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Alginate/Polypyrrole Hydrogels as Potential Extraction Phase for Determination of Atrazine, Caffeine, and Progesterone in Aqueous Samples

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Featured Application: Application of the hydrogel beads as extraction phases for determination of atrazine, caffeine, and progesterone.

Abstract: Hydrogels are smart-swelling 3D structures capable of incorporating/expelling water while maintaining their structures. When combined with electroactive materials, such as conducting polymers, the resulting composite may present tunable properties. Herein, the preparation and characterization of alginate-polypyrrole composite hydrogels is described using chemical polymerization to form polypyrrole inside and around alginate beads, employing two simple protocols. These materials were qualitatively tested as extraction phases, using the solid-phase extraction technique, for the pre-concentration of contaminants of emerging concern (atrazine, caffeine, and progesterone). Compared to alginate alone, the composite materials showed a modified extraction capacity, especially for the extraction of progesterone. It was shown that the alginate matrix also contributes to the extraction, not only acting as a support but also as an active extraction media, evidencing a good combination of materials.

Keywords: composite; hybrid; hydrogel; conducting polymers; solid phase extraction; contaminants of emerging concern; beads

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1. Introduction

Hydrogels are crosslinked hydrophilic polymers that form three-dimensional swelling networks that absorb water while maintaining their structures [1,2]. The swelling behavior of hydrogels can be triggered by external stimuli [3], such as temperature [4], pH [5], and electric fields [6], which lead to a huge variety of applications, from biomedical applications, such as 3D-Scaffolds for tissue engineering [7,8], to technological applications, such as electrolyte materials in supercapacitors [9]. Recently, hydrogels have also been used as new extraction phases since they can simultaneously extract organic compounds with different polarities from aqueous matrices [10–12].

The properties of hydrogels can be improved through the formation of composites [11]. One interesting combination can be made using conducting polymers (CPs) and hydrophilic polymers. The resulting composite hydrogel can maintain the structural stability of regular hydrogels while including the electrical activity of CPs [13,14]. Previous studies have shown successful combinations of polypyrrole (PPy) with polysaccharides, such as xanthan/polypyrrole scaffolds for tissue engineering [15] and chitosan/polypyrrole as an anticorrosive coating [16]. Alginates are also excellent candidates for forming composite hydrogels for their easy gelling properties, resulting from the cooperative binding of divalent and trivalent cations to their structure.

Previous works showed good interaction between conducting polymers and alginate [9], with increased conductivity [17], allowing their use in highly sensitive amperometric glucose biosensors [18,19], and for endocrine-disrupting compound extraction from water samples [20], where polypyrrole not only improved the adsorption of the pollutants, but also the stability and dispersibility in aqueous media.

In this work, two simple synthetic approaches were presented to prepare alginate-polypyrrole-based hydrogels. In the first approach, the conducting polymer was prepared by the chemical synthesis of pyrrole in an alginate matrix, followed by gelation with $CaCl_2$. In the second approach, the alginate hydrogel was directly prepared by gelation with $CaCl_2$, and then the pyrrole was chemically polymerized around the pre-formed alginate hydrogel beads. In the first case, polymer particles were dispersed all over the hydrogel matrix, while in the second case, the polypyrrole was only present around the hydrogel matrix.

Both hydrogels were used for the extraction of contaminants of emerging concern (CECs), which are a class of compounds with diverse origins that have not been deeply studied in the past, and in many countries are still not fully monitored, despite presenting adverse effects both in the environment and in human health [21–23]. CECs include many different molecules with various physical chemical properties. Thus, in this work, three contaminants with different characteristics were used to test the hydrogels as extraction phases: progesterone, atrazine, and caffeine. These molecules were selected not only because they are classes of CECs but also because they have different polarities, solubilities, and pKa, working as model molecules for the extraction studies.

The SPE (solid phase extraction) technique was applied, since it is a popular technique for sample preparation and removal of matrix interferents. It allows rapid, selective, and reproducible sample preparation, providing the isolation, extraction, and concentration of the target analytes [24,25].

