



Facile and rapid preparation of magnetic octadecylamine nanocomposite and its application as a capable adsorbent in magnetic dispersive solid phase extraction of some polycyclic aromatic hydrocarbons from wastewater samples

Mir Ali Farajzadeh^{1,2} · Nasim Fazli¹ · Sakha Pezhhanfar¹ · Mohammad Reza Afshar Mogaddam^{3,4}

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Abstract

In this research, modified magnetic nanoparticles were prepared to be served as a magnetic dispersive solid phase extraction adsorbent for the simultaneous extraction and preconcentration of some polycyclic aromatic hydrocarbons from different wastewater samples. This method was followed by a dispersive liquid–liquid microextraction procedure to achieve high sensitivity and enrichment factors. Ultimately, the analytes were analyzed by gas chromatography–flame ionization detection. The adsorbent was the octadecylamine co-precipitated by Fe_3O_4 which exhibited high adsorption capability towards the target compounds. The developed process was performed by dispersion of the octadecylamine@ Fe_3O_4 nanoparticles into an aqueous sample solution containing the target analytes by vortexing. Then, the magnetic adsorbent was collected by applying an external magnetic field followed by adding acetonitrile to elute the analytes from the adsorbent by vortexing for a few minutes. By utilizing an external magnet once again, the adsorbent was separated and the attained eluent was mixed with an extraction solvent at μL -level and speedily injected into deionized water. After centrifugation, an aliquot of the sedimented phase was injected into the separation system. The experimental parameters of both steps were investigated and optimized. Under the optimized extraction conditions, the proposed method provided low limits of detection (0.11 – $0.30 \mu\text{g L}^{-1}$) and quantification (0.40 – $1.0 \mu\text{g L}^{-1}$), and satisfactory precision with relative standard deviations in the ranges of 2–5% for intra- ($n=6$) and 3–6% for inter-day ($n=4$) precisions. Satisfactory extraction recoveries and high enrichment factors were obtained in the ranges of 63–84% and 506–676, respectively. The performance and results of this research unfold that the developed method is easy, practical, highly efficient, precise, and rewarding as the environmental perspective.

Keywords Magnetic dispersive solid phase extraction · Dispersive liquid–liquid microextraction · Gas chromatography · Polycyclic aromatic hydrocarbons · Octadecylamine@ Fe_3O_4 · Wastewater

Abbreviations

DLLME Dispersive liquid–liquid microextraction
EF Enrichment factor
ER Extraction recovery

FID Flame ionization detection
GC Gas chromatography
LOD Limit of detection
LOQ Limit of quantification
MDSPE Magnetic dispersive solid phase extraction
PAHs Polycyclic aromatic hydrocarbons
RSD Relative standard deviation

✉ Mir Ali Farajzadeh
mafarajzadeh@yahoo.com; mafarajzadeh@tabrizu.ac.ir

- ¹ Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, Iran
- ² Engineering Faculty, Near East University, 99138 Nicosia, North Cyprus, Mersin 10, Turkey
- ³ Pharmaceutical Analysis Research Center, Tabriz University of Medical Sciences, Tabriz, Iran
- ⁴ Food and Drug Safety Research Center, Tabriz University of Medical Sciences, Tabriz, Iran

Introduction

The term of polycyclic aromatic hydrocarbons (PAHs) covers a wide range of potent carcinogenic compounds defined to be comprised of two or more fused aromatic rings (Brazkova and Krastanov 2013; Manousi and Zachariadis 2020).

These compounds are prevailing environmental contaminants that are propounded by products of the incomplete combustion of organic substances such as wood, coal, petroleum, and fossil fuels (Zhang et al. 2006). Both natural and anthropogenic activities, urban runoff, industrial processes, exhaust fumes, and wastewaters are different sources of PAHs in the environment that spread over wide areas (Srivastava et al. 2018). It has been postulated that long-term exposure to PAHs is dramatically linked to human health threats such as lung and bladder cancers, reproductive abnormalities, DNA damage, and cardiopulmonary mortality (Kuo et al. 2003; Srogi 2007; Kim et al. 2013). To sum up, considering the biological stability and bioaccumulation risk of these compounds, development of a quick, sensitive, and simple analytical method for monitoring and determination of PAHs in various industrial and environmental wastewaters is highly demanded (Bai et al. 2010; Ma et al. 2010; Ghasemi and Zolfonoun 2013). Up to now, gas chromatography (GC) (Tian et al. 2017) and high performance liquid chromatography (Zhao et al. 2013) were the most successively used analytical instruments for analysis of PAHs. Nevertheless, due to the complexity of sample matrices, endogenous interferences, and also trace levels of PAHs, high proficiency clean up, extraction, and enrichment procedures are needed prior to their analysis (Olatunji et al. 2014; Ishizaki et al. 2010). Recently, magnetic dispersive solid phase extraction (MDSPE) was used as a new form of dispersive solid phase extraction method based on magnetic particles for the extraction and preconcentration of trace analytes (Zhang et al. 2017). In this method, a magnetic adsorbent is dispersed directly into an analyte-containing aqueous solution. After adsorption of the analytes onto the adsorbent, it is separated from the suspension using an external magnetic field and subsequently the supernatant is discarded. By adding an elution solvent the analytes are desorbed from the surface of adsorbent. Compared to the conventional procedures, using magnetic adsorbents makes the sample pretreatment method simple, rapid, and cost-effective because there is no need for some time-consuming stages such as filtration or centrifugation. Low consumption of organic solvents has also great importance from the aspect of green chemistry (Asfaram et al. 2020). In addition, the developed method which is a forward-looking technique for sample preparation thanks to the use of magnetic nanoparticles (MNPs) can be proficient, stable, time-consuming, and also cost-effective (Soylak et al. 2010). Among different MNPs, magnetite (Fe_3O_4) is the most commonly preferred compound due to its environmentally friendly behavior, highly magnetic property, high-yield synthesis process, favorable morphology, and large surface area due to its nanostructure (Aguilar-Arteaga et al. 2010; Hemmati et al. 2018; Mirzaei et al. 2020; Nejad et al. 2019). But oxidation and low adsorption capability of these naked MNPs impede the accurate

processing of them and to avoid these phenomena and also to preserve and enhance their stability, they are usually coated with several materials such as silica (Farajzadeh et al. 2019), carbon nanotubes (Rastkari and Ahmadvaniha 2013), octadecyl (Liu et al. 2009; Synaridou et al. 2014), etc. Among the mentioned coating materials, C_{18} modified MNPs offer outstanding points such as excellent stability, long life-time, nontoxicity, and ultimately proposing a fast, feasible, convenient, and highly efficient extraction process (Wang et al. 2012; Katsumata et al. 2006). Moreover, in order to achieve high sensitivity and high enrichment factors (EFs), implementation of dispersive liquid microextraction (DLLME) after MDSPE is recommended (Wu et al. 2019). DLLME is a developed method offering several advantages including easiness, usefulness, high EFs, and good precision. In addition, less solvent-consumption and low cost made it as a very popular sample preparation method. This method can be modified handily and combined with other sample preparation techniques (Rezaee et al. 2006; Zgoła-Grześkowiak and Grześkowiak 2011).

