



# Carbon nanotube-based benzyl polymethacrylate composite monolith as a solid phase extraction adsorbent and a stationary phase material for simultaneous extraction and analysis of polycyclic aromatic hydrocarbon in water<sup>☆</sup>

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## ABSTRACT

A composite of multi-walled carbon nanotubes incorporated into a benzyl methacrylate-co-ethylene dimethacrylate porous monolith was prepared, characterized and used as solid phase adsorbent and as stationary phase for simultaneous extraction and separation of ten polycyclic aromatic hydrocarbons, followed by nano-liquid chromatography analysis. The extraction and chromatographic parameters were optimized with regard to the extraction efficiency and the quality of chromatographic analytes separation. Under the optimized conditions, all PAHs were separated in 13 min with suitable resolution values ( $R_s = 1.74\text{--}3.98$ ). Addition of a small amount of carbon nanotubes (0.1% with respect to monomers) to the polymerization mixture increased the efficiency for the separation column to over 41,700 plates  $m^{-1}$  for chrysene at flow rate of  $0.5 \mu L \text{ min}^{-1}$ . The method showed a wide linear range ( $1\text{--}500 \mu g L^{-1}$  with  $R^2$  more than 0.9938), acceptable extraction repeatability (RSDs < 6.4%,  $n = 3$ ) and reproducibility (RSDs < 12.6%, five parallel-made solid phase extraction cartridges) and satisfactory detection limits ( $0.02\text{--}0.22 \mu g L^{-1}$ ). Finally, the proposed method was successfully applied to the detection of polycyclic aromatic hydrocarbons in environmental water samples. After a simple extraction procedure with preconcentration factor equal to 100, the average recovery values in ultra-pure, tap and sea water samples were found to be in the range 81.3–95.4% with %RSD less than 6.4. Again, the presence of carbon nanotubes (0.3% relatively to monomers) in native polymer enhanced the extraction performance for the solid phase adsorbent up to 78.4%. The application of the monoliths modified with CNTs in extraction and nano-scale liquid chromatography for analysis of environmental samples offered several advantages; it demonstrated an acceptable precision, low detection limits, good reproducibility, satisfying recoveries and wide dynamic linear ranges.

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## 1. Introduction

For many years, analysis of chemical pollutants in the environment has attracted a growing interest. The overall scheme of

analysis is crucial as many of the contaminants are very toxic for human and living organisms even at low concentrations [1]. Polycyclic aromatic hydrocarbons (PAHs) are a large class of organic compounds which contain at least two fused aromatic rings. PAHs are solids with low volatility at room temperature, soluble in many organic solvents and relatively insoluble in water. They are widespread products of the high-pressure processes or incomplete combustion of organic matter, and mostly result from burning of fossil fuels and waste incineration [2]. The PAH residues in the environment can induce air, soil or water pollution, as well as food contamination; they can also concentrate in human body through terrestrial or aquatic food webs [3]. PAHs are listed as priority harmful pollutants; they received more attention because of their

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carcinogenicity, lipophilicity and ubiquitous nature [4]. US Environmental Protection Agency (EPA) considers a list of 16 PAHs which are known as carcinogenic or mutagenic; this agency set the maximum contaminant level (MCLs) for most PAHs in drinking water between 0.1 and 0.4  $\mu\text{g L}^{-1}$  [5]. In view of the possible harmful effects of PAHs on human health and food safety, the development of fast, efficient and sensitive methods for analysis of PAH pollutants is of great importance.

A number of analytical techniques have been reported for determination of PAHs in different samples, such as fluorescence spectroscopy [6], capillary electrophoresis [7], immunoassay technique [8], gas chromatography [9] and high-performance liquid chromatography (HPLC) [10,11]. However, analysis of PAH compounds usually requires sample pretreatment including clean-up and preconcentration procedures because of the matrix complexity and the low content of PAHs in real environmental samples. Solid-phase extraction (SPE) has been one of the most common methods used for preconcentration of analytes in various media because of its advantages such as high enrichment factor, high recovery, rapid phase separation, low cost and low consumption of organic solvents [12]. However, the choice of appropriate adsorbents is a critical factor to obtain a good recovery and a high enrichment factor in the SPE procedure [13].

The use of organic monolithic polymers as separation material and as solid phase extraction adsorbent has continuously grown since the first report in 1992 [14,15]. While monolithic materials are commonly used in liquid chromatography, these porous media have also many applications in a variety of fields [16–20]. The monolith structure notably differs from that of conventional particulate materials, it does not require to be packed as it can be prepared by polymerization directly inside the separation column or SPE cartridge. The first generation of organic polymer monoliths exhibited fast and high flow analysis of large molecules such as proteins because of their high porosity and permeability, due to the presence of only large through pores (macropores) in their rigid structure which produce very low back pressure through the separation confines [20,21]. However, the lack of smaller pores (i.e. mesopores and micropores) in the polymer-based monoliths means a lower surface area, and hence less interaction sites in the monolithic structure, thus reducing the adsorptive properties of the native monoliths [22].

In the last few years, several methodologies have been developed to enhance the adsorptive and retentive properties of the monolithic materials. Since the type and percentage of polymerization mixture have strong effect on the final monolith morphology, many attempts tried to optimize the monomer, crosslinker and porogenic solvent composition as well as the polymerization conditions including time and temperature [23–25]. Other approaches tried to use a single crosslinker [26], to introduce an additional hypercrosslinking reaction [27] and to incorporate a small amount of nanoparticles into the naked porous monolithic structure such as polymeric latex nanoparticles [28,29], carbonaceous nanomaterials [30–34], metallic nanoparticles [35–38] and silica nanoparticles [39]. Due to the high surface area and good chemical and mechanical stability of carbon nanotubes (CNTs) [40], the small surface area and the lack of sufficient interaction sites in the native monolithic structure could be overcome through incorporation of these nanoparticles into the polymer monolithic columns.

As well as for many science and technology fields, analytical separation techniques have the potential nowadays to develop greener tools and methods to reduce their environmental impact. The miniaturization of the HPLC systems consisting of capillary and nano-LC scales is one of the most exciting prospects in separation technology [41]. Miniaturized liquid chromatography techniques use columns with internal diameter (i.d.) smaller than in conventional scale HPLC. Today, it is widely accepted in the literature

that capillary HPLC range corresponds to 100–500  $\mu\text{m}$  i.d. columns using less than 10  $\mu\text{L min}^{-1}$  mobile phase flow rate, while the column i.d. in nano-LC is between 10 and 100  $\mu\text{m}$  i.d., with a flow rate lower than 0.5  $\mu\text{L min}^{-1}$  [41–43].

In many cases, improving detection sensitivity that can be obtained as a result of reducing sample dilution during analysis is the main advantage for applying smaller i.d. columns [41–43]. This is an important aspect regarding detection limits and determination of compounds present at low concentration levels in limited sample volumes, such as for analysis of rare chemicals. Other advantages of using small diameter columns are the better compatibility of flow rate with mass spectrometric detectors, and a lower consumption of samples and solvents. This addresses both the cost of analysis and reduction of the environmental impact of toxic contaminants.

