

## Supplementary Information

### Study of alginate/polypyrrole hydrogels as potential extraction phase for determination of atrazine, caffeine, and progesterone in aqueous samples

#### Detailed description of the protocols for hybrid hydrogels formation

**Protocol 1.** First, a polypyrrole-alginate dispersion was formed using a previously described protocol [1]. Alginate was solubilized in water (2% m/v). After complete solubilization, 0.014 mol L<sup>-1</sup> of pyrrole was added, and the solution was kept under stirring for 30 min. Polymerization was carried out by adding 8 aliquots of 100 µL of APS 0.4 mol L<sup>-1</sup> at intervals of 10 minutes. The reaction was followed by UV-Vis spectroscopy (Agilent Cary 60 spectrophotometer) showing the characteristic absorption of PPy at 470 and 675 nm [2]. The resulting black dispersion was submitted to three washing steps, where the sample was centrifuged (30 min, 14500 rpm), and redispersed in ultra-pure water. The precipitate was dried in desiccator under reduced pressure and characterized by FTIR and transmission electron microscopy (Supplementary Material – Figs. S3 and S4). The Zeta potential (Stabino Control 2.00.23) of the purified PPy-ALG dispersion (2% m/V) was -75.8 mV.

PPy-ALG hydrogel disks were prepared by adding 1 mL of the polypyrrole-alginate dispersion into a 10 mL Becker. Then the crosslinker CaCl<sub>2</sub> solution was added in excess, forming the hydrogel, which was then removed from the Becker and washed with ultrapure water. PPy-ALG hydrogel beads were prepared using a 1.0 mL syringe filled with the PPy-ALG dispersion. The dispersion was dispensed into 5 mL of a 3% (m/v) CaCl<sub>2</sub> solution, at a rate of 0.8 mL min<sup>-1</sup>, under gentle stirring, using a home-made dispensing pump apparatus. The distance between the needle and the surface of the solution was 3.0 cm. The resulting beads had a diameter of approximately 0.5 cm. After the addition of the last drop, the beads were left in the solution for 120 min to ensure complete crosslinking. Then, they were collected by filtration with a nylon fabric and thoroughly rinsed with ultrapure water.

**Protocol 2.** In this protocol the hydrogel was prepared and then a layer of PPy formed. ALG@PPy disk were obtained by adding 1 mL of neat alginate solution into a 10 mL Becker, followed by the addition of CaCl<sub>2</sub> solution in excess. The alginate hydrogel disk

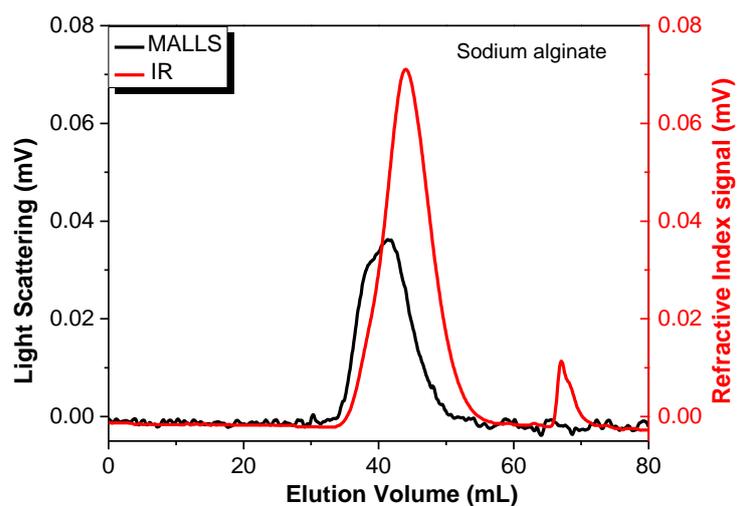
was dipped into a solution containing pyrrole (0.014 mol L<sup>-1</sup>) and the polymerization was induced by addition of APS (800 μL, 0.4 mol L<sup>-1</sup>) at 20°C. After 60 min, the ALG@PPy disk was filtrated and washed with ultrapure water. ALG@PPy beads were obtained by dispensing 1.0 mL of a 2% m/v alginate solution into a CaCl<sub>2</sub> solution (3% m/v) according to the same procedure previously described. The formed beads were left in the solution for additional 120 min. Then, the beads were collected from the solution by filtration and washed with ultrapure water. Neat alginate beads were added into the solution containing pyrrole (0.014 mol L<sup>-1</sup>) and the polymerization was induced by addition of APS (800 μL, 0.4 mol L<sup>-1</sup>) at 20°C. After 60 min, the ALG@PPy beads were filtrated and washed with ultrapure water.