2. Materials and Methods

2.1. Materials

Commercial sodium alginate (Mw~71.250 g $mol^{-1} \pm 6\%$ and dispersity 2.4—Supplementary Material, Figure S1) was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used as received. Pyrrole was purchased from Sigma-Aldrich, distilled under low pressure, and stored at 4 °C before use. Atrazine, caffeine, and progesterone were purchased from Sigma-Aldrich (Darmstadt, Germany) with purity >98% and used as received. Sodium chloride, hydrochloric acid, and calcium chloride were purchased from Sigma-Aldrich and used as received. Ammonium persulfate (APS) was purchased from Merck and used as received. Methanol (J.T. Becker) and ethyl acetate (Mallinckrodt Chemicals) of HPLC grade were used for the extraction procedure and chromatographic analysis. All solutions and dispersions were prepared using ultrapure water (18.2 MΩ cm at 25 °C).

2.2. Preparation of the Alginate/Polypyrrole Hydrogels Disks and Beads

The alginate-polypyrrole hydrogels were prepared according to two different protocols. Protocol 1 was used to form polypyrrole particles dispersed throughout the alginate matrix, and then used to form hydrogel beads. Pyrrole (0.014 mol L^{-1}) was dispersed in a 2% (m/V) alginate solution, and 8 aliquots of 100 μL of APS 0.4 mol L^{-1} at intervals of 10 min were added to chemically polymerize the monomer. The polymerization reaction was accompanied by UV-Vis spectroscopy (Supplementary Material, Figure S2). The resulting dispersion was washed three times (30 min, 14,500 rpm). The hydrogel beads were prepared by dispensing 1 mL of polypyrrole-alginate dispersion into 5 mL of a 3% (m/V) $CaCl_2$ solution, with a syringe, at a rate of 0.8 mL min^{-1}, under gentle stirring, using a home-made dispensing pump apparatus. This hydrogel contains polypyrrole particles dispersed throughout the alginate matrix and was named PPy-ALG.

Protocol 2 began with the preparation of a neat alginate hydrogel (ALG) by direct contact with $CaCl_2$. The alginate hydrogel beads were formed by dispensing 1.0 mL of a 2% (m/V) alginate solution into a $CaCl_2$ solution (3% m/V) according to the same procedure previously described. The beads were washed with ultrapure water and subsequently dipped in a pyrrole solution (0.014 mol L^{-1}), and the chemical polymerization was induced by the addition of APS (8 aliquots of 100 µL, 0.4 mol L^{-1}) at 20 °C. After 60 min, the beads were filtrated and washed with ultrapure water. This hydrogel contains polypyrrole only surrounding the alginate bead and was named ALG@PPy.

For each protocol, the hydrogels were prepared in two morphologies: beads and disks. Disks were employed to characterize the properties of the hydrogels, and the beads were used for the extraction experiments. Pure alginate hydrogels were also prepared for comparison purposes. Both procedures are depicted in Figure 1a. More details about the two different morphologies are available in the Supplementary Material.