In this study, a composite of carbon nanotube-benzyl polymethacrylate monolith was prepared and characterized as a SPE adsorbent and as a stationary phase material. Ten PAHs including naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene and dibenzo(a,h)anthracene were selected to test the extraction performance and separation efficiency of the composite materials. The ten pollutants were separated and detected by nano-LC after their extraction using the same material prepared inside SPE cartridges. The results obtained with carbon nanotube-benzyl polymethacrylate composite monoliths were compared with those of unmodified benzyl polymethacrylate monolith. Finally, the analytical method was validated and the composite materials were tested in analysis of environmental water samples including sea and tap water. So far, the combination of the outstanding advantages of CNTs, monolithic materials and nano-LC technique provided a fast, sensitive, efficient, green and economic method for routine analysis of water samples against PAHs and related pollutants.

## 2. Experimental

### 2.1. Chemicals and water samples

Toluene, NaOH, HCl, 1-propanol and acetic acid were purchased from BDH (Lutterworth, UK). PAHs (naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene and dibenzo(a,h)anthracene) were obtained from Acros Organics (Geel, Belgium) and from Aldrich (Steinheim, Germany). 3-(trimethoxysilyl)propyl methacrylate, ethylene dimethacrylate, benzyl methacrylate, azobis-isobutyronitrile (AIBN) and 1,4-butanediol were acquired from Aldrich (Steinheim, Germany). HPLC grade solvents acetonitrile, acetone, ethanol and hexane were purchased from Fisher Scientific (Leicestershire, UK). Multi-walled carbon nanotubes (95% purity) with 2–5 nm i.d., < 8 nm o.d. and 10–50  $\mu\text{m}$  length were purchased from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). Ultrapure water was produced using Millipore purification system (Milli-Q Advantage Elix, Millipore S.A.S. 67120 Molsheim, France).

Sea water and tap water, as environmental samples were used in this study for evaluation of the prepared SPE cartridges and separation columns. Sea water composite sample was generated by collecting various samples from Al-Dammam coast (Eastern Province of Saudi Arabia) from several locations at various days in brown amber glass bottles.

Tap water samples were taken after flowing for 3 min from various water taps in our college in different days, and then pooled and used to generate a composite water sample. All samples were collected from their sources by filling bottles with water to the top,

small amounts of HCl were added and samples were stored at 5 °C. All analysis was carried out in less than one week from sampling.

## 2.2. SPE cartridges and sample preparation

SPE process was performed using a Visiprep 12-port Vacuum Manifold (Supelco). SPE cartridges were prepared by synthesis of the adsorbents in empty 2 mL glass syringes (Poulten & Graf GmbH, Wertheim, Germany). In order to enhance the attachment of the monoliths with the inner glass wall, the syringes were flushed with acetone, water, 0.20 M NaOH solution (stand for 4 h), water, 0.20 M HCl solution (stand for 4 h), then ethanol. After this treatment, the empty syringes were then filled with 3-(trimethoxysilyl)propyl methacrylate in ethanol 20% (v/v) adjusted to pH 5 using acetic acid solution; they were stored overnight, then rinsed with ethanol and dried.

A polymerization mixture composed of 20% benzyl methacrylate, 12% ethylene dimethacrylate, 38% 1,4-butandiol, 30% 1-propanol and azo-bis-isobutyronitrile initiator (1% with respect to monomers) was incorporated with 3.0 mg mL<sup>-1</sup> CNT (0.3 wt% with respect to monomers). The mixture was homogenized by vortex for 3 min and degassed by purging with nitrogen for 5 min. The glass syringes were filled with the monomeric mixture and subjected to high-power sonication at 40 °C for 10 min. Then the polymerization reaction was completed in an oven at 70 °C for 20 h. As a control cartridge, benzyl methacrylate-co-ethylene dimethacrylate was prepared following the same steps but without incorporated nanotubes. For the reproducibility study, five CNT-benzyl methacrylate-co-ethylene dimethacrylate cartridges were prepared in parallel and used for extraction of PAHs.

After preparation, each SPE cartridge was equilibrated with 5 mL of acetonitrile and water, respectively. 100 mL of the aqueous sample was loaded into the cartridge at a flow rate of about 1.5 mL min<sup>-1</sup>. After washing with 1.0 mL of 5% acetonitrile, the retained compounds were eluted from the cartridge with 1.0 mL acetonitrile. The extract was filtered through a 0.45 µm Millipore syringe membrane. Finally, 4 nL of the eluate was injected into the nano-LC system at optimum conditions for analysis. In order to prepare the cartridge for next extraction, the adsorbent was washed with 5 mL acetonitrile and water, respectively.

## 2.3. Capillary columns preparation and characterization

Fused silica capillary with 0.100 mm i.d. and 0.365 mm o.d. and coated with polyimide was provided from Restek (Bellefonte, USA). The surface modification of the inner surface of the fused-silica capillary was carried out using almost the same previous process. In brief, the fused silica capillary was activated by flushing with acetone, water, 0.20 M NaOH solution, water, 0.20 M HCl solution then ethanol. The fused silica capillary was then flushed for 4 h with 3-(trimethoxysilyl)propyl methacrylate in ethanol 20% (v/v) adjusted to pH 5 using acetic acid solution; then, the capillary was rinsed with ethanol and dried with a stream of highly pure nitrogen.

The monomeric mixture was prepared in the following weight percentages: 24% benzyl methacrylate, 16% ethylene dimethacrylate, and 35% 1,4-butandiol with 25% 1-propanol as porogen and 1% (with respect to monomers) azo-bis-isobutyronitrile initiator. 1.0 mg mL<sup>-1</sup> CNTs (0.1 wt% with respect to monomers) was incorporated to the mixture, which was vortexed, purged with nitrogen for 5 min and subjected to high-power sonication for 10 min at 40 °C. This reaction mixture was then filled in the activated capillary column and both ends were plugged with two pieces of rubber. The polymerization was completed in a water bath at 70 °C for 20 h. Then, both rubber seals were removed; the capillary column was cut to 20 cm length, connected to a nano-LC pump and washed with acetonitrile. A control capillary monolithic column was prepared

with the same monomeric mixture percentages using the same procedure but without incorporated CNTs. Three successive columns were prepared to examine the effect of incorporation percentage on column reproducibility. Hydrodynamic parameters of both separation columns including porosity and permeability were evaluated as described elsewhere [22,24]. Flow method was used to determine the total porosity of the prepared columns; uracil was used as unretained solute in this study. Based on Darcy's equation, column permeability was determined at 0.5 µL min<sup>-1</sup> flow rate using acetonitrile as eluent.