The aim of this study was to find an effective, reliable, and facile analytical method for monitoring and determination of PAHs in industrial and environmental wastewater samples. For this purpose, a combination of MDSPE based on new MNPs and DLLME was developed and optimized. To gratify the qualification of magnetic separation, Fe_3O_4 particles were selected as the magnetic core and octadecylamine was chosen as the modifier. The utilized magnetic octadecylamine nanoparticles were prepared by co-precipitation method which has high and scalable reaction yield. The obtained results point that MDSPE based on octadecylamine@ Fe_3O_4 combined with DLLME coupled to GC-flame ionization detection (FID) is a persuasive and quick method for PAHs analysis in wastewater samples.

Experimental

Chemicals and solutions

The studied PAHs consisting of acenaphthene, phenanthrene, anthracene, pyrene, acenaphthylene, and benzo[a]pyrene were obtained from Merck (Darmstadt, Germany). Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), octadecylamine, and ammonia solution (25%, w/w) used in preparation of the adsorbent were also purchased from Merck. Acetonitrile (ACN), acetone, methanol (Merck) and iso-propanol (Caledon, Canada) were tested for desorption of the selected analytes in MDSPE and as the disperser solvents in DLLME. The extraction solvents used in DLLME including 1,2-dibromoethane (1,2-DBE), chloroform, carbon tetrachloride, 1,1,1-trichloroethane (1,1,1-TCE), and 1,1,2-trichloroethane

(1,1,2-TCE), all analytical grade, were acquired from Janssen (Beerse, Belgium). Sodium hydroxide, sodium sulfate, hydrochloric acid (37%, w/w), sodium chloride, and sodium nitrate were from Merck. A mixture stock solution of the selected PAHs at a concentration of 100 mg L⁻¹ (each analyte) was prepared in ACN. This solution was diluted with deionized water to prepare working standard solutions.

Samples

Several wastewaters including pharmaceutical, mine, petrochemical, and refinery wastewaters were obtained from Dana Pharmaceutical Company (Tabriz, Iran), Sungun copper mine (Ahar, East Azarbaijan, Iran), Tabriz Petrochemical Company (Tabriz, Iran), and Tabriz Refinery (Tabriz, Iran), respectively. Other aqueous solutions including municipality wastewater and fountain water (Tabriz, Iran) were also investigated.

Apparatus

All chromatographic measurements were carried out with a Shimadzu 2014 gas chromatograph equipped with a split/splitless injector (used in a splitless/split mode, split ratio of 1:10 min, and sampling time of 1 min) and an FID set at 300 °C. Separation of the selected PAHs was carried out on a Zerbon™ capillary column (95% dimethyl, 5% diphenyl poly siloxane, 30 m × 0.25 mm i.d., and a film thickness of 0.25 μm) (Phenomenex, Torrance, CA, USA). Helium (99.999%, Gulf Cryo, United Arab Emirates) was utilized as carrier and make up gases at a linear velocity of 30 cm s⁻¹ and flow rate of 30 mL min⁻¹, respectively. The initial column oven temperature was set at 100 °C for 3.0 min, elevated to 300 °C at a rate of 13 °C min⁻¹, and retained at 300 °C for 10 min. The provision of hydrogen as the fuel for FID was done by a hydrogen generator (OPGU-1500S, Shimadzu, Japan) at a flow rate of 30 mL min⁻¹. Also, the needed air as an oxidant for FID was supplied at a flow rate of 300 mL min⁻¹. Phase separation was carried out by a Hettich centrifuge model D-7200 (Tuttlingen, Germany) and an L46 vortex (Labinco, Breda, the Netherlands) was utilized for vortexing. All pH adjustments of aqueous solutions were performed using a Metrohm pH meter (model 654, Herisau, Switzerland). A magnetic heater stirrer (Heidolph MR 3001 K, Germany) was used in the adsorbent preparation step. X-ray diffraction (XRD) pattern of the prepared adsorbent was recorded by an X-ray diffractometer (Siemens AG, Karlsruhe, Germany). It was performed in the range of 4–73° operated at a voltage of 35 kV. Surface morphology and size of MNPs were studied by scanning electron microscopy (SEM) (Tescan, Czech) and the elemental analysis of the adsorbent was investigated by an energy dispersive X-ray (EDX) spectrometer (Tescan, Brno, Czech). Evaluating

magnetic property of the prepared adsorbent was done by a Lake Shore 7304 vibrating sample magnetometer (VSM) (Lakeshore, USA). Fourier transform infrared (FTIR) spectrum was recorded by a Bruker FTIR spectrophotometer (Billerica, USA).

Preparation of sorbent

The magnetic octadecylamine nanocomposite (octadecylamine@Fe₃O₄) was prepared by a chemical co-precipitation method. Briefly 100 mg of octadecylamine was added to 50 mL sulfuric acid solution (2 mol L⁻¹). In order to dissolve octadecylamine, temperature of the mixture was adjusted at 80 °C and stirred at a rate of 300 rpm for 20 min. After obtaining a clear solution, 0.53 g of FeCl₃·6H₂O and 0.36 g of FeSO₄·7H₂O were added to the solution. Afterward, 20 mL concentrated ammonia solution was added dropwise until emerging stable brownish color that is an indication of the generation of Fe₃O₄ nanoparticles. During the whole process, the solution temperature was maintained at 80 °C and it was stirred at 300 rpm. After 2 h, the produced MNPs were separated in the presence of an external magnet and washed with a mixture of deionized water: ethanol (50:50, v/v) and finally dried at room temperature.

Extraction procedure

MDSPE

Initially, 8 mL of deionized water spiked with 50 μg L⁻¹ of acenaphthene, phenanthrene, pyrene, and acenaphthylene, and 10 μg L⁻¹ of anthracene, and benzo[a]pyrene, or sample (see Section “Samples”) was added into a 12-mL glass test tube and 0.468 g NaCl (1 mol L⁻¹) was dissolved in it. Afterward, 20 mg of the prepared adsorbent was added and vortexed for 5 min. Then, the PAH-loaded octadecylamine@Fe₃O₄ MNPs was isolated by placing a magnet at the bottom of the tube and aqueous phase was discarded. Subsequently, 1.5 mL ACN was added on the collected adsorbent and vortexed for 3 min to elute the selected analytes. The eluent was isolated from the adsorbent in the presence of external magnetic field and utilized in the subsequent DLLME step as a disperser solvent.

DLLME

The eluent obtained from the MDSPE step was mixed with 26 μL 1,2-DBE as the extraction solvent and speedily injected into 5 mL sodium chloride solution (1 mol L⁻¹) placed in a 10-mL conical bottom glass test tube using a 2-mL glass syringe. Accordingly, a cloudy solution was emerged and centrifuged for 5 min at 7000 rpm. Eventually,

1 μL of the sedimented phase ($10 \pm 0.5 \mu\text{L}$) was taken and injected into GC–FID system.