### **Molar mass profile and homogeneity determination of sodium alginate**

HPSEC (high-performance size-exclusion chromatography) coupled with multidetector analyses were performed to determine the weight average molar mass  $\bar{M}_w$ , and polydispersity (PD =  $\bar{M}_w/\bar{M}_n$ ) of sodium alginate, on a Waters model 2410, equipped with four columns (Ultrahydrogel 2000, 500, 250, and 120, Milford, MA, USA) (**Fig. S1**). The columns were serially connected to a multidetector system, consisting of a Waters 2410 differential refractometer (RI) detector (Milford, MA, USA), and a DSP-F Wyatt Technology multiangle laser light scattering (MALLS) detector (Santa Barbara, CA, USA). A solution of NaNO<sub>2</sub> 0.1 mol L<sup>-1</sup> containing NaN<sub>3</sub> 0.5 g L<sup>-1</sup> was used as the eluent at a flow rate of 0.6 mL min<sup>-1</sup>. The sample was dispersed in the eluent at a concentration of 2.0 mg mL<sup>-1</sup>, and filtered (0.45 μm, cellulose acetate filters, Millipore). The experiments were conducted at 25°C. Before the analysis, the value of the refractive index increment  $dn/dc = 0.158 \text{ cm}^3 \text{ g}^{-1}$  was determined, later used in the treatment of the results of the chromatographic analyses by HPSEC. Data were analyzed using ASTRA 4.70.07 software (Table 1).

Table S1 –HPSEC-MALLS information of sodium alginate.

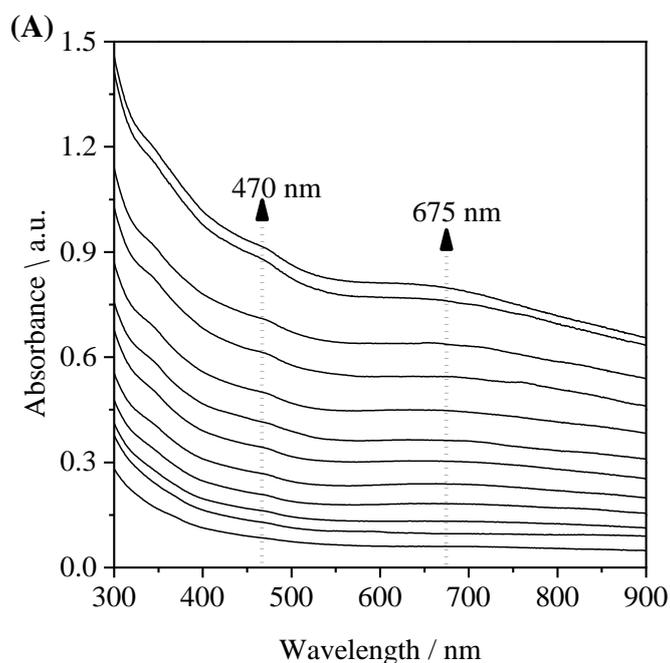
Sample	$\bar{M}_n$ (x10 <sup>4</sup> g mol <sup>-1</sup> )	$\bar{M}_w$ (x10 <sup>4</sup> g mol <sup>-1</sup> )	PD = $\bar{M}_w/\bar{M}_n$	% Recovery
Alginate (2.0 mg mL <sup>-1</sup> )	3.009 (10%)	7.125 (6%)	2.36 ± 0.30	87.1