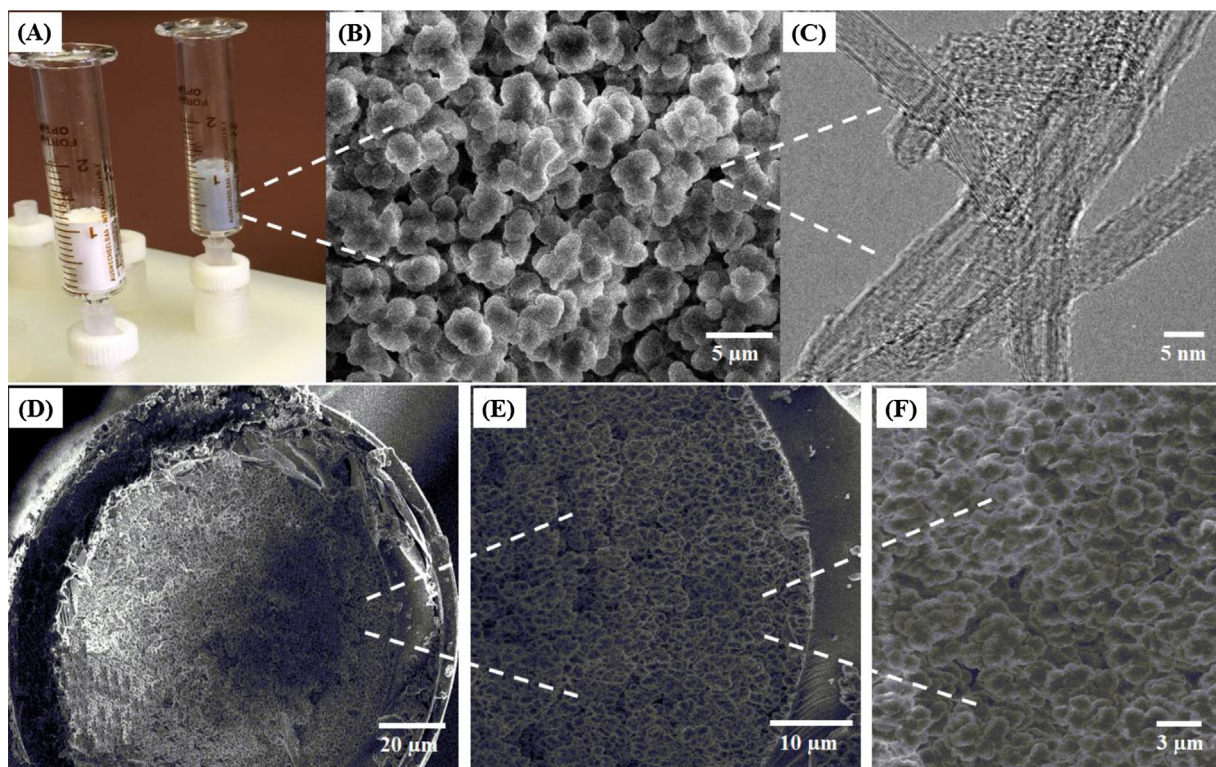
## 2.4. Instrumentation and conditions

All chromatographic experiments were performed with a Thermo Scientific™ UltiMate™ 3000 RSLC nano system (Sunnyvale, CA, USA), equipped with a 3 nL Ultimate 3000 variable wavelength detection cell and an electric actuator external injector with a 4 nL inner sampling loop (Vici Valco, Houston, USA). Simple gradient elution using a water/acetonitrile binary mixture was performed to separate the pollutants. The gradient elution program was as follows: 0 → 3 min (50% acetonitrile), 3 → 8 min (linear gradient 50% → 90% acetonitrile), 8 → 13 min (90% acetonitrile). The flow rate was 0.5 µL min<sup>-1</sup> at a column temperature of 50 °C. The detector wavelength was set at a 230 nm. Chromeleon 7.2 data package was used to control the nano-system and to acquire the chromatographic data. Peak area was used for quantitative evaluations, while each standard or sample was injected three times. Microsoft Office Excel software 2013 package was used for statistical parameters calculations.

The morphologies and structures of the synthesized monoliths were characterized on a Jeol (JSM-6380LA) analytical scanning electron microscope (SEM) at 5 kV and on a Jeol JEM-2100F transmission electron microscope (TEM) at 200 kV (Jeol, Ltd., Japan). For TEM images, the samples were prepared through grinding the CNT-monolith, dispersing it in pure ethanol by sonication and dropping the supernatant onto the copper grid followed by natural drying. Adsorption-desorption isotherm of liquid nitrogen was also used for measurement of the surface areas of the prepared materials using a Gemini VII 2390 surface area analyzer (Micromeritics, Norcross, Georgia, USA) at -196 °C. For this purpose, adsorbent samples corresponding to control cartridge (monolith without CNT), 0.1 and 0.3% CNT-incorporated cartridges were grinded and degassed at 200 °C before the measurements. Thermal stability of the monolithic materials was measured using thermogravimetric analysis (TGA) with a Mettler-Toledo TGA/DSC STARE system (Schwerzenbach, Switzerland). The samples were heated from 20 to 400 °C at a rate of 10 °C min<sup>-1</sup>.

## 2.5. Validation

The prepared cartridges and the proposed method were validated in terms of linearity, precision, sensitivity, repeatability, reproducibility and recovery. Calibration curves were obtained by analyzing 12 concentrations of standard mixtures prepared in HPLC grade acetonitrile, with three replicates at each concentration level. In order to study the method linearity and precision, each solution was injected in three replicates and peak areas were plotted versus the respective concentrations of analytes. The precision of the method in terms of peak area of all solutes was assessed by determining the intraday (three injections) and interday (three consecutive days) relative standard deviations (RSDs). The repeatability and reproducibility of the extraction were estimated in terms of percentage recovery, five parallel-made cartridges were used to evaluate the reproducibility of the method. The sensitivity of the method was evaluated by establishing the limit of detection (LOD) and the limit of quantitation (LOQ) which corresponded to



**Fig. 1.** (A) Photographs of the SPE benzyl methacrylate-co-ethylene dimethacrylate monolith control cartridge (left) and CNT-benzyl methacrylate-co-ethylene dimethacrylate composite monolith cartridge (right). (B) SEM image of the cross section of the CNT-benzyl methacrylate-co-ethylene dimethacrylate monolith. (C) TEM image showing the CNT structure incorporated into polymethacrylate monolith. (D & E) Cross-section SEM images of the prepared capillary column. (F) Bulk region SEM image of the synthesized composite monolith.

the solute concentrations that lead to signal-to-noise ratio of 3:1 and 10:1, respectively. In order to study the efficiency of the extraction at the optimal point, recovery tests were performed using the spiking method for the Milli-Q, sea and tap water samples injected in three replicates.