It is worth mentioning that, DLLME is an efficient micro-extraction process which benefits from brief extraction procedure, being inexpensive, and containing high enrichment factors (EFs) for analytes. But, actually the principle drawback of DLLME is its non-selective extraction feature that matrix components are also migrated into the extraction solvent resulting in noisy chromatograms which eventually makes it difficult to detect and determine the target compounds at low concentrations. So, suffering from high matrix effect and incomparable relative recovery data with deionized water due to the matrix complexity of the surveyed samples of this study (sewage, wastewater, and fountain samples) makes it impossible to apply just a DLLME procedure for the extraction of the analytes. For performing a clean-up step and relatively selective sorption of the analytes, application of MDSPE is inevitable. Also, DLLME is not directly applicable in real samples having suspended solids such as sewage samples. So, there is a high necessity for another extraction method to be coupled to DLLME in order to reduce the matrix effect of complex samples. Moreover, as you know, MDSPE suffers from lack of enrichment factor. This is due to the fact that the volume of the elution solvent in this study is 1.5 mL which is not analyte-enriched enough. So, the signals of the analytes would be small and consequently achieving low LODs and LOQs would be impossible. Due to the fact that concentrations of the studied analytes are at $\mu\text{g L}^{-1}$ level, detection and determination of such low concentrations are impossible by applying only MDSPE method. In this method, the adsorbent is directly added and dispersed into the sample solution and the clean-up goal was achieved by adsorbing the target compounds. Therefore, matrix effect is diminished and reaching lower LOD and LOQ values becomes possible. According to these facts, the developed process tries to benefit from the advantages of both MDSPE and DLLME. So, the combination of the two methods led to an effective method for the successful detection and determination of the analytes.

EF and extraction recovery (ER) calculation

EF is stated as the ratio of analyte concentration in the extracted phase (C_{sed}) in DLLME step to its initial spiked concentration in the aqueous solution (C_0).

$$\text{EF} = \frac{C_{\text{sed}}}{C_0} \quad (1)$$

Additionally, ER is calculated using Eq. (2) which denotes the percentage of the migrated amount of analyte into the extractant (n_{sed}) to the amount of analyte in the initial aqueous solution (n_0).

$$\text{ER} = \frac{n_{\text{sed}}}{n_0} \times 100 = \frac{C_{\text{sed}} \times V_{\text{sed}}}{C_0 \times V_{\text{aq}}} \times 100 = \text{EF} \times \frac{V_{\text{sed}}}{V_{\text{aq}}} \times 100 \quad (2)$$

where V_{sed} is volume of the sedimented phase and V_{aq} is volume of the aqueous solution.

Results and discussion

Characterization of sorbent

Characterization of the prepared MNPs was performed using FTIR, SEM, EDX, VSM, and XRD techniques. Figure 1a, b show the FTIR spectra of Fe_3O_4 and octadecylamine@ Fe_3O_4 MNPs, respectively. This technique is utilized to assure the desired chemical modification on the surface of MNPs. As it is clear from both spectra the absorption peak at 591.80 cm^{-1} represents the Fe–O stretching vibration in magnetite. In comparison to Fig. 1a, the advent of new peaks at 1115.06 , 1405.19 , and 1621.28 cm^{-1} in Fig. 1b is related to C–N stretching, C–H bending, and N–H bending bonds, respectively, confirming the successful modification of Fe_3O_4 MNPs with octadecylamine. The two absorption bands around 3041.59 cm^{-1} are assigned to N–H vibrations of the primary amino group. The characteristic peaks at 2847.81 and 2916.38 cm^{-1} are corresponded to the asymmetric and symmetric extension vibrations of $-\text{CH}_2$ in $-(\text{CH}_2)_{17}\text{CH}_3$ chain, respectively (Farajzadeh et al. 2020; <https://www.sigmaaldrich.com/US/en/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table.html>). The morphological features and size observation of the prepared adsorbent were examined by SEM technique. The obtained results show the agglomeration of nearly spherical-shaped particles (Fig. 1c) with a mean diameter of 40 nm (Fig. 1d) revealing a perfect platform for the adsorption of the analytes. Moreover, the performed elemental analysis on the product indicates the peaks denoting Fe, C, O, and N atoms with weight percentages of 21.60, 24.02, 42.82, and 9.00%, respectively (Fig. 1e). The outcome from VSM analysis illustrates the S-like magnetic hysteresis loop analysis of the adsorbent (Fig. 1f). The saturation magnetization value of the product was found to be 32 emu g^{-1} evincing its suitable magnetic property. Figure 1g also illustrates the XRD pattern of the final product. As can be observed, diffraction lines occur at 2θ angles of 32.84 , 35.8 , and 63.16° . These peaks indicate that the modification of Fe_3O_4 to form octadecylamine nanoparticles occurs without any phase change in the magnetite particles and the synthesized MNPs have a cubic crystalline structure (Hu et al. 2018; Maddah and Shamsi 2012).

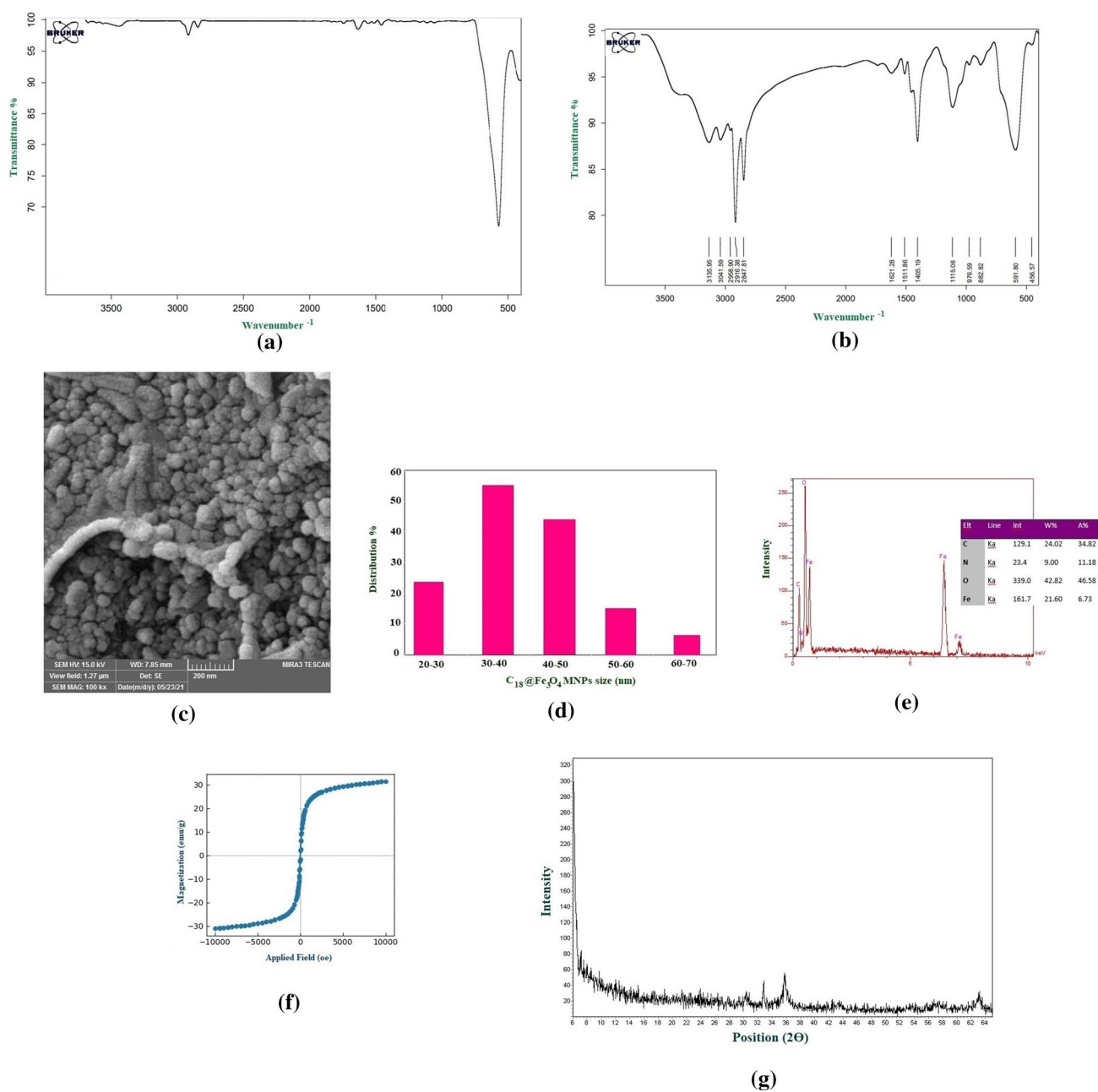


Fig. 1 FTIR spectra of Fe₃O₄ (a) and octadecylamine@Fe₃O₄ (b), and SEM image (c), size distribution (d), EDX spectrum (e), VSM curve (f), and XRD pattern of octadecylamine@Fe₃O₄ (g)