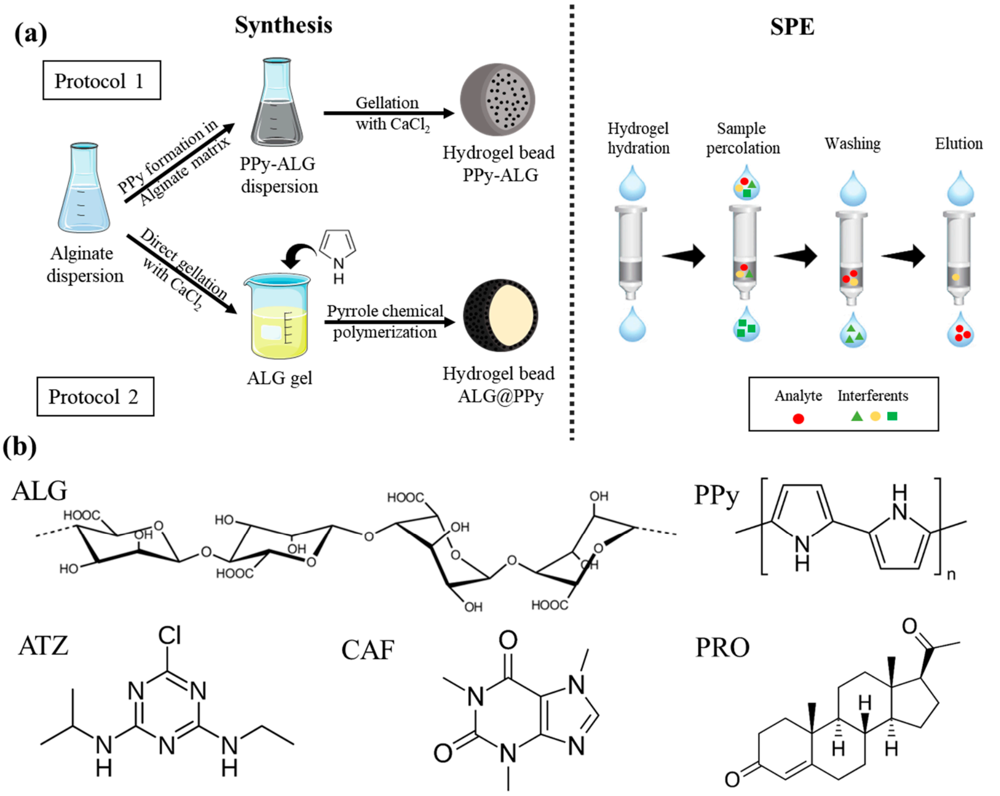

Figure 1. (**a**) Protocols for the formation of hydrogels modified with polypyrrole. In the first protocol, an alginate hydrogel containing polypyrrole particles is formed, while in the second protocol, alginate hydrogels are covered with a polypyrrole layer. All hydrogels were later applied as extraction phases in SPE (Solid Phase Extraction). (**b**) Structure of all chemicals used. ALG and PPy were used to form the hydrogels, and ATZ, CAF, and PRO were the CECs used to evaluate the extraction behavior of the composite.

2.3. Chemical, Physical Chemical, and Morphological Properties of Hydrogels

The dried hydrogel disks were characterized by attenuated total reflection in conjunction with infrared spectroscopy (ATR-FTIR) in a BRUKER Vertex 70 Infrared Spectrophotometer using a zinc selenide (ZnSe) crystal. Thermogravimetric analysis (TGA) was performed in a Netzsch, model STA 449 F3 Jupiter, employing N_2 as the purge gas, at a flow rate of 50 mL min^{-1}. The temperature was ramped from 25 to 900 °C at a heating rate of 10 °C min^{-1}.

The swelling index (SI) of the hydrogels (in wt%) was determined by the weight difference from the swollen hydrogel, left in ultrapure water, HCl 0.1 mol L^{-1} (pH 2.0) or NaCl 0.1 mol L^{-1} (pH 6.0) for 60 min, and the dried hydrogel. Water loss was evaluated by the difference between the previously swelled hydrogel (60 min in ultrapure water) and the dried hydrogel, at 60 °C.

The dried hydrogel beads were frozen in liquid nitrogen and fractured for SEM analysis. The samples were sputtered with a gold layer and observed in a TESCAN ©3 LMU equipment, operating at 5 kV.

