Electrochemical fabrication of polypyrrole/hazelnut shells modified carbon nanocomposite sorbent for determination of polycyclic aromatic hydrocarbons using headspace solid-phase microextraction-gas chromatography

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ABSTRACT
A novel composite of polypyrrole and modified activated carbon (AC) derived from hazelnut shell was electrodeposited by a chronoamperometry technique as a thin film coating on the pre-prepared stainless steel wire surface. Electrodeposition was done at ambient temperature and a fixed potential of 1 V for 1000 s. Five polycyclic aromatic hydrocarbons (PAHs) were extracted using headspace solid-phase microextraction (HS-SPME) and then detected by gas chromatography-flame ionization (GC-FID). Optimization of the extraction process was performed by the response surface methodology using the central composite design (CCD). The extraction method was optimized in terms of extraction temperature, extraction time, salt concentration, desorption temperature, and desorption time with the following results: 33°C, 45 min, 20% (W/V), 280°C, and 5 min, respectively. For the PAHs analyzed with the fiber under optimum conditions, the procedure was linear in the range of 2–200 μg/L, with detection limits of 0.1–0.5 μg/L and relative standard deviation (RSD%) of 0.2–5.4% (n = 3). Finally, the proposed method was effectively implemented to analyze PAHs in some water, tea, and vegetable samples. Flavored tea (19.0) and black tea (5.4) had the highest levels of Nap (μg/L), while Phe and Ant were not detectable in all the samples analyzed.

Introduction
SPME was first introduced in the early 1990s by Pawliszyn and Arthur, and now it has been used as a sampling method to investigate a broad range of analytes present in several matrices ranging from biological to environmental and pharmaceutical samples (1). Sample preparation, condensation, and extraction can be provided

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in a single step by SPME that resulted in the emergence of a straightforward, rapid, efficient, and environmentally friendly sample preparation technique (1,2). SPME fibers, which can be used for both headspace and direct sample analysis, can be immersed directly in the samples or located in air space over the samples. HS-SPME is preferable for volatile compounds and complex samples that may damage the fiber cover (3, 4). The SPME extraction efficiency is highly dependent on the partitioning of the analyte between SPME coating and the analyte matrix. The more analyte passes through the matrix and into the coating, the greater its concentrating power and effectiveness. Therefore, in this method, the coating plays a vital role in its extraction efficiency, sensitivity, and selectivity (1, 5, 6). In SPME, different coating materials, including polymeric (7, 8), ionic liquids (9), carbon-based materials (10, 11), and metal–organic frameworks (12, 13), have been used to extract different compounds. Improving the adsorptive characteristics of the coating materials is essential for applying SPME to new compounds and enhancing the effectiveness of this method for compounds that have already been studied. In addition to several different commercial SPME fibers, interest in the design of metal-based fibers has recently increased due to versatility, power of the body, easy handling, and long service life (8, 14). There are several methods for the deposition of a custom coating onto the fiber (6, 15, 16), among which electrochemical deposition offers a simple, convenient, inexpensive, and effective option (16, 17). Polyaniline, polystyrene, polypyrrole (PPy), and its conductive derivatives could be considered versatile and promising coatings that could significantly improve SPME performance. An electrochemical cell with working, counter, and reference electrodes are most often used in electrochemical methods (1, 15, 16, 18). The characteristics of conductive polymers as coating materials can be easily modified in SPME procedures by changing the type of ion, the concentration of monomers, and the application potential. The most commonly used conductive polymers as SPME coatings are PPy and its derivatives. A stainless steel slim fiber as an SPME supporting base can be coated by PPy using an aqueous solution’s electrodeposition (15, 19). AC, also known as activated charcoal, is a porous carbonaceous substance made from some carbon-rich materials other than graphite (20), such as widely available agricultural residues as low-cost precursors of AC (21–23). Nutshells are excellent choices for AC production because they are natural resources that have a high carbon content, pore length, pore size distribution, internal porosity, surface area, mechanical strength, physicochemical stability, functional groups on their pore surfaces, low ash content, and low initial cost, all of these have an effect on the AC adsorption performance (22, 24, 25). Chemical and physical modifications can be used to improve AC selectivity by introducing various functional groups based on the target analytes (1, 6). PAHs are a broad group of organic compounds with two or more fused aromatic rings. They are made when coal, oil, natural gas, garbage, and other organic materials such as tobacco or charbroiled meat are incompletely burned. They can be present in the air, water, soil, or anywhere else in the world. These materials are listed as essential pollutants by the US Environmental Protection Agency (EPA) and other government organizations. The analysis of PAHs in environmental samples has attracted some attention due to their carcinogenic and mutagenic characteristics (26–28). A composite material made of AC can be made from agricultural waste and conductive polymers, which can facilitate the manufacture of superior sorbent materials used in SPME. The main objective of this study was to use an easy and fast electropolymerization method to create a uniform and sticky composite coating of polypyrrole/modified activated carbon prepared from hazelnut shells (PPy/AC) on a steel wire. The coating was subsequently applied as an extraction phase for PAHs analysis using the HS-SPME-GC technique.