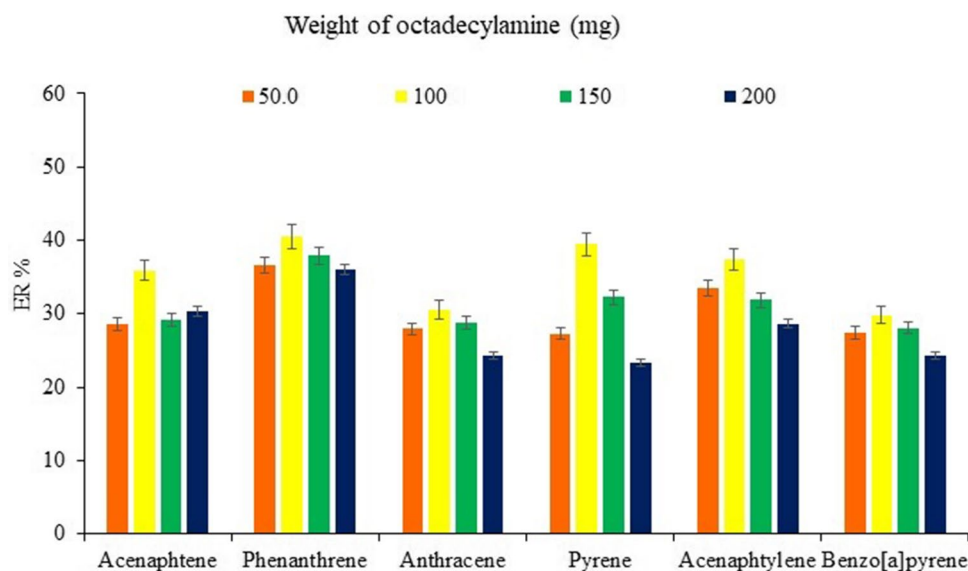
Optimization of parameters in MDSPE

Optimization of octadecylamine weight in the prepared nanocomposite

Fe₃O₄ nanoparticles were coated with octadecylamine to prevent the Fe₃O₄ nanoparticles oxidation in contact with air and to increase the selectivity of the adsorbent towards the studied analytes. It should be mentioned that by using bare

Fe₃O₄ nanoparticles' in the extraction process, the ERs of analytes were in the range of 5–10% while after modification with ODA the ERs were in the range of 63–84%. Therefore, Fe₃O₄ nanoparticles act as the magnetic core of the synthesized adsorbent and ODA is responsible for adsorption of the analytes in MDSPE step. So, the amount of modifier in the nanocomposite plays a critical role on ERs of the analytes. Accordingly, several amounts of octadecylamine (50, 100, 150, and 200 mg) were examined to be present in

Fig. 2 Optimization of octadecylamine weight. Extraction conditions: MDSPE procedure: aqueous sample, 8 mL deionized water spiked with $50 \mu\text{g L}^{-1}$ of each PAH; adsorbent weight, 30 mg; adsorption vortex time, 5 min; elution solvent, ACN (1 mL); and vortex time in desorption step, 3 min. DLLME procedure: 5 mL deionized water; extraction solvent, Chloroform ($48 \mu\text{L}$); centrifugation rate, 7000 rpm; and centrifugation time, 5 min. Both steps were done without any salt addition or pH adjustment. The error bars indicate standard deviation of three repeated determinations



the prepared octadecylamine@ Fe_3O_4 nanocomposite having 232 mg Fe_3O_4 . The results (Fig. 2) indicate that ER values increase up to 100 mg and then decrease noticeably. Due to the mentioned points, excessive use of ODA, decreases the magnetic property of the nanocomposite led to the deficient collection of the adsorbent particles in the presence of external magnetic field. Hence 100 mg was sufficient to certify an adequate efficiency and hence it was selected as the optimal amount of the octadecylamine for preparation of the adsorbent.

Optimization of adsorbent weight

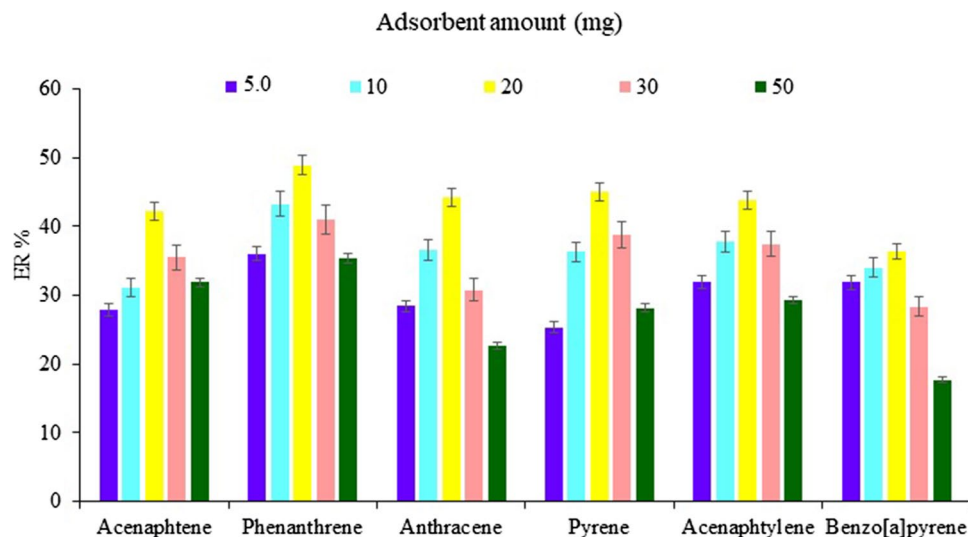
The amount of adsorbent was considered to be correlated to the number of active sites, and quantity of the adsorbed analytes. Accordingly, to access the optimum results, several

amounts of the MNPs varying in the range of 5–50 mg were studied. As shown in Fig. 3, 20 mg of the adsorbent is sufficient to assure an acceptable efficiency, hence it was selected as the optimum value. The decrease in the analytical signals at high weights occurs because of agglomeration of the adsorbent (lack of its efficient dispersion into the aqueous solution containing the analytes) or incomplete elution of the analytes during the desorption step. So, 20 mg was selected as the optimum sorbent weight to continue the optimization steps.

