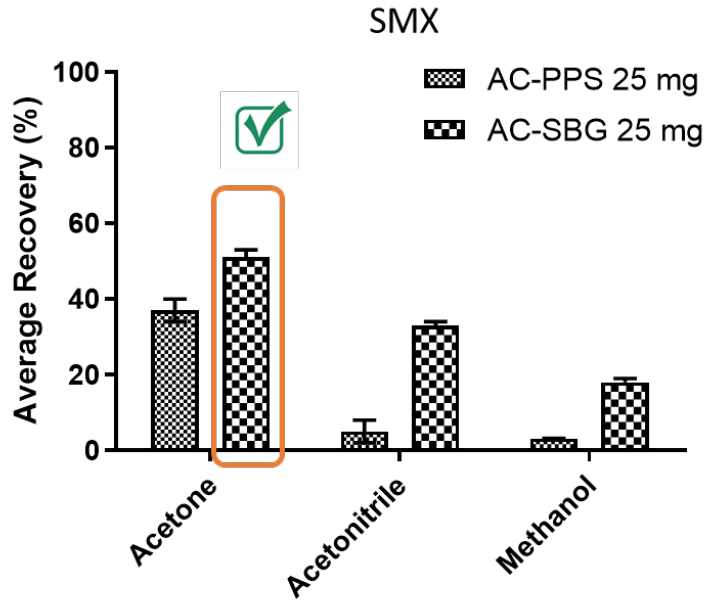


Figure 3. Extraction recovery for sulfamethoxazole (100 µg/L), using different mass of AC-SBG and different eluents (n=3). Volume of eluent used: 5 + 5 mL and 10 min of contact time. Volume of standards loaded: 100 mL.

RESULTS:

2. Evaluation of the pre-concentration procedure

2.2. Elution Conditions

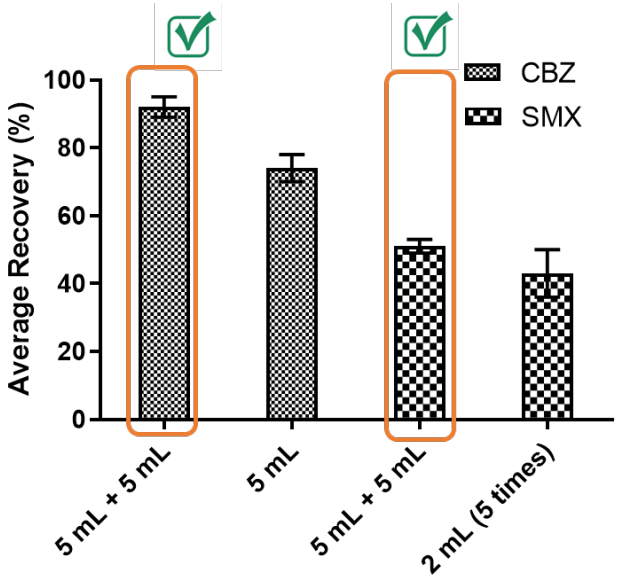


Figure 4. Eluent volume effect on the recovery of carbamazepine (CBZ) and sulfamethoxazole (SMX) using cartridges containing 25 mg of AC-PPS and 25 mg of AC-SBG, respectively (n=3). Eluent: Acetone; Contact time: 10 minutes

2.3. Sample Volume

Table 2. Recovery results obtained for carbamazepine (CBZ) and sulfamethoxazole (SMX) using different sample volumes and different concentrations (n=3).

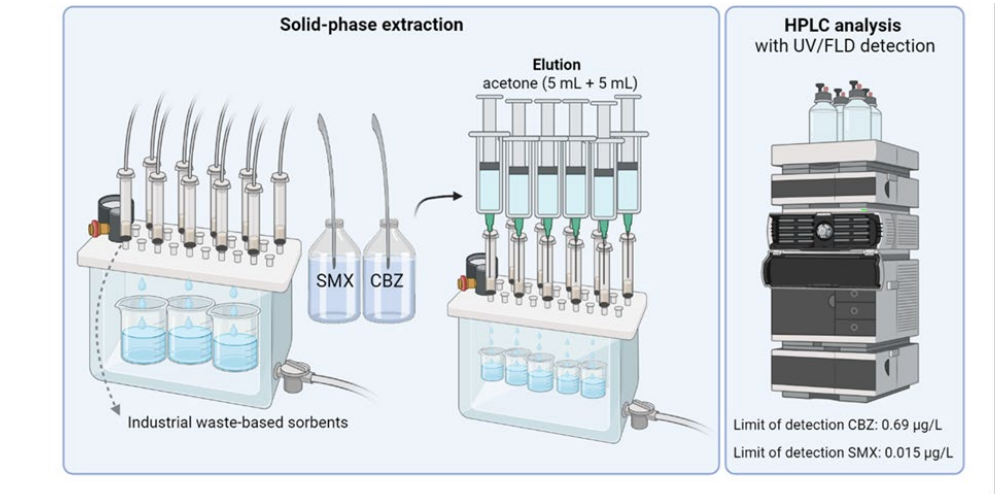
		Sample Volume = 1 L		Sample Volume = 100 mL	
	Concentration (µg/L)	Loaded mass (µg)	Recovery rate (%)	Loaded mass (µg)	Recovery rate (%)
CBZ	1000	1000	65 ± 5	100	92 ± 1
	100	100	90 ± 1	n.d.	n.d.
SMX	100	100	51 ± 3	10	51 ± 2
	10	10	47 ± 5	n.d.	n.d.