### 3. Results and discussion

#### 3.1. SPE cartridges preparation and characterization

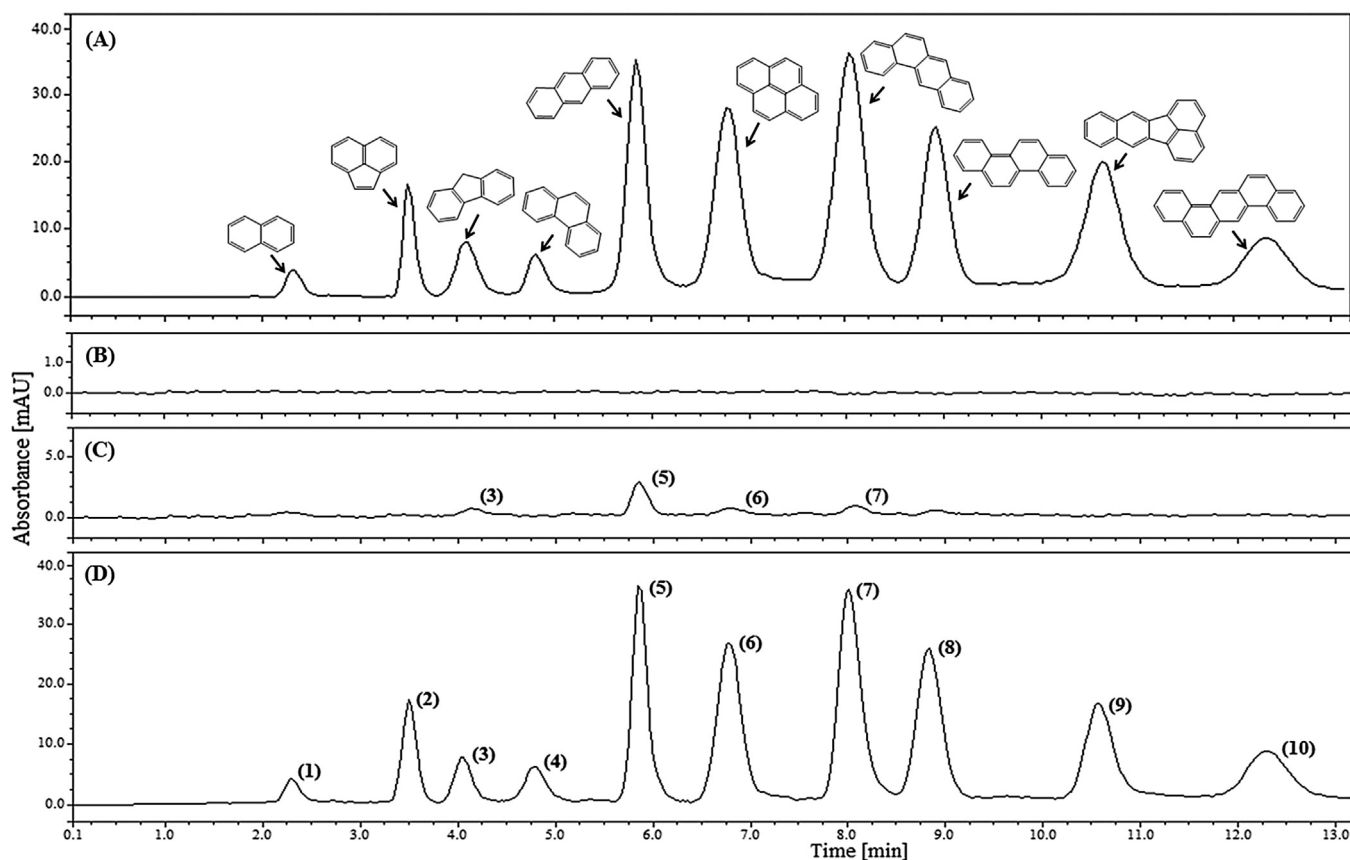
Preparation procedure of both the solid phase adsorbent inside glass syringes and the stationary phase inside capillary columns consists of two main steps: activation of the glass inner surface and *in-situ* polymerization of monomeric mixture in the confines. Various works studied the effect of monomeric mixture composition type and percentages as well as the polymerization conditions on the final morphological properties and performance of the prepared material [23–25].

In this study, a composite adsorbent made of small amount of MWCNTs incorporated to benzyl methacrylate based monolithic polymer was prepared in glass cartridges. The content of MWCNTs in the monomeric mixture composition was set based on previous studies and preliminary experiments [30,31]. In contrast to particulate materials such as silica and carbon, monoliths are not required to be packed since they can be directly synthesized inside the SPE cartridges and attached to their inner glass surface. This could contribute to obtain a more rigid adsorbent and to minimize the voids between the inner surface of the SPE cartridge and the adsorbent. As a control SPE cartridge, benzyl methacrylate-co-ethylene dimethacrylate has been prepared using the same procedure but without incorporated nanotubes. Benzyl methacrylate has benzyl groups which are supposed to provide  $\pi$ - $\pi$  interactions between the adsorbent and aromatic analytes. On the other side, CNTs are

hydrophobic in nature. Under these circumstances, both benzyl methacrylate polymer and CNTs are strong candidates for interacting with most environmental pollutants including PAHs.

Fig. 1(A) displays the SPE cartridges made of benzyl methacrylate-co-ethylene dimethacrylate monolith (white colored monolith) and CNT-benzyl methacrylate-co-ethylene dimethacrylate composite monolith (grey colored monolith). Fig. 1(B) shows the SEM image of the cross section of the CNT-benzyl methacrylate-co-ethylene dimethacrylate monolith. Fig. 1(C) corresponds to the TEM micrograph which characterizes the MWCNTs incorporated into the monolith structure. The presence of nanotubes is mainly dispersed through the monolith and cross the larger bed pores. They contribute to decrease the polymethacrylate monolith channels size, inducing more interaction sites, enhancing the surface area and improving the interaction performance of the final medium. This effect was accompanied by an increase in cartridge resistance to the solvent and sample flow, which, in turn, limits the applicable elution rates. However, this could be compensated by increasing the percentage of porogenic solvents in the monomeric mixture at the expense of monomer and crosslinker contents. On the other side, this is not a big obstacle in the case of liquid chromatography since the nano-LC system could be run under higher pressures, in addition to the ability to reduce the column back pressure by increasing the oven temperature that was set at 50 °C in this work.

The specific surface area of the native nanotubes provided by the supplier is 500 m<sup>2</sup> g<sup>-1</sup>. The values measured for the prepared polymeric materials corresponding to 0 (control monolith), 0.1 and 0.3% MWCNT incorporation using liquid nitrogen physisorption according to the BET method, were 25.63, 38.04 and 55.84 m<sup>2</sup> g<sup>-1</sup>, respectively. Obviously, these results confirmed that incorporation of small amounts of MWCNT into the polymethacrylate monolith induced significant increase of its specific surface area, which is beneficial to the adsorption of PAHs. TGA measure-



**Fig. 2.** (A) Chemical structures and chromatogram of the standards PAH compounds separated at optimum conditions using CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary column. All PAHs ( $100 \mu\text{g L}^{-1}$  for each PAH) detected at UV 230 nm. Typical chromatograms of PAH pollutants using CNT-benzyl methacrylate-co-ethylene dimethacrylate composite monolith in real water samples for (B) blank, (C) SPE of the unspiked sea water, (D) SPE of the spiked sea water. Peaks identification by order of elution: (1) naphthalene, (2) acenaphthylene, (3) fluorene, (4) phenanthrene, (5) anthracene, (6) pyrene, (7) benzo(a)anthracene, (8) chrysene, (9) benzo(k)fluoranthene and (10) dibenzo(a,h)anthracene.