Effect of salt addition

Salt addition is notably applied for the augment of extraction efficiency due to dwindling solubility of the selected analytes in aqueous solution (known as salting-out effect) and

Fig. 3 Optimization of octadecylamine@ Fe_3O_4 amount. Extraction conditions: All conditions are the same as those used in Fig. 2, except 100 mg of octadecylamine was utilized in preparation of the adsorbent



hence increasing their migration onto the sorbent surface. However, high concentrations of salt can increase viscosity of aqueous phase which can unfavorably decrease the analytes diffusion coefficients and adversely affect the extraction efficiency (known as salting-in effect). Due to the stated reasons NaCl, NaNO₃, and Na₂SO₄ were added separately at a concentration of 1 mol L⁻¹ (each salt) into the aqueous phase including the analytes. Among the tested salts, NaCl provides the highest ERs for the selected PAHs (Fig. 4). Moreover, to study the salt concentration, several concentrations of it (0.5, 1.0, 1.5, and 2.0 mol L⁻¹) were studied. The obtained analytical results depicted that by increasing NaCl concentration up to 1 mol L⁻¹, ERs of the analytes enhanced and then steadily dropped (data not shown here). It is obvious that salt addition has salting-out effect until 1 mol L⁻¹ salt concentration and then salting-in effect emerges more dominant. With regard to the obtained results, 1 mol L⁻¹ NaCl was chosen for the further investigations.

Effect of solution pH

Efficiency of the proposed method in the extraction and pre-concentration of the selected analytes can be altered with varying solution pH because it not only influences the adsorbent surface charge but also stability of the MNPs. Since the studied PAHs are neutral and do not ionize, it is anticipated that no considerable effect of pH would be found due to the negligible impact of pH on them. Therefore, pH of the aqueous solution was varied in the range of 3–13 (with 2-unit intervals) by using 1 mol L⁻¹ HCl or NaOH solutions. The results (data not shown here) indicated that the highest ERs were obtainable at the pH range of 5–9 which is well assorted with the pH of all sample solutions utilized in the present study. So, as it was expected the further analyses were performed without any pH adjustment.

Optimization of vortexing time in adsorption step

In adsorptive-based analytical methods an appropriate vortexing time is necessary for acquiring high ERs because it leads to enough contact surface area between the adsorbent and analytes. To fulfill the effect of this parameter, 1–6 min vortexing time periods were tested. ERs of the analytes increased by increasing the vortex time until 5 min and remained constant in the vortex time of 6 min (data not shown here). Therefore, 5 min vortexing was selected for the further investigations.

Optimization of the type and volume of desorption/disperser solvent

In order to obtain an efficacious desorption of the adsorbed PAHs from the surface of the nanocomposite, opting an appropriate eluent is of great importance. Moreover, it can influence dispersion efficiency of the extraction solvent used in DLLME step into aqueous phase. Additionally, the chosen solvent should be miscible in both aqueous solution and extraction solvent. For this purpose, 1 mL of different solvents including ACN, methanol, acetone, and iso-propanol were tested. Referring to the results in Fig. 5, the highest ERs are achieved in the presence of ACN as the desorption/disperser solvent. Furthermore, to investigate the sufficient volume of the opted disperser solvent, its volume was studied in the range of 0.50–2.0 mL. Based on the obtained results (data not shown here), 1.5 mL of ACN was superior over the other studied volumes and it was selected as the optimum volume of the desorption/disperser solvent for the following experiments.

Fig. 4 Study of ionic strength. Extraction conditions: are the same as those used in Fig. 3, except 20 mg of the adsorbent was utilized

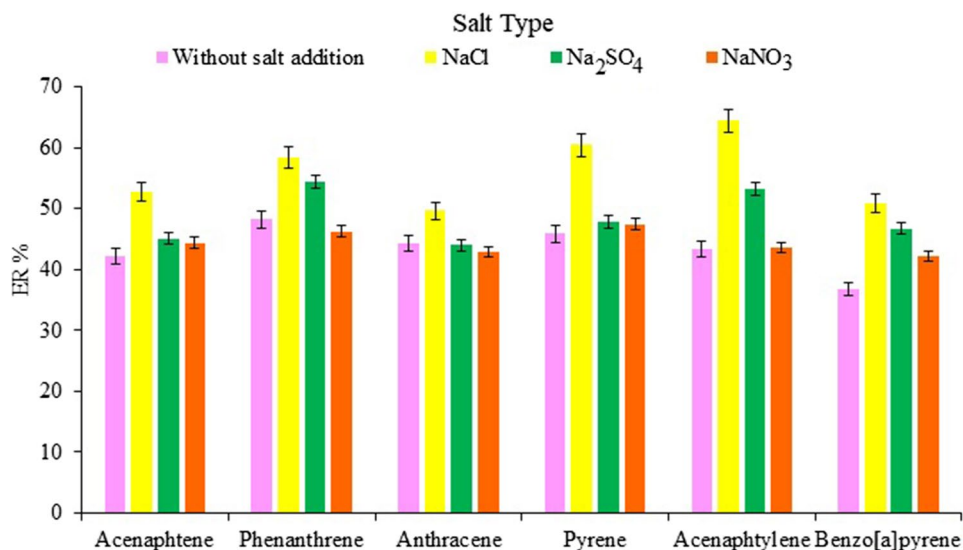
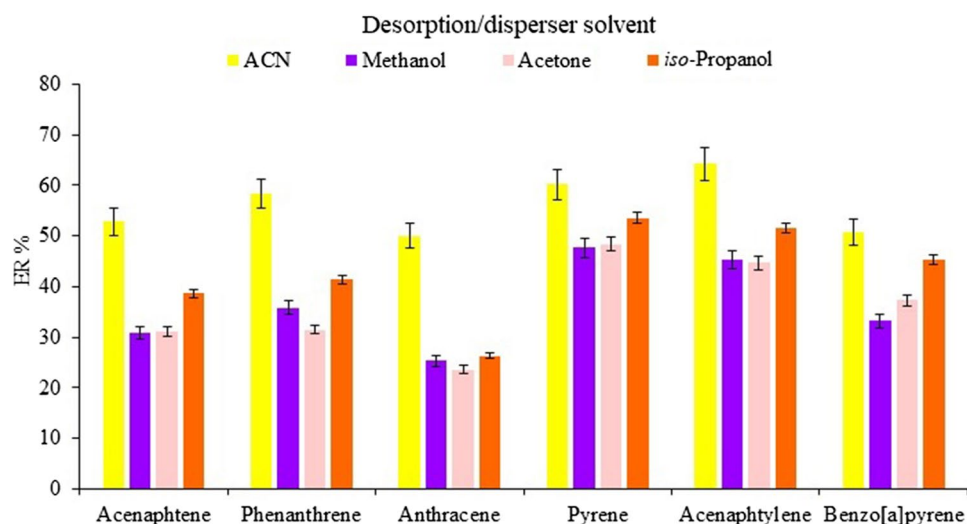


Fig. 5 Selection of desorption/disperser solvent type. Extraction conditions: are the same as those utilized in Fig. 4, except 1 mol L⁻¹ NaCl was used in MDSPE step



Optimization of vortexing time in desorption step

To obtain an optimum time for desorption of the analytes, various vortexing times were tested in the range of 1–5 min. Considering the outcomes (data not shown here) vortexing for 3 min was the best time for elution of the selected PAHs from the surface of the adsorbent.