2.4. Application of Hydrogel Beads as Extraction Phases for Determination of Atrazine, Caffeine, and Progesterone

The composite hydrogels were evaluated as the extraction phase for atrazine (ATZ), caffeine (CAF), and progesterone (PRO) (Figure 1b). For this, 0.5 g of each hydrogel was hydrated with 10 mL of ultrapure water. Then, 50 mL of the mixed analyte solution (0.5 mg L^{-1}) were percolated though the hydrogel beads in a Visiprep (Supelco®, Bellefonte, PA, USA) manifold system at a flow rate of 3 mL min^{-1}, for the Solid Phase Extraction (SPE) step. The system was connected to a vacuum pump (Prismatec®, Porto Alegre, Brazil) for drying and the analytes were desorbed from the beads by percolation of 5 mL of methanol. The extracts were dried and reconstituted in 1 mL of ethyl acetate and, finally, injected into the GC-MS system (GCMS2010 Plus (Shimadzu®, Kyoto, Tokyo) gas chromatograph coupled to a TQ8040 mass spectrometer with an AC5000 for determination of the analytes. Chromatographic separation was performed in an SH-Rtx-5MS column (30 m × 0.25 mm × 0.25 µm—Shimadzu®) with helium 5.0 as the carrier gas and a constant flow rate of 1.0 mL min^{-1}. The injection volume was 1 µL in split injection mode (1:10 ratio). Both injector and ion source temperatures were maintained at 250 °C. The transfer line temperature was 300 °C. The initial GC oven temperature was kept at 180 °C for 4 min, followed by an increase in 25 °C min^{-1} to 300 °C (4 min). The total analysis time was 13 min, and the mass spectrometer operated in single ion monitoring (SIM) mode with electron ionization at 70 eV. One quantification ion (for ATZ, m/z = 200, for CAF, m/z = 194, and for PRO, m/z = 124) and two confirmation ions (for ATZ, m/z = 173 and 215, for CAF, m/z = 109 and 193, and for PRO, m/z = 91 and 191) were employed for each analyte. GCMS solution software was used for data analysis.

3. Results and Discussion

ATR-FTIR spectra of ALG, PPy-ALG, and ALG@PPy hydrogels are shown in Figure 2a, where characteristic bands of alginate and polypyrrole were identified [26], indicating the successful formation of the composite.

The thermal stability of ALG, PPy-ALG, and ALG@PPy (Figure 2b) showed a loss of adsorbed water occurring up to 164 °C for all samples, but the weight loss of the composite hydrogels was smaller when compared to neat ALG. ALG and PPy-ALG showed degradation of the main alginate chains in the range from 164 °C to 420 °C, associated to the dehydration of ALG, fracture of glycosidic bonds, decarbonylation, and decarboxylation. The weight loss above 420 °C may be the result of an additional thermal degradation of previously formed residues [27–29]. ALG@PPy displayed the first loss of mass event at a lower temperature, possibly due to the higher content of polypyrrole on this sample's surface. It is expected that polypyrrole degrades around 290 °C and 750 °C [26].

The SEM images of the beads are in Figure 2c–e and indicate that neat alginate is homogeneous, whereas in the composite hydrogels, dispersed particles are observed. The morphology of the composite included the characteristics of both the neat alginate hydrogel and pure polypyrrole (Supplementary Material—Figure S4a and Figure S4b, respectively). In the PPy-ALG hydrogel, a homogeneous surface and randomly distributed polypyrrole nanoparticles are observed inside the ALG matrix, since the small structures formed inside the hydrogel, as observed in Figure 2d, can be attributed to polypyrrole (see Figure S4c). Conversely, in the ALG@PPy (Figure 2e), a rough surface and a shell of polypyrrole is observed, as expected from the protocol employed.