**Experimental**

**Chemicals**

Pyrrole, Anthracene (Ant), ethanol (HPLC grade), Fluorene (Flu), sodium chloride (reagent grade), Phenanthrene (Phe), nitric acid, Naphthalene (Nap), and Pyrene (Pyr) was acquired by Merck (Darmstadt, Germany). In order to prepare stock solutions, each PAH (1000.0 μg/mL) was dissolved separately in ethanol. A standard mixture of PAHs was also prepared, each with a 10.0 μg/mL concentration in ethanol. Then, standard working solutions in distilled water were prepared daily from these stock solutions. To keep stock and working solutions in their most stable conditions, they were stored at a temperature of 4°C. Hazelnut shells were bought from the local market as a source of AC preparation (Kerman, Iran).

**Apparatuses**

An Agilent (U.S.A.) model 7890A gas chromatograph, equipped with a split-splitless injector, flame ionization detector (FID) and a capillary column HP-5 (30, 0.320 mm i.d.) with a film thickness of 0.25 μm was used for chromatographic analysis of PAHs. Nitrogen
(with a purity of 99.999%) was the carrier gas applied by a flow rate of 0.8 mL/min in the splitless mode. The initial temperature of the GC column was determined to be 40°C, which was maintained for 4 min. Then the column temperature was raised to 220°C at a rate of 30°C/min, and when 220°C was reached, it was maintained for 20 min. The temperature of the injector and the detector were set at 280°C and 300°C, respectively. Pyrrole was electro-polymerized by using a potentiostat/galvanostat model 302N from Autolab (Netherlands). The working electrode was the American Orthodontics steel wire (WI, U.S.A.) and the reference electrode Ag/AgCl and Pt counter electrode from Azar Electrode were used in the electrochemical process (Urumieh, Iran). In this study, a laboratory-manufactured SPME device consisted of a 22 gauge, and used a 4.0 cm stainless steel medical syringe needle, which was installed in a Hamilton syringe (25.0 µL) and glued to the syringe. The other side of the Hamilton syringe was glued to a piece of rubber septum. The SPME fiber was a steel wire 18.0 cm passed through the septum, and 1.5 cm of the fiber length was coated with Polypyrrole/modified AC composite (PPy/AC). A hot plate-stirrer model RH basic 2 obtained from IKA (Germany) was used to stir and heat the samples during the SPME process. For sonication purposes, ultrasonic bath model 3000865 from Selecta (Spain) was used. A scanning electron microscope (SEM), FEI Quanta 200 (U.S.A.) was used to study the fiber surface. Tensor 27 FTIR spectrometer recorded the FTIR spectra (Bruker, Ettlingen, Germany).

**Preparation of AC from hazelnut shells**

To remove dust and other inorganic impurities from the hazelnut shell it was rinsed several times with distilled water. It was then dried for 24 h in the oven at 105°C to lower the moisture level. Afterward, a high-speed mill and a standard sieve (mesh 150) were used for crushing and sieving, respectively. The size of particles that passed through the sieve was 106 µm. The carbonization process for obtaining charcoal from the starting material, and the activation of the generated charcoal, were all carried out in a furnace at 800°C for 30 min (21, 22).