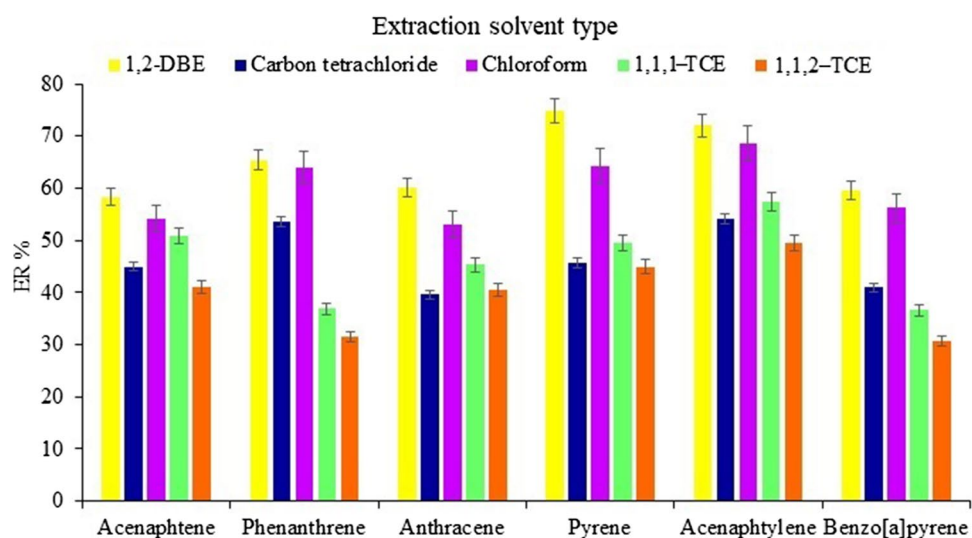
Optimization of parameters in DLLME

Selection of the type and volume of extraction solvent

Selection of a suitable extraction solvent is the pivotal parameter in DLLME-based methods. It has to acquire various criteria including low solubility in aqueous phase, having higher density than water, high extraction

efficiency towards the target PAHs, and forming a stable cloudy state in the presence of ACN. Based on these points 1,2-DBE, 1,1,1-TCE, 1,1,2-TCE, chloroform, and carbon tetrachloride with the volumes of 26, 31, 30, 48, and 26 μ L, respectively, were examined to get 10 \pm 0.5 μ L of the sedimented phase after centrifugation. Regarding the outcomes illustrated in Fig. 6, 1,2-DBE is preferred over the surveyed extractants due to resulting higher ER values. Subsequently, the effect of extraction solvent volume on the EF values was tested using several volumes of 1,2-DBE (26, 31, 36, 41, and 46 μ L). It is noted that increasing volume of the extraction solvent in the mentioned range led to obtaining 10, 13, 15, 19, and 23 μ L of the sedimented phase, respectively, at the end of the procedure. So, the EF values decreased by increasing the extractant volume due to dilution effect (data not shown)

Fig. 6 Selection of extraction solvent type in DLLME. Extraction conditions: are the same as those used in Fig. 5, except 1.5 mL ACN was used as the desorption/disperser solvent



here). Accordingly, the volume of 26 μL was chosen as the optimum volume of the extraction solvent.

Ionic strength study

As explained before, salt addition can improve extraction efficiency of the method by decreasing solubility of the selected analytes in aqueous solution and also it can decrease mass transfer rate of the analytes via increasing viscosity of the aqueous solution which results in decreasing the extraction efficiency. To investigate this parameter, several salts including NaCl, Na_2SO_4 , and NaNO_3 (1 mol L^{-1} of each) were studied in which NaCl utilization provided higher ERs (data not shown here) similar to the DSPE step. Then various concentrations of NaCl (0.5, 1.0, 1.5, and 2.0 mol L^{-1}) were added to aqueous solution and in order to keep volume of the sedimented phase constant, different volumes of 1,2-DBE (31, 36, 41, and $46 \mu\text{L}$) were used for 0.5, 1.0, 1.5, and 2.0 mol L^{-1} of NaCl, respectively. The outcomes (Fig. 7) evince that ERs of the target PAHs increase by increasing the concentration of NaCl up to 1 mol L^{-1} and then decrease slightly by the further increasing NaCl concentration. Hence, 1 mol L^{-1} NaCl was selected.

Reusability of the sorbent

Reusability is an important factor when evaluating the efficiency of sorbents. In order to investigate the reusability of the sorbent, repetitive extractions were done using the same sorbent according to Section “Extraction procedure”. Before repeating the experiment, the recycled sorbent was washed twice using ACN (each time by 1 mL along with vortexing for 3 min) to prevent carry-over. The obtained results indicated that the sorbent was capable to adsorb the analytes after three desorption cycles without a significant

change in the ERs of the analytes which indicates that octadecylamine@ Fe_3O_4 is a suitable sorbent for usage in repetitive analytical cycles.

Validation of the developed analytical method

The practical applicability of the proposed MDSPE–DLLME–GC–FID method was validated through evaluating various analytical values including ER, EF, linear range (LR), limits of detection (LOD) and quantification (LOQ), and relative standard deviation (RSD). The LOD is the lowest concentration of the analyte in a sample that can still be detected by applying the analytical method and using the analytical detection system but should not be quantified as an appropriate value. However, the LOQ is the lowest concentration of the sample that can still be quantitatively determined with acceptable precision and accuracy. The most common method to estimate the LOD of a chromatographic method is to measure the signal of the smallest detected analyte peak with a height equals to three times of the neighbor noise ($\frac{S}{N} = 3$). The concentration related to this signal is called LOD. On the other hand, LOQ is determined by a signal-to-noise ratio of 10. So, the concentration in which the resulted signal is 10 times taller than the neighbor noise is called LOQ. To evaluate these figures of merit several solutions with different spiked concentration of the analytes were prepared and injected into GC–FID after performing the method on them. For each of analytes, the spiked concentrations in which the signal-to-noise ratios found to be 3 and 10, were chosen as LODs and LOQs, respectively.

The obtained results of the above-mentioned figures of merit are listed in Table 1. The LODs and LOQs for the selected PAHs (based on signal-to-noise ratios of 3 and 10, respectively) were found to be in the ranges of 0.11–0.30

Fig. 7 Study of NaCl concentration in DLLME step. Extraction conditions: All conditions are the same as those used in Fig. 6, except 1,2-DBE was used as the extraction solvent

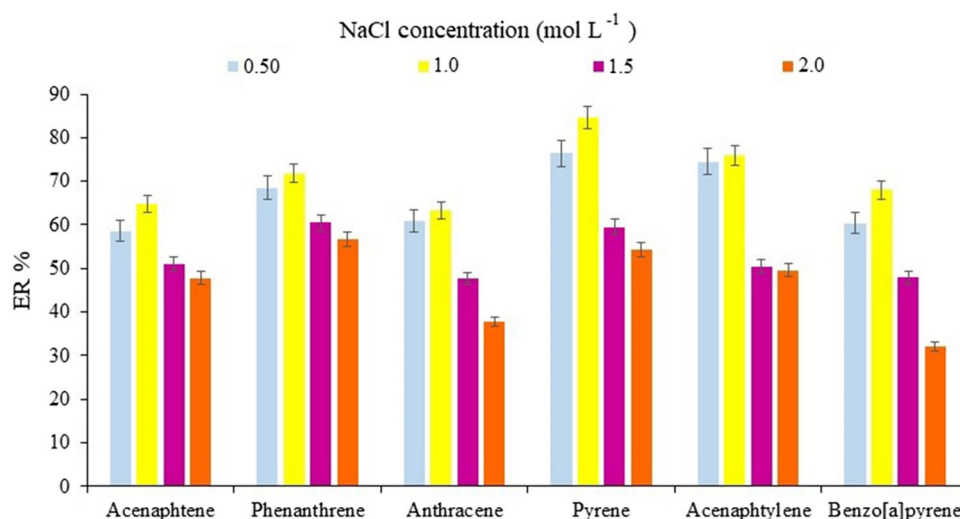


Table 1 Quantitative features of the developed approach for the selected PAHs

Analytes	LOD ^a	LOQ ^b	LR ^c	r^2 ^d	RSD% ^e		EF \pm SD ^f	ER \pm SD ^g
					Intra-day	Inter-day		
Acenaphthene	0.17	0.58	0.58–1000	0.998	3	4	519 \pm 10	64 \pm 2
Phenanthrene	0.14	0.47	0.47–1000	0.993	2	5	571 \pm 15	71 \pm 4
Anthracene	0.11	0.40	0.40–30	0.991	3	6	506 \pm 20	63 \pm 4
Pyrene	0.30	1.0	1.0–100	0.997	5	6	676 \pm 10	84 \pm 3
Acenaphtylene	0.16	0.53	0.53–1000	0.998	2	3	608 \pm 25	75 \pm 5
Benzo[a]pyrene	0.18	0.61	0.61–10	0.996	4	6	544 \pm 20	68 \pm 5