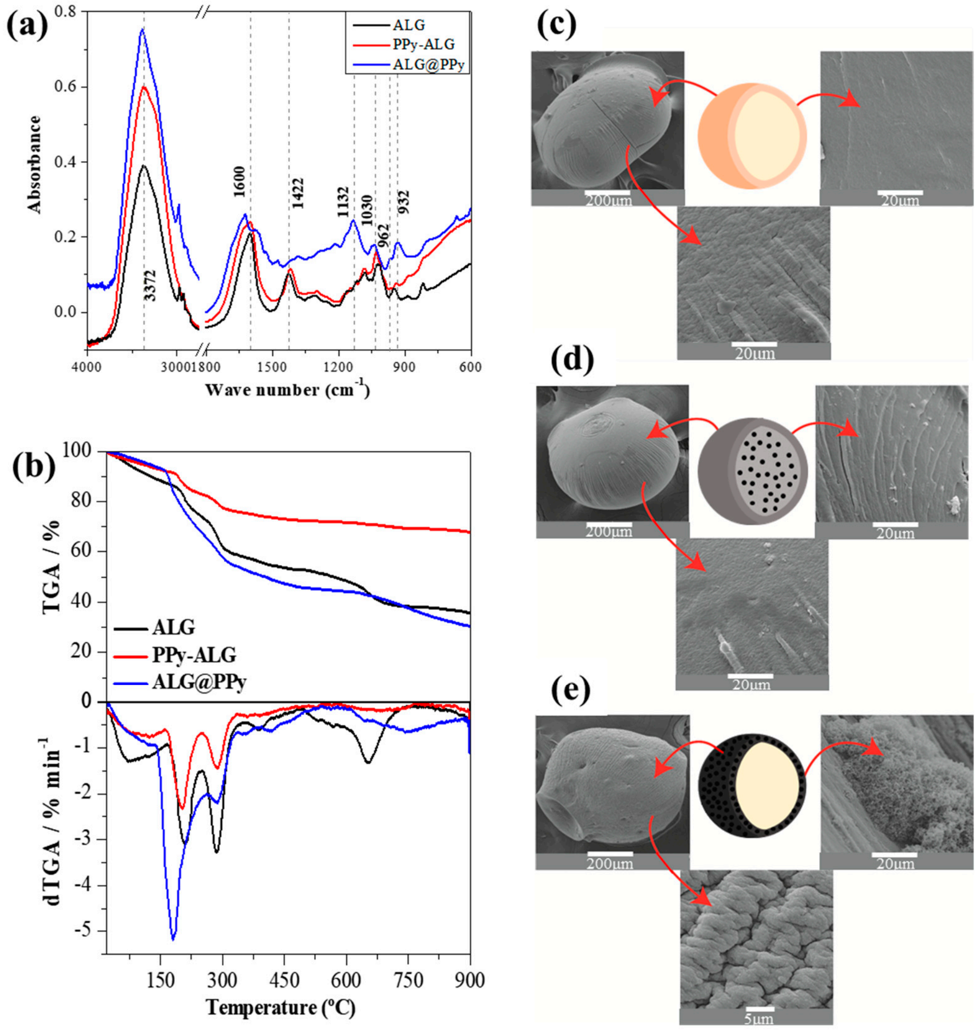

Figure 2. (**a**) ATR-FTIR spectra of the ALG, PPy-ALG and ALG@PPy hydrogels disks. (**b**) TGA and dTGA curves for ALG, PPy-ALG and ALG@PPy hydrogels. SEM images showing the morphology of (**c**) ALG, (**d**) PPy-ALG and (**e**) ALG@PPy hydrogels.

The composite hydrogels were exposed to different pH values. In alkaline conditions (pH 12.0), the material completely loses its physical integrity due to calcium ion displacement and gel network breakdown [30–32]. Thus, these materials are only applicable in neutral to acidic media (pH 1 up to 6).

The swelling index (SI) in all tested media is shown in Figure 3. The samples were evaluated in ultrapure water, HCl 0.1 mol L^{-1}, pH 1, and NaCl 0.1 mol L^{-1}, pH 6. The ALG@PPy presented the higher SI in all 3 media, followed by the PPy-ALG and pure ALG. For example, in water, the content of absorbed water of ALG@PPy (68.3 wt%) hydrogel was 1.7 times higher than that of the PPy-ALG (39.3 wt%) hydrogel and 2.1 times that of ALG (32.4 wt%) hydrogel. Water uptake is generally related to the number of hydrophilic groups available in the hydrogel network, such as -OH, -COOH, and -COO^{-}. The higher SI of the samples containing polypyrrole may indicate that less hydrophilic groups of alginate are available to interact with the media since they are preferably interacting with polypyrrole or committed to intra and intermolecular bonds. Another factor is the crosslinking degree of the alginate matrix, which may be lower in the presence of polypyrrole. Finally, a higher hydrogel porosity facilitates the entrance of water and increases SI. Although the hydrogel porosity was not determined, it is possible to infer that polypyrrole particles, when occupying some sites in the alginate matrix, may contribute to the increase in the number of voids in the alginate matrix, hindering alginate-alginate interactions responsible for the matrix cohesivity.