Results indicated that a volume of 1 L can be used maintaining high recoveries for a loaded mass lower than 100 µg.

RESULTS:

3. Evaluation of the SPE-HPLC optimized method

3.1. Analytical performance



Scheme 2. Solid phase extraction and chromatographic analysis

Conditions for the calibration curves:

- 25 mg of sorbent (AC-PPS for CBZ and AC-SBG for SMX)
- **Conditioning** with 10 mL of H_2O
- **Loading:** Standards/Samples (1 L) in triplicate
- **Elution with acetone** (2 x 5 mL, each fraction ketp inside the cartridge for 10 min)
- Analysis by HPLC

RESULTS:

3. Evaluation of the SPE-HPLC optimized method

3.1. Analytical performance

Table 3. Quantitative parameters for analytical curves obtained by SPE–HPLC.

Analyte	Linear range (µg/L)	Correlation Coefficient (*r*)	Linearity (%)	Limit of detection (µg/L)	Extraction Recovery (%)	Enrichment factor[c]
CBZ	1-10	0.9768	95.5	0.69		
	10-250	0.9988	99.1	3.5	90 ± 1[a]	90 ± 1
SMX	0.05-1	0.9999	99.1	0.015		
	0.1-25	0.9995	97.4	0.94	47 ± 5[b]	47 ± 5

[a]Values obtained for a 100 µg/L concentration (n=3).
[b]Values obtained for a 10 µg/L concentration (n=3)
[c]Mean value ± standard deviation (n=3).

RESULTS:

3. Evaluation of the SPE-HPLC optimized method

3.2. Matrix effects

Table 4. Average recoveries of carbamazepine (CBZ) and sulfamethoxazole (SMX) in river and effluent water solutions of 1 L with different levels of spike with the pharmaceutical (n=3)

Analyte	Level of spike (µg/L)	Recovery in river water (%)	Recovery in effluent water (%)
CBZ	10[a]	71 ± 6	45 ± 10
	100[b]	81 ± 3	20 ± 0
	250[b]	85 ± 4	12 ± 4
SMX	1[c]	92 ± 3	19 ± 1
	10[d]	99 ± 9	14 ± 2
	25[d]	115 ± 3	6 ± 2

[a]Calculated using the calibration curve with concentrations ranging from 1-10 µg/L; [b]Calculated using the calibration curve with concentrations ranging from 10-250 µg/L; [c]Calculated using the calibration curve with concentrations ranging from 0.05-1 µg/L; [d]Calculated using the calibration curve with concentrations ranging from 0.1-25 µg/L.

CONCLUSIONS

- Two microporous carbonaceous sorbents, derived from waste materials (SBG and PPS) were successfully produced through chemical activation and pyrolysis
- Using 25 mg of the AC-PPS for CBZ and 25 mg of the AC-SBG for SMX as SPE sorbent, recoveries of 92 ± 3 % for CBZ and 51 ± 2 % for SMX in ultrapure water were achieved under optimal conditions (elution using 5 mL + 5 mL of acetone and a contact time of 10 min)
- The SPE procedure coupled to HPLC allowed to reach a LOD of 0.69 µg/L for CBZ and of 0.015 µg/L for SMX
- Finally, the recovery efficiency in river water was maintained for both pharmaceuticals for a wide range of concentrations, however for wastewater it decreased significantly, due to pH implications for SMX, and high DOC values for both SMX and CBZ

CONCLUSIONS

A reliable pre-concentration and sample clean-up methodology based on the use of biomass-based sorbents was successfully developed and suitable for the analysis of the target pharmaceuticals in surface water samples

Thank you for your attention!!

diana.lima@ua.pt;
diana.lima@estesc.ipc.pt

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