^aLimit of detection ($S/N=3$) ($\mu\text{g L}^{-1}$)

^bLimit of quantification ($S/N=10$) ($\mu\text{g L}^{-1}$)

^cLinear range ($\mu\text{g L}^{-1}$)

^dCoefficient of determination

^eRelative standard deviation for intra- ($n=6$) and inter-day ($n=4$) precisions at a concentration of $10 \mu\text{g L}^{-1}$ of each analyte

^fEnrichment factor \pm standard deviation ($n=3$)

^gExtraction recovery \pm standard deviation ($n=3$)

and $0.40\text{--}1.0 \mu\text{g L}^{-1}$, respectively. EF values of the proposed approach (calculated from Eq. 1) were in the range of 506–676. Also, the ERs (calculated from Eq. 2) were between 63 and 84%. Intra- ($n=6$) and inter-day ($n=4$) RSDs at a concentration of $10 \mu\text{g L}^{-1}$ of each PAH were in the ranges of 2–5 and 3–6%, respectively. The method presented wide LRs with a good linearity ($r^2 \geq 0.991$) for the target analytes. The listed validation parameters including low LODs and LOQs, good repeatability, and high EFs and ERs are the significant assurance of an acceptable and reliable approach.

Analysis of real samples

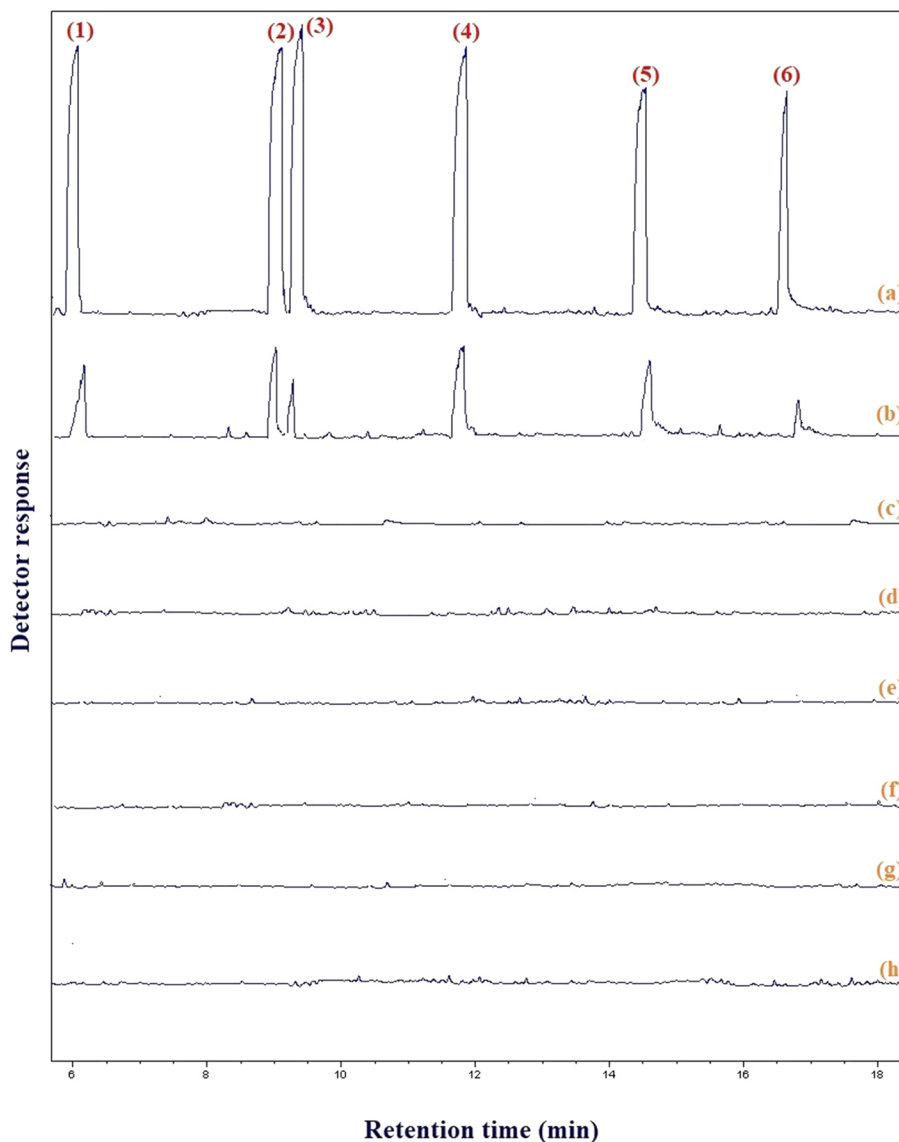
In order to evaluate efficiency of the modified Fe_3O_4 MNPs for the successful clean up and also applicability of the MDSPE–DLLME procedure, the validated method was further assessed with analyzing several real samples including pharmaceutical sewage, sewage of the refinery unit of copper mine, sewage of distillation unit (petrochemical and refinery wastewaters), municipality wastewater, and fountain water samples. According to the outcomes, none of the target analytes was detected. Figure 8 illustrates GC–FID chromatograms of standard solution of the analytes (100 mg L^{-1} of each PAHs), aqueous standard solution ($50 \mu\text{g L}^{-1}$ of acenaphthene, phenanthrene, pyrene, and acenaphtylene, and $10 \mu\text{g L}^{-1}$ of anthracene, and benzo[a]pyrene) and all real samples after performing the method on them, except the standard solution prepared in 1,2-DBE in which direct injection without preconcentration was done. Moreover, to

investigate the method's accuracy and matrix effect in various samples, added-found method was employed. According to the relative recovery values (86–114%) (Table 2) obtained at the spiked concentrations of 5 and $10 \mu\text{g L}^{-1}$ of each PAH, the matrices of samples have a negligible effect on the method's performance. Hence, the proposed method is applicable for the determination of the target PAHs in the studied samples.

Comparison of the method with other approaches

The analytical figures of merit of the developed extraction method in combination with GC–FID for the determination of the selected PAHs were compared with the other similar analytical methods. As it can be concluded from the listed results in Table 3, the proposed method has better RSDs, lower LODs (in most cases), and wider LRs in comparison to the other methods. Also the obtained EF values of the method are higher than the EFs of the mentioned methods. It is worthwhile to notify that the presented method benefits from several aspects such as good precision, easy operation, good repeatability, high EFs, and low LODs and LOQs. Moreover, utilizing a magnetic and efficient adsorbent accelerates separation process via avoiding laborious and time-consuming centrifugation or filtration procedures. Regarding to all aforementioned points, the developed method seems to be accessible, quick, and sensitive, and it can be applied effectively for monitoring the selected PAHs in various industrial wastewater samples.