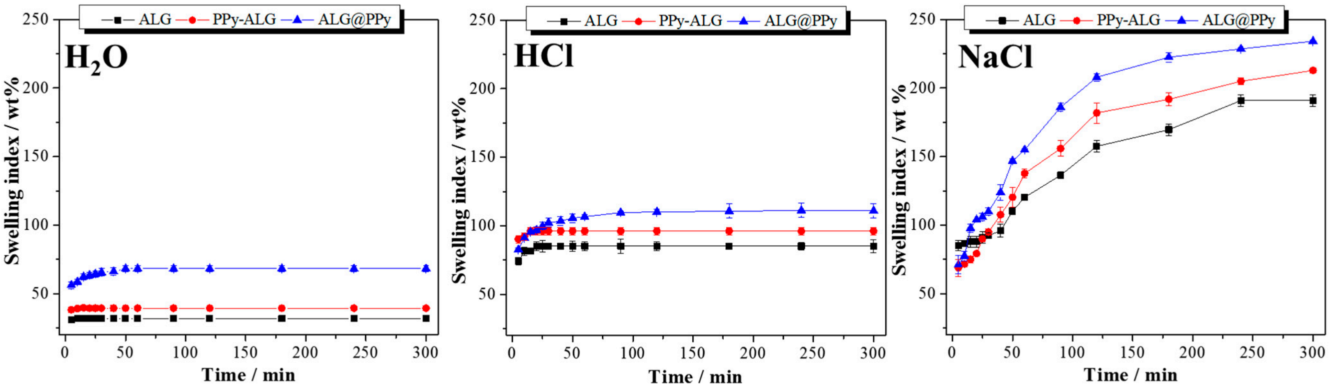

Figure 3. Swelling index (in wt%) of ALG, PPy-ALG and ALG@PPy hydrogels disks in (**left**) ultrapure water, (**center**) HCl 0.1 mol L^{-1} and (**right**) NaCl 0.1 mol L^{-1} (replicates = 3).

Considering the effect of media, the SI of all samples increased in the order: water < HCl << NaCl. The results are most probably related to alginate matrix behavior in different media. The pK_a value of uronic acids in the alginate chains is around 3–4 [32,33], meaning that in ultrapure water, the carboxylic acid groups are mainly deprotonated and interact with calcium ions to form the hydrogel network [34,35]. In an acidic medium, some of the Ca^{2+} ions in the -COO-Ca-OOC- groups of the hydrogel network are replaced by H^+ to form -COOH groups. The Ca-ALG network is partially undone, increasing the mobility of the polymeric segments and their interaction with the solvent. The SI was even greater in NaCl because of the replacement of Ca^{2+} with Na^+, loosening the hydrogel network [36].

The loss of water, at 60 °C, in wt% with respect to the swollen sample, is shown in Figure S5 (Supplementary Material). The maximum weight loss was around 95 wt% for the three samples, reaching equilibrium mass in 3 h. Thus, the presence of polypyrrole inthe hydrogel did not importantly affect the loss of water behavior.