**Fig. S1.** HPSEC profiles of sodium alginate obtained from Sigma-Aldrich.

### UV-Vis characterization

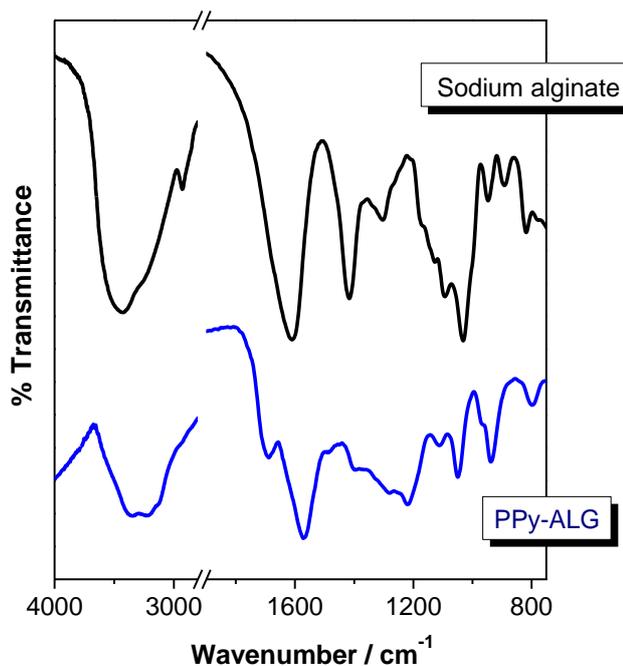
The pyrrole polymerization was accompanied by UV-Vis absorption spectroscopy (Agilent Cary 60 spectrophotometer) and revealed the presence of typical bands of polypyrrole.



**Fig. S2.** UV-Vis spectra for PPy-ALG dispersion synthesis. The oxidizing agent  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ;  $0.4 \text{ mol L}^{-1}$ ) was added to the alginate-pyrrole solution in aliquots of  $100 \mu\text{L}$  at intervals of 10 min for 120 min. The reaction was conducted at  $20^\circ\text{C}$ .

## FTIR characterization

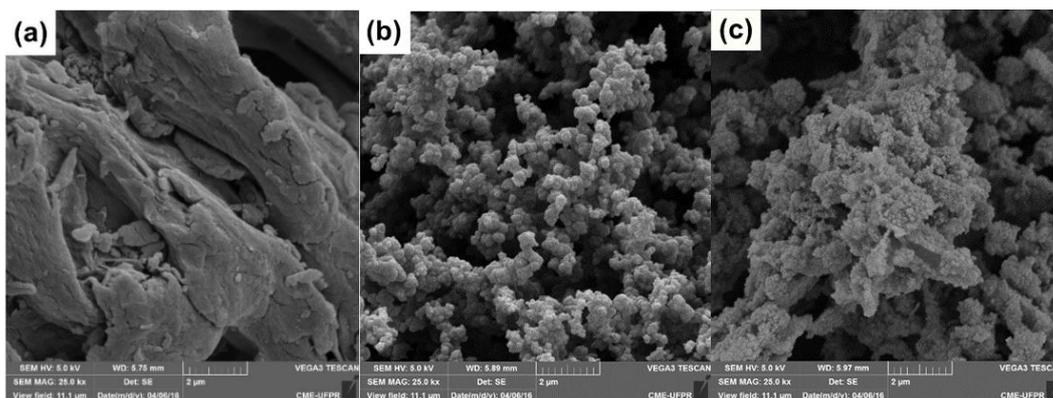
Fourier transform infrared spectroscopy (FTIR) was performed in a BioRad Excalibur model. Spectra were recorded between 4000-400  $\text{cm}^{-1}$ , in transmittance mode with a resolution of 4  $\text{cm}^{-1}$  using 32 scans. The samples were prepared in KBr pellets at a mass ratio of 9:1 (KBr:sample).