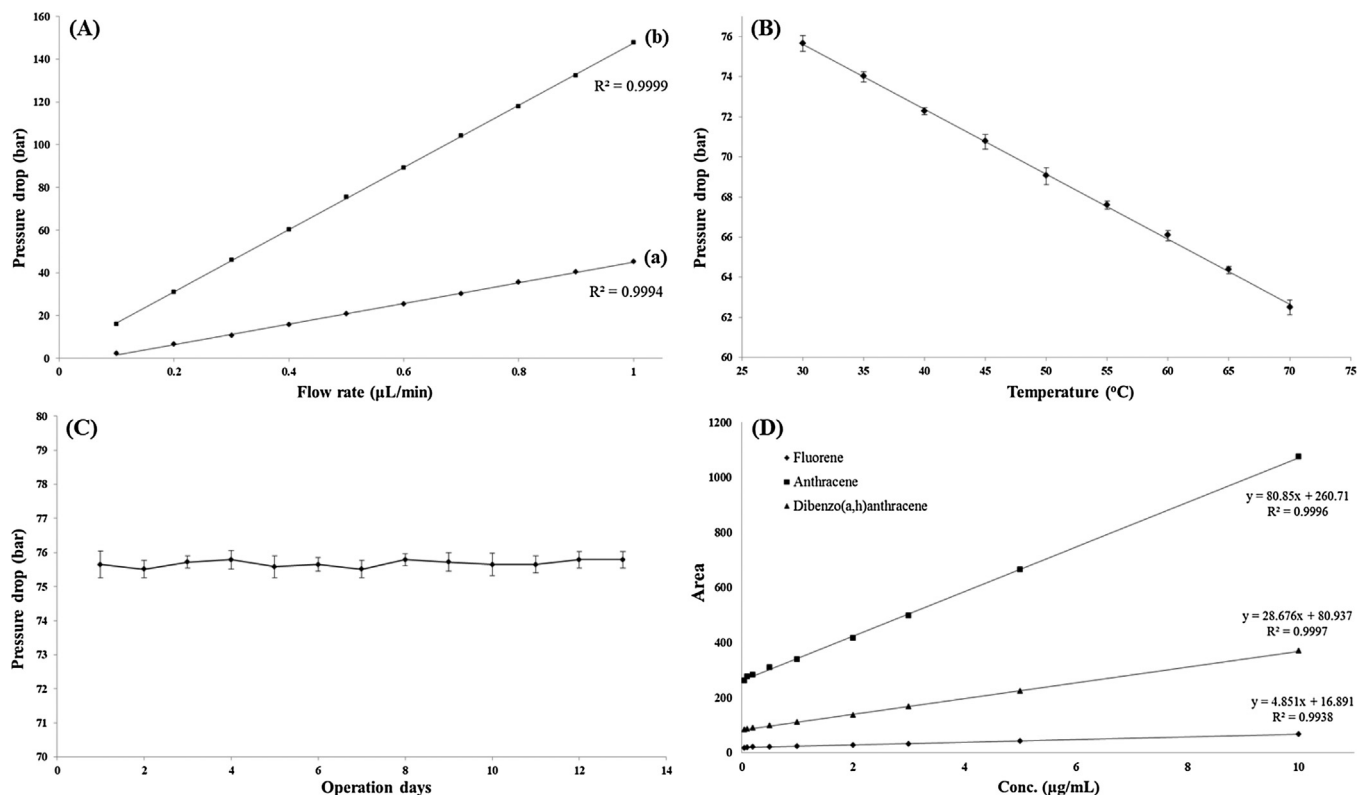
ments indicated that the CNT-benzyl methacrylate-co-ethylene dimethacrylate composite monolith (with 0.3% MWCNT) did not undergo any significant thermal decomposition before  $310^\circ\text{C}$ , while the degradation of unmodified benzyl methacrylate-co-ethylene dimethacrylate monolith started at about  $220^\circ\text{C}$ . This result indicates that the addition of small amounts of nanotubes remarkably enhances the degree of thermal stability for the monolithic composite polymer. It is in agreement with several previous works which demonstrated that addition of carbon nanotubes to various polymers led to improvement in their thermal properties [44–47]. Furthermore, the notable increase in the decomposition temperature observed for our prepared composites can be explained by the fact that MWCNTs are added to the monomeric mixture before polymerization step. This procedure allowed a better dispersion of carbon nanotubes in the composite and resulted in smaller pores with thermally more stable materials. On the other hand, these properties suggest that the prepared monoliths should be promising for future applications in gas chromatography.

### 3.2. Capillary columns preparation and properties

Fig. 1(D & E) show SEM images of the cross section of the CNT-benzyl methacrylate-co-ethylene dimethacrylate capillary column. Fig. 1(F) illustrates the SEM micrograph of bulk region of the synthesized composite monolith. These SEM pictures indicate that the morphology was permeable with a uniform structure and completely linked to the inner capillary wall. The continuous microglobules that appear in the figures have an approximate diameter in the range of  $1\text{--}2 \mu\text{m}$ . To explore the effect of CNT

incorporation into the polymethacrylate monolith for separation of PAHs, a comparative study was performed between the control (no MWCNTs) and the composite (0.1% MWCNTs) capillary columns to separate the aromatic mixture. Both columns have been pushed to their optimum chromatographic performance. While the control column failed to separate the ten analytes completely under various isocratic and gradient elution trials, the ten PAHs were totally separated with suitable resolution values ( $R_s = 1.74\text{--}3.98$ ) in about 13 min at  $0.5 \mu\text{L min}^{-1}$  flow rate using gradient conditions at  $50^\circ\text{C}$  on the CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary monolithic column. Fig. 2(A) shows the typical separation chromatogram for PAH compounds at optimum chromatographic conditions. The enhancement in separation efficiency is probably due to the smaller pores introduced by the addition of CNTs and the higher specific surface area of the composite compared to the native monolith. However, the presence of benzyl group within the monolith structure also had an important role in the separation of the PAHs through the strong  $\pi\text{--}\pi$  interactions. While the performance in terms of the number of theoretical plates for the column with no CNTs exhibited an efficiency not exceeding  $7200 \text{ plates m}^{-1}$ , the efficiency obtained for CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary column was in the range between  $11,500 \text{ plates m}^{-1}$  for naphthalene and  $41,700 \text{ plates m}^{-1}$  for chrysene at optimum conditions.