Fig. 8 Typical GC–FID chromatograms of **a** direct injection of standard solution (100 mg L^{-1} in 1,2-DBE, each PAH), **b** deionized water spiked with $50 \text{ } \mu\text{g L}^{-1}$ of acenaphthene, phenanthrene, pyrene, and acenaphthylene, and $10 \text{ } \mu\text{g L}^{-1}$ of anthracene, and benzo[a]pyrene, **c** pharmaceutical sewage, **d** mine wastewater **e** petrochemical wastewater **f** refinery wastewater **g** municipality wastewater and **h** fountain water. In all cases, except chromatogram (a) the proposed method was performed and $1 \text{ } \mu\text{L}$ of the sedimented phase was injected into the separation system. Peaks identification: (1) acenaphthene, (2) phenanthrene, (3) anthracene, (4) pyrene, (5) acenaphthylene, and (6) benzo[a]pyrene



Conclusions

The proposed MDSPE method based on a new magnetic adsorbent (octadecylamine@ Fe_3O_4) was an effective, convenient, and rapid method for the simultaneous extraction and preconcentration of PAHs in several obscure matrices such as environmental and industrial wastewater samples. On account of effectual hydrophobic–hydrophobic interactions, PAHs were adsorbed by the C_{18} group of

the nanoparticles. The GC–FID method combined with MDSPE–DLLME acquired low LODs ($0.11\text{--}0.30 \text{ } \mu\text{g L}^{-1}$) and LOQs ($0.40\text{--}1.0 \text{ } \mu\text{g L}^{-1}$), satisfactory repeatability ($\text{RSD} \leq 6\%$), and high EFs ($506\text{--}676$). Taking into account that the desired adsorbent inherits virtues of being cost-effective, easy for preparation, having higher efficiency, and easy to separate and dispersion, this method is considered to be promising for the detection and determination of PAHs and other pollutants from various real samples.

Table 2 Mean relative recovery obtained from several samples spiked at different concentrations

Analyte	Mean relative recovery (%) \pm standard deviation ($n=3$)					
	Fountain water	Municipality wastewater	Sewage of petrochemical company	Sewage of refinery	Output of copper mine	Pharmaceutical sewage
<i>All samples were spiked with each analyte at a concentration of 5 $\mu\text{g L}^{-1}$</i>						
Acenaphthene	90 \pm 5	93 \pm 3	92 \pm 5	97 \pm 4	90 \pm 4	93 \pm 4
Phenanthrene	96 \pm 4	86 \pm 5	90 \pm 3	104 \pm 2	95 \pm 3	86 \pm 3
Anthracene	87 \pm 3	91 \pm 3	96 \pm 5	98 \pm 3	98 \pm 4	89 \pm 4
Pyrene	96 \pm 3	89 \pm 4	92 \pm 2	94 \pm 4	95 \pm 5	92 \pm 5
Acenaphthylene	92 \pm 2	94 \pm 5	91 \pm 4	96 \pm 2	94 \pm 3	109 \pm 3
Benzo[a]pyrene	108 \pm 3	110 \pm 3	90 \pm 3	95 \pm 4	96 \pm 4	103 \pm 2
<i>All samples were spiked with each analyte at a concentration of 10 $\mu\text{g L}^{-1}$</i>						
Acenaphthene	94 \pm 4	96 \pm 3	88 \pm 4	93 \pm 3	90 \pm 2	97 \pm 4
Phenanthrene	102 \pm 5	91 \pm 4	96 \pm 3	96 \pm 5	103 \pm 3	93 \pm 5
Anthracene	88 \pm 3	95 \pm 4	95 \pm 4	101 \pm 5	96 \pm 5	86 \pm 2
Pyrene	98 \pm 2	95 \pm 3	88 \pm 3	91 \pm 4	96 \pm 3	103 \pm 3
Acenaphthylene	108 \pm 3	101 \pm 3	94 \pm 2	97 \pm 5	95 \pm 4	97 \pm 4
Benzo[a]pyrene	97 \pm 4	112 \pm 5	95 \pm 5	90 \pm 3	114 \pm 3	105 \pm 3

Standard deviations were obtained from three repeated determinations

Table 3 Comparison of the presented method with the other methods used in the preconcentration and determination of the selected PAHs

Analyte	Method	Sample	LR ^a	RSD% ^b	LOD ^c	EF ^d	Refs.
Phenanthrene	SPE–RP–HPLC–DAD ^e	River water samples	0–1000	≤ 2.26	11.2	–	Moja et al. (2013)
Benzo[a]pyrene	DLLME–GC–FID ^f	Seawater and wastewater	1.5–17	4	0.29	321	Ramos-Dorta et al. (2013)
Pyrene	D–LPME–HPLC–UV ^g	Water samples	1.2–12	6	0.6	156	Hou and Lee (2002)
Anthracene	HLLME–FA–GC–FID ^h	Water samples	50–1000	10	41	–	Hosseini et al. (2013)
Acenaphthene	LLME–HPLC–DAD ⁱ	Honey samples	1.6–1000	4	0.52	586	Farajzadeh et al. (2016)
Benzo[a]pyrene	MIL-based SBDLME-TD-GC-MS ^j	Water samples	–	8.9	0.008	32	Juan et al. (2017)
Anthracene	D- μ SPE-GC-MS ^k	Fresh and marine water samples	0.0039–0.070	4.01	0.0012	461	Nascimento et al. (2019)
Acenaphthene	MDSPE–DLLME–GC–FID ^l	Industrial and environmental wastewaters	0.58–1000	3	0.17	519	This study
Phenanthrene			0.47–1000	2	0.14	571	
Anthracene			0.40–30	3	0.11	506	
Pyrene			1.0–100	5	0.30	676	
Acenaphthylene			0.53–1000	2	0.16	608	
Benzo[a]pyrene			0.61–10	4	0.18	544	

^aLinear range ($\mu\text{g L}^{-1}$)

^bRelative standard deviation

^cLimit of detection ($\mu\text{g L}^{-1}$)

^dEnrichment factor

^eSolid phase extraction–reversed phase high performance liquid–liquid chromatography–diode array detector

^fDispersive liquid–liquid microextraction–gas chromatography–flame ionization detector

^gDynamic liquid–phase microextraction high performance liquid chromatography–ultraviolet detector

^hHomogenous liquid–liquid microextraction–flotation–assisted–gas chromatography–flame ionization detector

ⁱLiquid liquid microextraction–high performance liquid chromatography–diode array detector

^jMagnetic ionic liquid-based stir bar dispersive liquid microextraction–thermal desorption–gas chromatography–mass spectrometry

^kDispersive micro solid phase extraction–gas chromatography–mass spectrometry

^lMagnetic dispersive solid phase extraction–dispersive liquid–liquid microextraction–gas chromatography–flame ionization detector

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Declarations

Conflict of interest Mir Ali Farajzadeh declares that he has no competing interest. Nasim Fazli declares that she has no competing interest. Sakha Pezhhanfar declares that he has no competing interest. Mohammad Reza Afshar Mogaddam declares that he has no competing interest.

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