**Modification of the AC**

To distribute the AC in the composite network, the following modifications were accomplished: in a round-bottom glass flask, 0.10 g of AC and 7 mL of nitric acid were added, and the mixture was sonicated in an ultrasonic bath for 10 min. Afterward, the mixture was refluxed at 150°C for 3 h. After cooling, the resultant oxidized AC was collected using a Whatman No. 42 filter paper, and neutralized with purified water, and subsequently was left to dry at room temperature (6). Owing to the existence of –COOH, –OH, etc. as hydrophilic functional groups, the acid-treated sample of the AC can be easily dispersed in the solution.

**The composite coating preparation**

The oxidized AC (0.02 g) was homogenously dispersed using an ultrasonic bath in 10 mL of distilled water–ethanol mixture for 1 h at 28°C to prepare the composite coating. Next, 250 µL of pyrrole monomer was added to the mixture and sonicated for 15 min (7). By applying a constant potential of 1 V for 1000 s, the composite polymer coating is deposited directly from this solution on the surface of the wire. Potentiostatic polymerization at room temperature performed the electrodeposition process. Since an electrolyte must be present for electropolymerization, so, in this work, the polar functional groups created during the AC oxidation process may act as the necessary electrolyte. Therefore, without any other supporting electrolyte, electropolymerization was carried out. Till the polymerization process, the surface of the wire was first roughened with smooth sandpaper to improve the effectiveness of the coating’s adherence to the surface and then washed in acetone subsequently with distilled water while sonicating. Before using the fiber in HS-SPME experiments, the treated fiber was heated to 100°C for 1 h in the oven and then to 300°C in the GC injector port for 2 h under the atmosphere of nitrogen to condition it. Fiber conditioning will remove the remaining volatile compounds of the fiber that can produce a smooth baseline for chromatography.

**HS-SPME procedure**

From the stock solutions prepared previously, 0.10 µg/mL of each, working solution of the PAHs mixture was prepared daily in distilled water. On every HS-SPME analysis, 5 mL of water sample was put into a 10 mL glass vial which was capped with a septum to avoid evaporation of the sample. By placing the extraction vial in a glass water bath, which was put on a magnetic stirrer, the extraction temperature was adjusted. During the extraction procedure, the sample solution was stirred at a constant speed with a small Teflon-coated magnetic stir bar. The stainless steel needle, which housed the fiber, was then pushed through the septum of the vial. The fiber was then driven out from the housing and exposed in optimal conditions to the headspace above the specimen. The fiber was withdrawn from the sample back into the
needle after the extraction, which was then retrieved from the vial of the sample, and immediately introduced for thermal desorption into the injector port of GC.

**Preparation of the real samples**

**Water:** Various water samples, including a specimen of well water, representing agricultural water, were collected from the University water well (IAUK, Iran), and a rainwater sample collected, and the recommended method was subsequently used to extract the PAHs from these samples. In order to eliminate any suspended material, each water sample was filtered. The water specimens were stored in a refrigerator at 4°C in amber glass bottles before the analysis.

**Tea:** A variety of tea samples were obtained from a local market, including green tea, black tea, and aromatized tea (Kerman, Iran). Specimens were prepared in all tests by soaking 2.50 g of dried tea leaves into 100 mL of hot ultra-pure water for 5 min, then filtering the sample and allowing it to cool down to room temperature.

**Vegetables:** Some vegetable samples, including lettuce, potato, and radish obtained from the local market (Kerman, Iran). To remove the airborne dust and deposited soil particles on the vegetables, they were washed with tap water. Using a juice extractor, as the vegetable dried, vegetable samples were thoroughly homogenized and sealed in bottles of amber glass. The samples were placed in a fridge at −20°C to maintain their properties until analysis.