The stability of the prepared capillary columns was also evaluated. Fig. 3(A–C) illustrates back pressure as a measure of columns stability versus acetonitrile flow rate, operation days and temperature, respectively. Acetonitrile was used as eluent for the measurement of the pressure drop across the column at differ-



**Fig. 3.** (A) Columns back pressure as a function of acetonitrile flow rate curves of (a) benzyl methacrylate-co-ethylene dimethacrylate control column and (b) CNT-benzyl methacrylate-co-ethylene dimethacrylate composite monolithic column. (B) Back pressure as a measure of the composite column stability versus temperature. (C) Back pressure versus operation days for CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary column. (D) External calibration curves of fluorene, anthracene and dibenzo(a,h)anthracene compounds using a CNT-benzyl methacrylate-co-ethylene dimethacrylate composite column at optimum chromatographic conditions.

ent flow rates ranging from 0.10 to 1.0  $\mu\text{L}/\text{min}$ . Fig. 3(A) shows a directly proportional relationship between the acetonitrile flow rate and columns pressure drop at 30  $^{\circ}\text{C}$  for the control and composite (0.1% MWCNTs) capillary columns. A linear dependence with regression factors 0.9994 and 0.9999 indicates excellent permeability and mechanical stability for both columns. As demonstrated in Fig. 3(B) for the composite capillary columns, an inversely proportional linear relationship was obtained for the temperature versus the pressure drop curve, using acetonitrile as mobile phase at 0.5  $\mu\text{L}/\text{min}$  flow rate over a temperature range from 30 to 70  $^{\circ}\text{C}$ . The significant reduction in the column back pressure with the increasing temperature is due to the reduction of the mobile phase viscosity.

A stability study was also performed on a CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary column to investigate its repeatability and durability over 13 successive days. As shown in Fig. 3(C), the composite column also exhibits very good pressure drop stability over the operating days at the same flow rate of 0.5  $\mu\text{L}/\text{min}$  using acetonitrile as a mobile phase at 30  $^{\circ}\text{C}$ . The linear dependence of the CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary column back pressure versus eluent flow rate, temperature and over successive operation days confirms that there is no bleeding of the CNT from the column and indicating the excellent stability of the CNT-benzyl methacrylate-co-ethylene dimethacrylate stationary phase inside the capillary tubes.

The permeability of the two capillary columns was determined using acetonitrile as mobile phase through the columns at a volumetric flow rate of 0.5  $\mu\text{L}/\text{min}$ . The permeability values of the prepared columns were  $2.55 \times 10^{-14}$  and  $6.51 \times 10^{-15} \text{ m}^2$  corresponding to the measured pressure drop of 20.96 and 75.57 bar for benzyl methacrylate-co-ethylene dimethacrylate and CNT-benzyl

methacrylate-co-ethylene dimethacrylate columns, respectively. On the other hand, the total porosity values were 0.74 and 0.68 for benzyl methacrylate-co-ethylene dimethacrylate and CNT-benzyl methacrylate-co-ethylene dimethacrylate columns, respectively; they were calculated using uracil as unretained solute. Three successive columns were prepared with the same composition in order to evaluate the reproducibility of the proposed procedure. The %RSD in terms of column porosity and permeability were less than 6.4% ( $n=3$ ) and 10.2% ( $n=3$ ). As expected, addition of a small amount of CNTs to the monomeric mixture exhibited lower permeability and porosity values and higher column back pressure. Both permeability and porosity values of the prepared columns are in good agreement with that published previously for polymethacrylate based monolithic capillary columns [24,30,31].

### 3.3. PAHs analysis and method validation

The influences of mobile phase flow rate, gradient mobile phase composition and column temperature on the separation of the ten PAHs were examined to reach a good compromise between run time and peak resolution. The sample injection volume was fixed at 4 nL using an external automatic injector. Fig. 2(A) represents the typical separation chromatogram of the PAHs. At optimum chromatographic conditions, the ten pollutants were completely separated with an acceptable resolution in about 13 min at 0.5  $\mu\text{L}/\text{min}$  flow rate using CNT-benzyl methacrylate-co-ethylene dimethacrylate composite capillary monolithic column. The detector wavelength was set at 230 nm to obtain the highest intensity and lowest detection limit for all compounds.

In order to validate the suitability of the prepared column for determination of PAH compounds, the developed chromatographic method was validated in terms of linearity, limit of detection and

**Table 1**  
Analytical parameters of the developed method.

PAH	Regression equation	Range ( $\mu\text{g L}^{-1}$ )	R <sup>2</sup>	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )
Naphthalene	$y = 0.395x + 9.047$	5–500	0.9955	0.22	0.6
Acenaphthylene	$y = 7.634x + 17.523$	2–500	0.9963	0.055	0.15
Fluorene	$y = 4.851x + 16.891$	5–500	0.9938	0.1	0.3
Phenanthrene	$y = 0.845x + 11.623$	5–500	0.9981	0.14	0.45
Anthracene	$y = 80.85x + 260.71$	1–500	0.9996	0.02	0.06
Pyrene	$y = 82.73x + 206.097$	1–500	0.9990	0.03	0.1
Benzo(a)anthracene	$y = 104.02x + 412.11$	1–500	0.9993	0.025	0.08
Chrysene	$y = 48.006x + 106.93$	1–500	0.9985	0.035	0.1
Benzo(k)fluoranthene	$y = 53.743x + 93.46$	2–500	0.9996	0.046	0.15
Dibenzo(a,h)anthracene	$y = 28.676x + 80.937$	5–500	0.9997	0.11	0.35

quantitation, precision and recovery. Calibration curves were plotted by injecting 12 concentrations of standard mixtures, with three replicates at each concentration level. A wide linear range for PAHs was obtained with correlation coefficients higher than 0.9938. When peak areas were used for signal evaluation, the developed method was found to be linear in the following dynamic concentration ranges: 5–500  $\mu\text{g L}^{-1}$  for naphthalene, fluorene, phenanthrene and dibenzo(a,h)anthracene, 2–500  $\mu\text{g L}^{-1}$  for acenaphthylene and benzo(k)fluoranthene, and 1–500  $\mu\text{g L}^{-1}$  for other aromatic hydrocarbons. As examples, the external calibration curves of fluorene, anthracene and dibenzo(a,h)anthracene are shown in Fig. 3(D), while the whole calibration curves data for the ten pollutants are presented in Table 1.

The precision of the method in terms of peak area was checked by calculating the intraday ( $n = 3$ ) and interday ( $n = 3$ ) RSDs. As an example, the intraday and interday RSDs values for anthracene were 1.3% and 4.2%, respectively, and below 5.1% for all solutes. All precision values confirmed that the developed assay has a good precision. The sensitivity was evaluated by the LOD and the LOQ based on the signal/noise ratios criteria. The respective values for LODs and LOQs were in the range of 0.02–0.22  $\mu\text{g L}^{-1}$  and 0.06–0.6  $\mu\text{g L}^{-1}$ , respectively. The values of LOD and LOQ for all investigated PAHs are summarized in Table 1.