Finally, the extraction efficiency of the hydrogel beads was determined for the extraction of atrazine (ATZ), caffeine (CAF), and progesterone (PRO) in aqueous medium by applying the SPE technique. Although SPE is a well-established technique, low-cost commercial phases, such as octadecylsilane (C18), have several disadvantages, including poor selectivity that leads to co-extraction of interferents, and difficulty in extracting polar compounds from aqueous matrices, since they mostly have hydrophobic character [12]. Polymeric sorbents, such as Oasis HLB and Strata X, have better performance for polar compounds but have cost limitations. To overcome these problems, several new materials have recently been developed to reach high sorption capacities, selectiveness, stability, longer lifetimes, and low costs [37–39]. Especially for aqueous samples, hydrogel-based materials are very promising extraction techniques because of their structure formed by a highly hydrophilic polymeric network and their ability to be easily modified or functionalized. These materials, both naturally occurring and synthetic, are capable of absorbing and retaining large amounts of water without dissolving [11,40], enabling interactions between analytes from aqueous samples and the polymeric hydrogel network.

In this study, all hydrogels were able to extract the three analytes in the investigated media. The chromatogram after water extraction is shown in Figure S5 (Supplementary Material). The peak area of each analyte after extraction is shown in Figure 4. As observed in Figure 4a, neat alginate (ALG) beads were able to extract all compounds, indicating that the polysaccharide contributes to the extraction process, acting as an effective extraction phase, as previously reported [11]. The addition of polypyrrole to the alginate hydrogel did not affect the extraction of CAF or ATZ from water, indicating that these compounds are being majorly extracted by the alginate. CAF ($\log(K_{ow}) = 0.07$) and ATZ ($\log(K_{ow}) = 2.61$) are expected to interact better with alginate. However, it is clear that the presence of polypyrrole in the hydrogel beads increased the peak area of PRO ($\log(K_{ow}) = 3.87$). The extraction of PRO from NaCl aqueous solutions followed the same trend. Although the extraction of PRO from HCl aqueous solution resulted in higher peak areas, statistical differences were not observed when comparing the three samples. The results demonstrated that polypyrrole particles contribute to an increase in the hydrophobic character of the composite. The capacity of extracting compounds with different polarities indicates the versatility of the composites [41], and the presence of polypyrrole at the surface increases the lipophilic character of the composite even more, improving the extraction of more hydrophobic molecules, such as PRO.

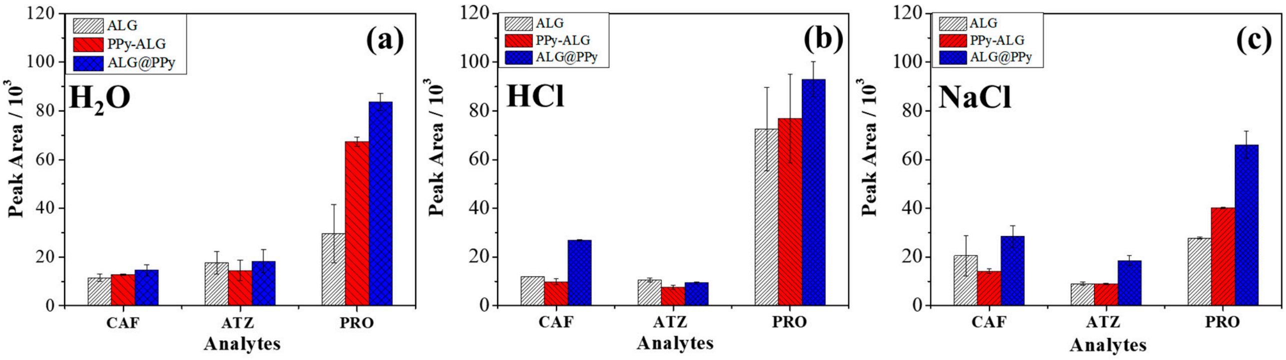

Figure 4. GC-MS peak area (replicates = 2) of CAF, ATZ, and PRO (0.5 mg mL^{-1}) after extraction using ALG, PPy-ALG and ALG@PPy hydrogel beads in (**a**) ultrapure water, (**b**) HCl 0.1 mol L^{-1} and (**c**) NaCl 0.1 mol L^{-1}. The order of increasing polarity of the contaminants is: CAF > ATZ > PRO.