**Results and discussion**

**Coating optimization**

Since in the fiber coating stage, two variables of potential and coating time were considered, to optimize the parameters of the coating process, the method of one variable at a time (OVAT) was used. The experimental design method, which is usually used for a large number of variables to reduce time and cost, does not seem to be much preferred in this case. After fiber coating, thermal conditioning was applied in each

![Figure 1. Effect of coating parameters on the extraction efficiency: (a) deposition potential and (b) deposition time; (N = 3). Conditions: sample volume: 5 mL; concentration of PAHs: 0.1 μg/mL of each; extraction time: 45 min; extraction temperature: 33°C; desorption time and temperature; 5 min and 280°C.](image-url)
optimization step and then the fibers were used for PAHs HS-SPME and the corresponding extraction efficiencies were evaluated. To optimize the deposition potential, electrodeposition was performed on the solutions containing 0.02 g modified AC and 250 µL pyrrole monomer, at potential levels of 0.8, 0.9, 1.0, and 1.2 V versus Ag/AgCl, at a deposition time of 800 s. As illustrated in Figure 1(a), 1.0 V was the most appropriate potential for obtaining the highest extraction efficiency. The amount of PAHs extracted is considered as a measure of the efficiency of the coating. In this potential, as in many other reports, the highest degree of polymerization occurs at the 1.0 V potential. The effect of the deposition time was also investigated in order to optimize the thickness of the composite layer. The deposition time ranged from 600 to 1200 s with a constant deposition potential of 1.0 V. As shown in Figure 1(b), the deposition time of 1000 s was optimal for most PAHs for electropolymerization except for Nap which was reduced. Increased adsorption in most cases is probably related to increasing the thickness of the coating and thus increasing the coating extraction capacity. On the other hand, reducing the extraction efficiency at more times is probably due to reduced adhesion of the coating on the fiber surface resulting in reduced fiber efficiency and the decreased lifetime of coated fiber.

**Characterization of PPy/AC composite layer**

The composite’s composition and morphology have been characterized by FTIR spectroscopy and SEM. FTIR spectra of modified AC and PPy/AC composite were shown in Figure 2(a) and 2(b), respectively. The modification is observed to introduce different functional groups on the AC surface. The peak at 3447 cm\(^{-1}\) in the modified AC spectrum can be attributed to O─H stretching vibration. The peaks at 1245, 1630, and 1711 cm\(^{-1}\) can be contributed to the stretching vibrations of C─O, C═C, and C═O, respectively. The peak at 2962 and 2929 cm\(^{-1}\) can be assumed to be caused by the sp\(^3\) C─H bonds. These functional groups enhance the dispersive behavior of modified AC in aqueous solutions. In the case of PPy/AC composite, the peak at 1630 cm\(^{-1}\) could be assigned to C═C stretching vibration in the polypyrrole ring. The peak at 1245 cm\(^{-1}\) can be attributed to the C─O or C─N stretching vibration. The peak at 1168 cm\(^{-1}\) could be attributed to the C─N stretching band. The peak at 3447 cm\(^{-1}\) is assigned to the stretching vibration of the O─H of the modified AC, which was superimposed on the N─H stretching band of pyrrole.

The SEM magnified micrographs of the coating are displayed in Figure 3(a–d). It is seen that the surface of the polymer coating has a cauliflower-like structure. The morphology of the PPy/AC composite coating surface, consisting of a coarse and highly porous structure, significantly enhances the surface area, which is

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**Figure 2.** FTIR spectra of (a) modified AC, (b), PPy, and (c) PPy/AC composite.
favorable for the adsorption and desorption of target analytes. The lifespan of the fiber was such that a single fiber could be used at least 150 times for HS-SPME of PAHs. The fiber was rubbed against a piece of white paper to study the mechanical adhesion of the coating that no black particles were removed from the fiber. This indicated the strength of the mechanical integrity of the coating. Also, the thermal stability of the coating seems to be good enough with regard to the lack of weight loss of the adsorbent, acceptable reproducibility of repeated injections at 300°C. However, a TGA should be performed to confirm such thermal stability of the coating.

**HS-SPME optimization**

The effects of different parameters on SPME process efficiency such as ionic strength, extraction time and temperature, desorption time, and temperature have been evaluated. Results showed that the optimum condition for extraction and desorption are as follows: 33°C, 45 min, 20% (W/V), 280°C, and 5 min for extraction temperature, extraction time, salt concentration, desorption temperature, and desorption time, respectively.

One other important parameter that could have a significant impact on the effectiveness of the SPME process is stirring, since it reduces the time needed to achieve equilibrium, by accelerating the transfer of mass between the sample solution and the headspace phase (29). Throughout the extraction, the aqueous specimens were stirred with a magnetic stirring bar.