For the repeatability and reproducibility tests, one CNT-benzyl methacrylate-co-ethylene dimethacrylate cartridge was used for extraction of a water sample spiked with 1.0  $\mu\text{g L}^{-1}$  PAHs for three replicates under the same conditions. The obtained RSDs expressed in terms of PAHs percentage recovery were 3.0% for anthracene and less than 6.4% for all analytes. On the other hand, five parallel-made SPE cartridges of CNT-benzyl methacrylate-co-ethylene dimethacrylate composite were used to detect 1.0  $\mu\text{g L}^{-1}$  PAHs spiked in Milli-Q water sample. The RSD values were 9.8% for anthracene and below 12.6% for all solutes, indicating a satisfactory reproducibility. All these results gave evidence to demonstrate that the prepared SPE cartridges and the proposed chromatographic method were unbiased and could be applied to investigate real environmental water samples.

#### 3.4. Extraction efficiency and water samples analysis

The prepared cartridges and developed method were applied for the extraction and analysis of ten PAHs in two real environmental water samples including tap and sea water. No signal corresponding to any of the ten PAHs was detected in the tap water sample according to our procedure. On the other hand, investigation of the same pollutants in sea water showed presence of fluorene, anthracene, pyrene and benzo(a)anthracene, with trace amounts of naphthalene and chrysene. As listed in Table 2, the concentrations of these pollutants in sea water were found to be 0.86, 0.64, 0.14 and 0.19  $\mu\text{g L}^{-1}$  for fluorene, anthracene, pyrene and benzo(a)anthracene, respectively. According to the EPA, the detected concentrations are higher than the MCLs admitted for

**Table 2**  
Determination of PAHs in environmental water samples.

Pollutant	Residue level ( $\mu\text{g L}^{-1}$ ) (% RSD, $n = 3$ )	
	Tap water	Sea water
Naphthalene	ND <sup>a</sup>	Trace <sup>b</sup>
Acenaphthylene	ND	ND
Fluorene	ND	0.86 (3.2)
Phenanthrene	ND	ND
Anthracene	ND	0.64 (5.8)
Pyrene	ND	0.14 (6.1)
Benzo(a)anthracene	ND	0.19 (4.4)
Chrysene	ND	Trace
Benzo(k)fluoranthene	ND	ND
Dibenzo(a,h)anthracene	ND	ND

<sup>a</sup> ND: non-detected (not present or less than the LOD).

<sup>b</sup> Trace:  $\text{LOD} \leq \text{result} < \text{LOQ}$ .

PAHs in drinking water [5]. The chromatograms of the blank, unspiked and spiked sea water samples extracted using the CNT-benzyl methacrylate-co-ethylene dimethacrylate SPE cartridge are shown in Fig. 2(B–D).

The applicability and reliability of the prepared SPE cartridges and separation columns, and the developed method for the analysis of PAH pollutants in water samples were demonstrated by evaluation of recovery. For this purpose, 100 mL of each aqueous solution containing the spiked PAHs were extracted by 1.0 mL HPLC grade acetonitrile; then, 4 nL of each extracted sample were injected into the nano-LC system operated under the optimum conditions. According to this extraction procedure, the theoretical preconcentration factor is equal to 100 and the targeted concentration for each pollutant corresponds to 100  $\mu\text{g L}^{-1}$ . The typical chromatogram of the spiked sea water sample pretreated with the CNT-benzyl methacrylate-co-ethylene dimethacrylate SPE cartridge is shown in Fig. 2(D).

The recovery percentage values for all studied compounds extracted with the CNT-benzyl methacrylate-co-ethylene dimethacrylate adsorbent ranged between 81.3–95.4% in Milli-Q, tap and sea water samples. In comparison with the PAHs extracted with the benzyl methacrylate-co-ethylene dimethacrylate control SPE cartridge, the recovery percentages using CNT-benzyl methacrylate-co-ethylene dimethacrylate cartridge have been improved by a factor 48.6–78.4%. The total extraction efficiency values of both adsorbents in Milli-Q water are compared in Table 3. The recovery percentage values CNT-benzyl methacrylate-co-ethylene dimethacrylate adsorbent demonstrate good extraction efficiencies. The respective values of %RSD performed in three extraction replicates were <6.4% for Milli-Q water, <6.0% for tap water and <5.2% for sea water. %RSD results indicate that the precision was satisfactory at this concentration level. Results of recovery percentages and %RSD values of the ten PAH compounds in Milli-Q and real water samples are presented in Table 3. The data indicated that the prepared adsorbents and proposed SPE

**Table 3**  
Recovery (%) and method precision (%RSD, n = 3).

PAH	Recovery (%) (% RSD, n = 3)			
	Control cartridge	CNTs-incorporated cartridge		
	Milli-Q water	Milli-Q water	Tap water	Sea water
Naphthalene	47.2 (3.2)	83.3 (6.4)	85.6 (4.8)	82.2 (5.2)
Acenaphthylene	59.6 (4.6)	90.5 (5.2)	92.6 (5.8)	90.2 (4.2)
Fluorene	48.4 (6.2)	82.7 (4.8)	81.3 (5.3)	81.8 (4.5)
Phenanthrene	61.8 (6.1)	93.5 (6.4)	90.2 (3.4)	88.7 (5.0)
Anthracene	64.2 (3.5)	95.4 (3.0)	94.7 (4.2)	94.3 (2.3)
Pyrene	52.0 (2.2)	89.5 (2.4)	87.3 (6.0)	85.5 (4.7)
Benzo(a)anthracene	51.0 (6.2)	87.4 (4.1)	85.6 (5.5)	85.7 (4.6)
Chrysene	57.3 (5.2)	91.6 (3.2)	90.7 (4.7)	89.3 (3.2)
Benzo(k)fluoranthene	49.5 (5.7)	88.3 (3.6)	90.2 (4.7)	88.7 (3.6)
Dibenzo(a,h)anthracene	57.9 (6.3)	93.8 (2.1)	91.6 (3.0)	93.9 (2.6)

**Table 4**  
Comparison of the proposed method with other extraction methods for the determination of PAHs in water samples.