Moreover, the Relative Standard Deviation (RSD) values for extractions using polypyrrole were lower (from 2.8% to 28.8% for PPy-ALG and between 4.3% and 26.1% for ALG@PPy) when compared to neat ALG (from 12.6% to 40.7%), which indicates that the composite material is promising for extraction applications.

This work complements previous publications regarding these types of composites. Here, we present a composite with an amphiphilic character capable of extracting low-to-medium polarity compounds, where a change in morphology—increasing the availability of polypyrrole at the surface—could improve the extraction of low polarity compounds (PRO).

Castilhos and coworkers [11] developed an alginate/zein (ALG:Z) hydrogel supported on polypropylene fiber, capable of extracting medium-to-high polarity compounds. The device resulted in a simple and efficient sorption phase. In this case, the ALG hydrogel also presented better results for more polar analytes, such as ATZ, while the ALG:Z combination inferred an amphiphilic character in the extraction phase, since better extraction efficiency was reached for PRO. This work also evaluated the reusability of the material, performing 5 consecutive extractions with satisfactory standard deviation values (0.8–19.3%) and maintaining the mechanical integrity of the material.

In another study, de Lazzari and coworkers [22] evaluated polypyrrole alone, in two different morphologies (globular and nanotubular), such as the extraction phase for ATZ, CAF, and PRO, using SPE and electrochemically controlled solid-phase extraction (EC-SPE) as pre-concentration techniques. In this case, polypyrrole again showed improved extraction of PRO, which can be associated with π-π interactions between the analyte PRO and PPy. Despite not being very selective, the morphology of PPy nanotubes showed the best performance associated with the increased surface area of the nanostructures. An increase was observed in the extraction efficiency of all compounds with lower RSD values (CV < 4.3%) due to the higher surface area.

4. Conclusions

Alginate and polypyrrole hydrogel composites (ALG, PPy-ALG and ALG@PPy hydrogel beads) were successfully prepared and characterized. As a future application perspective, the composite hydrogels were employed as the sorbent phase for ATZ, CAF, and PRO, and showed potential for the extraction of compounds with different polarities from aqueous matrices. The physical-chemical properties of these materials indicate that the hydrogel matrix and its functional groups, associated with the conducting polymer chains, are very important to ensure satisfactory amphiphilic interactions with the analytes.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app122010609/s1, Detailed description of the protocols for hybrid hydrogels formation, Table S1: HPSEC-MALLS information of sodium alginate; Figure S1: HPSEC profiles of sodium alginate obtained from Sigma-Aldrich; Figure S2: UV-Vis spectra for PPy-ALG dispersion synthesis; Figure S3: FTIR spectrum of sodium alginate and PPy-ALG composite; Figure S4: Scanning electron microscopy images: (a) neat ALG, (b) neat PPy, and (c) PPy-ALG composite; Figure S5: Loss of water (in wt%) of ALG, PPy-ALG and ALG@PPy hydrogels at 60 °C (replicates = 3); Figure S6: Representative chromatogram showing peaks for ATZ, CAF, and PRO for extraction performed with ALG, PPy-ALG and ALG@PPy beads in ultrapure water.

Author Contributions: Conceptualization, B.J.G.S., M.V. and I.C.R.-V.; methodology, B.J.G.S., M.V. and I.C.R.-V.; investigation, S.C.J., A.C.d.L. and N.M.F.M.S.; resources, B.J.G.S., M.V. and I.C.R.-V.; data curation, S.C.J., A.C.d.L. and N.M.F.M.S.; writing—original draft preparation, S.C.J.; writing—review and editing, G.d.A.; visualization, G.d.A.; supervision, B.J.G.S., L.F.M., M.V. and I.C.R.-V.; project administration, B.J.G.S., M.V. and I.C.R.-V.; funding acquisition, B.J.G.S., M.V. and I.C.R.-V. All authors have read and agreed to the published version of the manuscript.

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