**Desorption parameters**

Desorption variables comprising desorption time, and desorption temperature, play a vital role in the complete desorption of the fiber analytes and any memory or carryover effect avoided (1). Extracted analytes desorbed at various temperatures in the range of 220–300°C. According to the results, the highest peak areas were obtained at 280°C for all analytes (Figure 4(a)). Desorption time optimization was accomplished by putting the fiber inside the GC injection port for 1–5 min. Desorption time at 280°C was set at 5 min based on the optimum conditions obtained (Figure 4(b)). In these conditions,

**Figure 3.** The scanning electron micrographs of the surface of PPy/Ac composite coated on a steel wire with a magnification of (a) 500x, (b) 5000x, (c)20,000x, and (d) 40,000x.
no residual effects were observed after desorption of PAHs from the surface of the fiber.

**Design of experiment (DoE)**

In the extraction step, the effect of extraction temperature, extraction time, and ionic strength were investigated. The partition coefficient of analytes in the sample solution and the headspace phase is strongly affected by the extraction temperature. Equilibrium plays a prominent role in the HS-SPME extraction method, and since the extraction time is a crucial factor in reaching the equilibrium in the concentration of the analytes between the sample and the fiber, it is an essential parameter in determining the efficiency of the HS-SPME procedure (30). The other very important parameter affecting the extraction efficiency by HS-SPME is the ionic strength of the sample solution. To enhance the partitioning of PAHs from the sample solution to the spaces of the samples (HS), the existence of salt in an aqueous solution would be beneficial. Adding salt to the aqueous solution increases the ionic strength but reduces the water solubility of the analytes (6). To identify essential parameters to optimize the extraction conditions of the HS-SPME process, the design of the experiment approach in combination with response surface methodology was used. It has been demonstrated that statistical methods, such as DoE, could significantly decrease the cost and the time of a study by drastically reducing the number of runs required. Due to this high efficiency, DoE has been used for various applications in analytical chemistry. DoE is composed of three fundamental steps. The first step is to identify the parameters that could affect the results, which is called screening. The second step, which is also known as the optimization step, is to find the optimal

![Figure 4. Effect of desorption parameters on the extraction efficiency: (a) desorption temperature and (b) desorption time; N = 3. Conditions: sample volume: 5 mL; concentration of PAHs: 0.1 μg/mL of each; extraction time: 45 min; extraction temperature: 33°C; desorption time and temperature: 5 min and 280°C.](image-url)
set of parameters, using statistical methods. Moreover, finally, the third step is to experimentally verify the predictions made in the second step, referred to as the validation of the model (31). DoE and data processing were carried out by Design-Expert statistical tool. For this respect, a factorial design was first used to measure the importance of the leading and interaction effects of the parameters. The screening step was then carried out with 11 experiments at high (+1) and low (−1) levels, that for temperature was 20 and 46°C, time of 10 and 80 min, and salt concentration of 10 and 30% (w/v) including three replicates at the center of the experimental domain to evaluate the experimental error designed by the software, according to Table S1, which was filled after the experiments. The low and high values for each factor were selected after initial testing and paper reviewing (29, 31, 32). The sequence of the tests was randomly assigned to prevent any potential memory effect of the analytical apparatus. The findings obtained revealed that all the chosen parameters had significant effects on the extraction efficiency of PAHs on the PPy/AC composite. Summary of the experimental design for each analyte has been shown in Figures S1 through S5. To achieve the optimal level of variables, the response surface methodology and CCD was used, because in this method variables can be studied at the optimal level of variables, the response surface has been shown in Figures S1 through S5. To achieve validation of the model (predictions made in the second step, referred to as the third step) is to experimentally verify the predicted model for all analytes (Table S2) that was filled after the experiments with responses. The peak area value of each of the target analytes after the extraction was considered as the response and based on these values, the optimum extraction conditions were evaluated. As shown in Table 1, the best model suggested by the software for all of the analytes is the quadratic model, since the p-value of the suggested model is less than 0.05, and the lack of fit of the recommended models are greater than 0.05, indicating that it is a reliable model. In addition, adjusted R2 and predicted R2 calculated for the most analytes are greater than 0.8 and the difference between them is less than 0.2. The results of the analysis of variance (ANOVA) method for the quadratic model for all analytes are shown in Table 2. ANOVA results showed that the model was significant for all of the analytes, with a p-value of less than 0.05. Also, based on the ANOVA results, the extraction temperature and ionic strength for Nap and Flu, the extraction time and ionic strength for Phe, and the extraction temperature and extraction time for Ant and Pyr, exhibited a significant effect on the response (p-value was less than 0.05). It is recommended to use the three-dimensional model plots (3D) for the visual description of the relationships. This is useful to imagine the relationship between the responses and each experimental factor level. Figure S6 represents the surface response curves corresponding to the most critical PAH extraction variables. As the figure shows, temperature is a variable that is effective for extracting all PAHs, but has different effects in extracting each, so that it is more effective for Nap and Flu at low temperatures and more effective for Phe, Pyr, and Ant at high temperatures. This effect may be related to the weight of different molecules of these compounds and their boiling point, which is effective in extracting from the headspace. Time and salt concentration have different effects, but in general both have optimal ranges for their effect so that their effect is reduced to a greater or lesser extent.