Adsorbent	HPLC column (length × diameter) and detection technique	Number of targeted PAHs	Dynamic range ( $\mu\text{g L}^{-1}$ )	LOD ( $\mu\text{g L}^{-1}$ )	Recovery (%)	Run time (min)	Mobile phase consumption (mL/h)	Ref.
Stir plate sorptive coated with PDMS/ $\beta$ -CD/divinylbenzene	Lichrospher ODS (200 × 4.6 mm, 5 $\mu\text{m}$ ), FL	6 PAHs	0.001–1	0.001–0.003	88–110	25	60	[10]
Graphene functionalized silica gel	Eclipse XDB-C18 (150 × 4.6 mm, 5 $\mu\text{m}$ ), UV	6 PAHs	0.01–600	0.003–0.05	89.0–115.4	26	30	[11]
MWCNTs, off/on-site $\mu$ -SPE	Zorbax SB-C18 (100 × 2.1 mm, 3.5 $\mu\text{m}$ ), UV	5 PAHs	0.1–100	0.014–0.59	77.3–107.2	8	12	[48]
BakerBond SPE C18	Supelcosil LC-PAH (250 × 2.1 mm, 5 $\mu\text{m}$ ), FL	16 PAHs	5–100	0.008–0.17	67.4–91.5	32	24	[49]
Stir bar sorptive coated with PDMS	H5-ODS C18 (150 × 4.6 mm, 5 $\mu\text{m}$ ), UV	5 PAHs	0.02–400	0.007–0.01	84.4–98.0	19	48	[50]
Magnetic nanoparticles-nylon 6 composite	Acquity UPLC BEH C18 (50 × 2.1 mm, 1.7 $\mu\text{m}$ ), UV	4 PAHs	1–50	0.05–0.58	80–111	4.5	30	[51]
Sulfur microparticles	Nucleosil LC-PAH (250 × 4.6 mm, 5 $\mu\text{m}$ ), UV	10 PAHs	0.05–80.0	0.007–0.048	78–108	21.5	90	[52]
Copper(II) isonicotinate	Zorbax SB-C18 5 (150 × 4.6 mm, 5 $\mu\text{m}$ ), UV	8 PAHs	0.005–4.8	0.002–0.014	–	20	60	[53]
MWCNTs	C18 column (250 × 4.6 mm, 5 $\mu\text{m}$ ), UV	10 PAHs	0.04–100	0.005–0.058	78.7–118.1	33	60	[54]
Bis-(2,4,4-trimethylpentyl)-dithiophosphinic acid on $\text{Fe}_3\text{O}_4$ @Ag core@shell nanoparticles	ODS-3 (125 × 4.0 mm, 3 $\mu\text{m}$ ), UV	5 PAHs	0.05–100	0.02–0.1	95.2–109.0	14	48	[55]
$\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ -MIL-101	C18 (150 × 4.6 mm, 5 $\mu\text{m}$ ), UV	6 PAHs	0.001–250	0.003–0.03	81.3–105	16	60	[56]
Ionic liquid-coated $\text{Fe}_3\text{O}_4$ nanoparticles	Ultimate XB-C18 (250 × 4.6 mm, 5 $\mu\text{m}$ ), FL	6 PAHs	0.001–1.25	0.0003–0.008	73–104	19	60	[57]
Mixtures of polyoxyethylene-10-lauryl ether with non-ionic surfactants Triton X-114 and Brij 30	Vydac201TP54-C18 (250 × 4.6 mm, 5 $\mu\text{m}$ ), FL	13 PAHs	0.3–80	0.023–0.23	72–98.8	31	60	[58]
Cetyltrimethylammonium bromide modified $\text{TiO}_2$ nanotube arrays	SunFire C18 (150 × 4.6 mm, 5 $\mu\text{m}$ ), UV	16 PAHs	0.2–100	0.026–0.82	75–114	53	60	[59]
Barium alginate caged $\text{Fe}_3\text{O}_4$ @C18 magnetic nanoparticles	Diamonsil C18 (250 × 4.6 mm, 5 $\mu\text{m}$ ), FL	8 PAHs	0.01–20	0.002–0.059	72–108	35	60	[60]
$\text{Fe}_3\text{O}_4$ /graphene oxide nanocomposites	UltimateXB-C18 (250 × 4.6 mm, 5 $\mu\text{m}$ ), UV	5 PAHs	0.5–100	0.09–0.19	76.8–101.2	16.5	60	[61]
CNT-poly(benzyl methacrylate)	CNT-poly(benzyl methacrylate) (200 × 0.1 mm), UV	10 PAHs	1–500	0.02–0.22	81.3–95.4	13	0.03	this work



method could be used for simple extraction of PAHs pollutants and in the analysis of real environmental water samples.

### 3.5. Comparison with previously published methods

In order to evaluate the method performance, the characteristics of the proposed method have been compared with other methods, which were used for the extraction and determination of PAHs (Table 4). For convenience, the developed method was compared with different reported analytical approaches for extraction of PAHs from environmental water samples using various solid adsorbents followed by HPLC analysis. Although some of the new approaches show better sensitivity, the LODs and percentage recovery values obtained with the CNT-poly(benzyl methacrylate) as adsorbent were comparable to most other solids. This fact can be ascribed to the use of fixed UV wavelength (230 nm) as detection technique instead of fluorescence detector or multiple UV wavelengths detection with time. For example, Huang et al. have demonstrated that fluorescence detector provides LODs values 95–100 times lower than UV for the determination of the PAHs [62]. On the other side, the present method shows some advantages, such as wider linear dynamic ranges and shorter separation time. In general, monolithic columns have higher porosity and permeability compared to the particulate ones, which contributes to reduce the analysis time and to decrease the column backpressure [15,17].

As it can be seen in Table 4, the main advantage of the presently described method is the solvent consumption which is notably lower with capillary scale columns (0.03 mL/h) than with commercial packed columns (from 12 to 90 mL/h). In addition, it requires smaller sample injection volumes, 4 nL in comparison with 5–20  $\mu$ L for conventional columns. Moreover, the preparation of capillary monolithic columns needs only small amounts of chemicals. As a result, the amount of toxic wastes generated using this method is very trivial relative to other works, which makes this procedure easy, convenient, cheap and environmentally friendly.

## 4. Conclusions

Because of the high maturity, availability and versatility of the silica and carbon based particulate materials, few quantitative application studies have been developed using monoliths in spite of their promising characteristics. In the present work, a composite of CNT-benzyl methacrylate-co-ethylene dimethacrylate monolith was fabricated, characterized and used as a SPE adsorbent and as a chromatographic stationary phase. The composite was successfully applied for extraction and separation of ten PAHs, then determination of these pollutants in environmental water samples by nano-LC technique. The whole optimized process showed an acceptable precision, low detection and quantitation limits, good reproducibility, satisfactory extraction recovery and wide dynamic linear range. Under the optimum conditions of extraction and chromatographic procedures, the detection limits values obtained for the ten PAHs were lower than the MCLs set by the EPA for drinking water. The performance of monolithic materials can be still improved, and more investigations are needed to enhance the efficiency and applicability of these promising structures. Beside their application in nano-LC, porous monoliths with incorporated CNTs could be very useful as GC stationary phases, since they exhibit enhanced thermal stability compared to other monoliths. In other scenario, CNTs could be functionalized and used together with monoliths for more specific extractions. The obtained results show that the validated method is suitable to be used as a reliable and routine tool for quantifying PAHs in water samples.

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