**Fig. S3.** FTIR spectrum of sodium alginate and PPy-ALG composite.

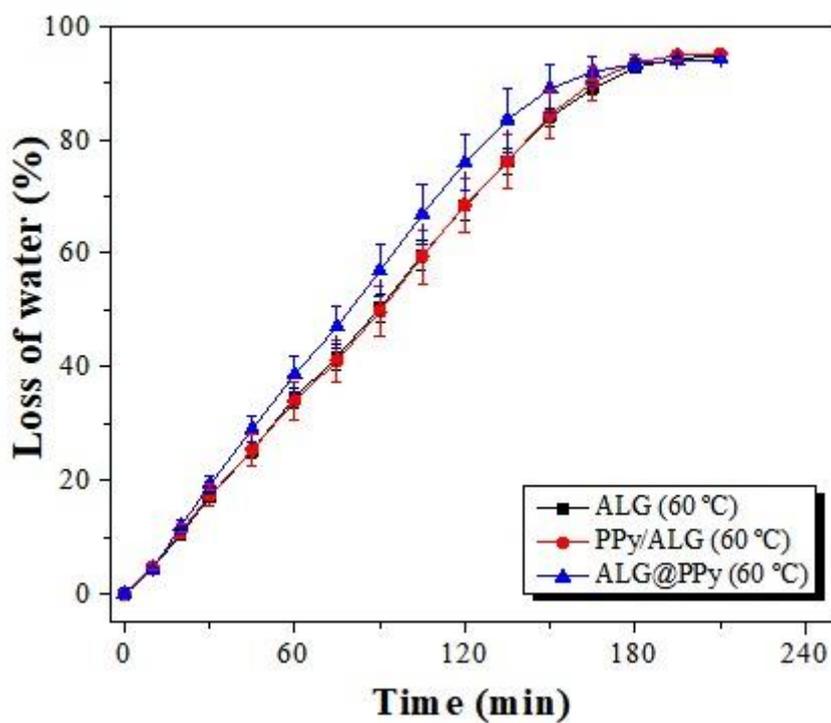
## SEM characterization

The samples were deposited on aluminum stubs and sputtered with gold on a Balzers Union-SCD 030 metallizer. SEM images were obtained using a Tescan Vega3LMU equipment, operating at 5 kV.



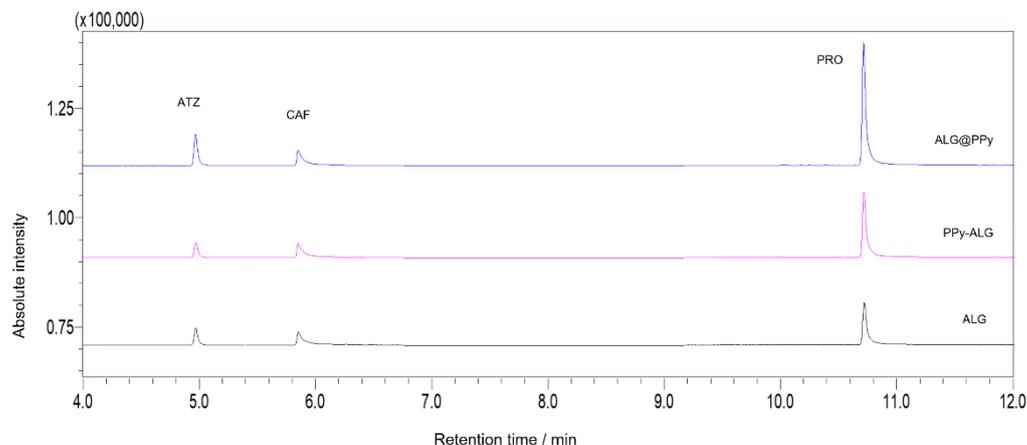
**Fig. S4.** Scanning electron microscopy images: a) neat ALG, b) neat PPy and c) PPy-ALG composite.

### Loss of water at 60°C



**Fig. S5.** Loss of water (in wt%) of ALG, PPy-ALG and ALG@PPy hydrogels at 60°C (replicates = 3).

## Chromatogram for extraction of ATZ, CAF and PRO



**Fig. S6.** Representative chromatogram showing peaks for ATZ, CAF and PRO for extraction performed with ALG, PPy-ALG and ALG@PPy beads in ultrapure water.

### References:

1. Lopes, L.C.; Simas-Tosin, F.F.; Cipriani, T.R.; Marchesi, L.F.; Vidotti, M.; Riegel-Vidotti, I.C. Effect of Low and High Methoxyl Citrus Pectin on the Properties of Polypyrrole Based Electroactive Hydrogels. *Carbohydr Polym* **2017**, *155*, 11–18, doi:10.1016/j.carbpol.2016.08.050.
2. Tavoli, F.; Alizadeh, N. In Situ UV-Vis Spectroelectrochemical Study of Dye Doped Nanostructure Polypyrrole as Electrochromic Film. *Journal of Electroanalytical Chemistry* **2014**, *720–721*, 128–133, doi:10.1016/j.jelechem.2014.03.022.