Table 1. Summary of the obtained results for suggested model of each analyte.

| Analyte | Source | Model p-value | Lack of Fit p-value | Adjusted R² | Predicted R² |
|---------|--------|---------------|---------------------|-------------|-------------|
| Nap     | Quadratic | < 0.0001 | 0.6631 | 0.9005 | 0.8136 |
| Flu     | Quadratic | < 0.0001 | 0.0753 | 0.8837 | 0.6375 |
| Phe     | Quadratic | 0.0002 | 0.0557 | 0.8543 | 0.5545 |
| Ant     | Quadratic | 0.0095 | 0.1097 | 0.7328 | 0.2406 |
| Pyr     | Quadratic | < 0.0001 | 0.0506 | 0.9743 | 0.9160 |

Table 2. ANOVA results (p-values) for response surface quadratic model in the optimization of HS-SPME of PAHs (p-values less than 0.0500 indicate model terms are significant).

| Source | Nap | Flu | Phe | Ant | Pyr |
|--------|-----|-----|-----|-----|-----|
| Model  | < 0.0001 | < 0.0001 | 0.0002 | 0.0040 | < 0.0001 |
| A-Temp | < 0.0001 | < 0.0001 | 0.0774 | 0.0004 | < 0.0001 |
| B-Time | 0.4476 | 0.2629 | 0.0001 | 0.0051 | < 0.0001 |
| C-Ionic strength | 0.0015 | 0.0064 | 0.0094 | 0.6486 | 0.8598 |
| AB     | 0.3624 | 0.0177 | 0.0002 | 0.1532 | 0.0092 |
| AC     | 0.4932 | 0.2016 | 0.9654 | 0.3097 | 0.0336 |
| BC     | 0.7279 | 0.3330 | 0.8200 | 0.9408 | 0.6425 |
| A2     | 0.0006 | 0.0049 | 0.0067 | 0.0101 | 0.9243 |
| B2     | 0.0023 | 0.0012 | 0.0001 | 0.0092 | < 0.0001 |
| C2     | 0.8415 | 0.8659 | 0.0911 | 0.2691 | 0.0029 |
| Lack of fit | 0.6631 | 0.0753 | 0.0557 | 0.1097 | 0.0506 |
Method validation

The analytical method figures of merit were investigated to validate the efficiency aspects of the current method and to verify its ability to analyze PAHs. Valuable analytical data comprising linear dynamic range (LR), detection limit (LOD), and RSD% were computed under the optimum conditions for the studied analytes (Table 3). In the concentration ranges of 2.0–50.0 µg/L for Phe and Ant; 2.0–25.0 µg/L for Nap; 5.0–50.0 µg/L for Flu; and 25.0–200.0 µg/L for Pyr, the obtained plots were linear.

### Table 3. Figures of merit of the presented method for determination of PAHs.

| Analyte | LOD (µg/L) | LOQ (µg/L) | RCC (µg/L) | CE                           | Rec  | r       | A     | B     |
|---------|------------|------------|------------|------------------------------|------|---------|-------|-------|
| Nap     | 0.5        | 1.7        | 2.0–25.0   | $y = 10.943x + 6.672$        | 93.2 | 0.9999  | 3.3   | 8.3   |
| Flu     | 0.2        | 0.6        | 5.0–50.0   | $y = 15.833x − 1.995$        | 67.4 | 0.9994  | 0.5   | 6.2   |
| Phe     | 0.2        | 0.5        | 2.0–50.0   | $y = 17.838x − 1.974$        | 88.9 | 0.9995  | 5.4   | 7.1   |
| Ant     | 0.1        | 0.3        | 2.0–50.0   | $y = 13.629x − 0.424$        | 90.6 | 0.9997  | 1.8   | 4.5   |
| Pyr     | 0.2        | 0.8        | 25.0–200.0 | $y = 17.307x − 1.865$        | 89.1 | 0.9995  | 0.2   | 5.1   |

RCC, Range of Calibration Curve; CE, Calibration Equation; Rec: Recovery (%); A: Intraday precision using one fiber in one day; B: Interday precision using three fibers (fiber to fiber repeatability) in three different days.

Figure 5. The chromatograms obtained by GC-FID for (a) standard solution of the mixture of PAHs before SPME (PAHs concentration: 0.1 µg/mL of each), (b) standard solution of the mixture of PAHs after SPME (PAHs concentration: 0.01 µg/mL of each). Extraction conditions: extraction temperature: 33°C; extraction time: 45 min; salt concentration: 20% (W/V); desorption temperature: 280°C; and desorption time: 5 min.
For all PAHs, the ‘r’ (correlation coefficient) was in the appropriate range of 0.9995–0.9999.

The precision of the method was determined by calculating the RSD percent of the results obtained under optimal conditions by performing consecutive fiber extractions from the aqueous solution. Since chromatograms obtained by direct injection of PAHs with concentrations of 0.01 µg/L had no detectable peaks, direct injection of standard PAH solutions with concentrations of 0.01 µg/L had no detectable peaks, direct injection of standard PAH solutions with concentrations of 0.10 µg/L of each was performed (Figure 5(a)). In contrast, due to the concentrating ability of the SPME method, a standard concentration of 0.01 µg/L of each PAH (Figure 5(b)) was used for analytes from the samples. Therefore, in the optimum conditions, the RSD% were obtained and found to be in the range of 0.2–8.3% (n = 3), and the detection limits (based on S/N = 3) for the target analytes were also found to be between 0.1 and 0.5 µg/L. Considering SPME is an equilibrium extraction method, recovery was calculated by comparing the AUC of the authentic samples spiked with a certain amount of PAHs, such as rainwater, well water, tea infusion, and some vegetables, to the AUC of standard samples prepared in pure water with the same concentration. The results showed that except for Flu that the recovery was as much as 67%. For all other PAHs, the recovery was more remarkable than 89%. Figure 5(a,b) demonstrate the chromatograms of standard PAHs solutions before and after SPME application, respectively. A significant increase in the height of the peaks and, consequently, the AUC, demonstrates the efficiency of the SPME to concentrate the PAHs and provide the ability to detect and quantify them at very low concentrations. Comparing the outcome of the extraction and determination of PAHs using PPy/AC coating with the corresponding results found in the literature (6, 17, 33–35) demonstrated that the developed composite coating is equivalent to or better than the ones reported earlier (Table 4).

### Table 4. Comparison of analytical characteristics for PPy/AC coating with other fibers in determination of PAHs. All the concentrations are in µg/L.

| Method                  | SP Composition | Parameter | N: PAHs | Nap µg/L | Flu µg/L | Phe µg/L | Ant µg/L | Pyr µg/L | Ref. |
|-------------------------|----------------|-----------|---------|----------|----------|----------|----------|----------|------|
| HS-SPME-GC-FID          | PPy/AC         | LR 5      | 2.0–25  | 5.0–50   | 2.0–50   | 2.0–50   | 25–200   | This work|      |
|                        |                | LOD 0.5   | 0.2     | 0.2      | 0.1      | 0.2      |          |          |      |
|                        |                | RSD 3.3   | 0.5     | 5.4      | 1.8      | 0.2      |          |          |      |
| HS-SPME-GC-MS           | PPTMCNT        | LR 8      | 0.01–100| 0.01–100 | 0.01–100 | 0.01–100 | 0.01–300 | (6)      |      |
|                        |                | LOD 0.005 | 0.005   | 0.004    | 0.001    | 0.004    |          |          |      |
|                        |                | RSD 5.9   | 5.9     | 6.7      | 4.8      |          |          |          |      |
| HS-SPME-GC-MS           | CNTPOA         | LR 8      | 0.05–20 | 0.01–20  | 0.01–20  | 0.01–20  | 0.05–20  | (20)     |      |
|                        |                | LOD 0.01  | 0.003   | 0.002    | 0.002    | 0.01     |          |          |      |
|                        |                | RSD 6.2   | 5.6     | 7.8      | 9.3      |          |          |          |      |
| SPME-GC-MS              | PA             | LR 5      | 0.05–10 | 0.02–10  | –        | 0.02–10  | –        | –        | (29) |
|                        |                | LOD 0.0060| 0.0001  | –        | 0.0007   | –        |          |          |      |
|                        |                | RSD 16.8  | 10.5    | –        | 12.4     |          |          |          |      |
| HS-SPME-GC-FID          | BC6HTSO        | LR 8      | 0.5–200 | 0.1–200  | –        | –        | –        | –        | (32) |
|                        |                | LOD 0.16  | 0.03    | –        | –        |          |          |          |      |
|                        |                | RSD 3.8   | 4.5     | –        | –        |          |          |          |      |
| HF-SPME-HPLC-UV         | MWCNT/ZrO2     | LR 6      | 10–2000 | 2–2000   | 2–2000   | 20–2000  | 20–2000  | (33)     |      |
|                        |                | LOD 0.33  | 0.16    | 0.11     | 2.09     | 0.98     |          |          |      |
|                        |                | RSD 6.16  | 11.60   | 3.89     | 7.81     | 9.81     |          |          |      |

BC6HTSO: Benzoxy-C(6)/OH-TSO fiber; CNTPOA: Carbon nanotubes/poly-ortho-aminophenol; HF: Hollow Fiber; LOD: Limit of Detection (µg/L); LR: Linear Range (µg/L); PA: Polyaniline; PPTMCNT: Poly (o-phenylenediamine-co-o-toluidine)/modified carbon nanotubes composite; RSD: Relative Standard Deviation%; SP: Solid Phase; N: Number.

### Table 5. PAHs concentrations in real samples.

| Sample             | Concentration of PAHs (µg/L) |
|--------------------|-----------------------------|
|                    | Nap | Flu | Phe | Ant | Pyr |
| Rain water         | 0.29| 1.98| ND  | ND  | 1.85|
| Well water         | ND  | 2.33| ND  | ND  | 0.64|
| Green tea          | ND  | ND  | ND  | ND  | ND  |
| Black tea          | 5.36| 0.6 | ND  | ND  | ND  |
| Flavored tea       | 19.02| ND | ND  | ND  | ND  |
| Lettuce            | 2.0 | ND  | ND  | ND  | ND  |
| Potato             | 1.14| ND  | ND  | ND  | ND  |
| Radish             | ND  | ND  | ND  | ND  | ND  |

ND means not detected.

### Analysis of the real specimens

To show the efficiency of the proposed procedure it was used to adsorb the PAHs and determine their concentrations in various water, tea, and vegetable samples. Each sample was analyzed in triplicate at optimum SPME condition using the PPy/AC coated fiber. The results are shown in Table 5 and typical chromatograms are shown in Figure 6. The results showed that Phe and Ant could not be detected in any samples and Pyrene could be detected only in rainwater and well water. Nap showed the highest value in flavored tea (19.0) and black tea (5.4).
Conclusion

The combination of the activated carbon, which was prepared from hazelnut shells, with polypyrrole, as a conductive polymer, in a composite form, created excellent opportunity to produce a new adsorbent for solid-phase microextraction. Thus, for the first time in this report, a novel composite was introduced for the headspace solid-phase microextraction method of polyaromatic hydrocarbons. The polypyrrole/activated carbon composite was made by

Figure 6. The chromatograms obtained by GC-FID for (a) standard solution of the mixture of PAHs, (b) flavored tea, (c) rain water, (d) green tea, (e) raddish, and (f) potato.
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Disclosure statement

No potential conflict of interest was reported by the author(s).

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