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Carbon nanofibers decorated with magnetic nanoparticles as a new sorbent for the magnetic solid phase extraction of selected polycyclic aromatic hydrocarbons from water samples

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Abstract

A novel nano-adsorbent, magnetic carbon nanofibers (CNFs-Fe_3O_4), was prepared by impregnating magnetic Fe_3O_4 nanoparticles onto the surfaces of carbon nanofibers based on electrostatic interactions. The resulting nanoparticles were used as the adsorbent for the magnetic solid phase extraction of polycyclic aromatic hydrocarbons from the environmental water samples. The experimental parameters affecting the extraction efficiency, including the amount of sorbents, desorption conditions, extraction time and salt concentration were investigated and optimized. Under the optimal conditions, the detection limits of the method (S/N=3) were in the range of 0.008–0.03 ng mL^{-1} and the limits of quantification (S/N=10) were between 0.025–0.08 ng mL^{-1}. Repeatability of the method was assessed through five consecutive extractions of independently prepared solutions at concentrations of 0.1, 10, and 100 ng mL^{-1} of the compounds. The observed repeatability ranged between 3.2–11.2% depending on the considered compounds. The developed method was successfully applied to the real water samples while the relative recovery percentages obtained from the spiked water samples at three level concentrations (0.1, 10 and 100 ng mL^{-1}) were from 90.1 to 100.9%.

Keywords: Magnetic solid phase extraction; Carbon nanofibers; Polycyclic aromatic hydrocarbons; Water samples.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of hydrophobic organic contaminants (HOC) comprised of two or more fused benzene rings. PAHs are one of the most well-known classes of environmental pollutants. Some of these compounds are carcinogenic and mutagenic. They are omnipresent pollutants widen in all compartments of the environment (atmosphere, soil and water) and seriously dangerous to human health and living organisms.[1–3] On the basis of their occurrence and carcinogenicity, 15 PAHs have been identified as priority hazardous substances by the European Union (EU)[4] and 16 PAHs by US Environmental Protection Agency (EPA)[5], 12 of them are identical in both lists. The sources of these pollutants can be created as follows: traffic pollution, oil spills, volcanic activity, industrial processing and incomplete combustion of organic materials.[6] In order to reduce the human intake of these hazardous substances a chemical control (and consequently methods of analysis) is required. There is a major problem for the monitoring due to the very low concentrations of these compounds and complexity of matrix samples.[7] Therefore, sample preparation and preconcentration steps are very necessary.

Solid-phase extraction (SPE) is the most common pre-treatment method for sample matrix simplification and pre-concentration of trace amounts of analyte in samples.[8] Recently, a new SPE technique based on the use of magnetic nanoparticles (MNPs), called magnetic solid phase extraction (MSPE) has been introduced for the separation and preconcentration of organic and inorganic species from complex matrixes.[9,10] The powdery magnetic adsorbent can be reversibly agglomerated and re-dispersed in solution or suspensions by the application and removal of an appropriate magnetic field, thus

realizing the phase separation conveniently. Therefore, the time-consuming for the passage of solvent through the column for desorption of the analytes and also the filtration operations encountered in SPE are avoided. In addition, owing to its nano-nature, MNPs possesses large specific surface area, and the equilibrium time between the sorbents and also the sample solutions are thus greatly shortened, and at the end resulting in relatively higher extraction capacity and detection sensitivity.[11–13] Among the magnetic nano-sized materials, iron oxides have been extensively used as adsorbent in MSPE because of their super paramagnetism, high magnetic saturation, low toxicity, simple preparation process and low price. However, the drawbacks of utilizing MNPs to sample preparation are their low selectivity toward the target analytes, low stability in strong acidic aqueous media and low dispersion ability in various sample matrices. The stability and selectivity of the MNPs can be significantly improved by the modification of the surface of the adsorbent with special functional groups.

In recent years, a large number of carbon-based nanoparticles have been investigated as sorbent materials in the sample preparation, including nanodiamonds, fullerenes, carbon nanotubes, graphene, carbon nanofibers, carbon nanocones-disks and nanohorns, as well as their functionalized forms.[14,15] Recently, carbon nanofiber (CNF) has been extensively studied under recognition as a unique carbon material.[16–18] Carbon nano-fibers could be defined as sp^2-based linear filaments with a diameter of ca. 100 nm that is characterized by flexibility and their aspect ratio (above100). CNFs are hydrophobic materials with ability to establish π–π interactions with our target analytes. The combination of high specific area, flexibility, and high mechanical strength make them as a very attractive adsorbents.[19]

As mentioned, CNFs have been considered as excellent sorbents because of their large surface area and high affinity towards the various organic compounds. In the present case, the CNFs were decorated with magnetic nanoparticles. As a result, the magnetic CNF, which combines merits of strong adsorption property and magnetic separation, should show great potential as sorbents for MSPE. In fact, the intersection of CNFs science with MSPE essentially allows the proposed method to integrate the advantages of both, the CNFs and MSPE. To the best of our knowledge, the use of CNFs modified with magnetic Fe_3O_4 as an adsorbent has not been reported. In the present work, we prepared magnetized CNFs as a new adsorbent for MSPE of selected polycyclic aromatic hydrocarbons (PAHs) (naphthalene, fluorine and anthracene as model compounds) from the real water samples using gas chromatography–flame ionization detector (GC–FID).

2. Experimental

2. 1. Chemicals and materials

Polycyclic aromatic hydrocarbons (PAHs) include naphthalene (Naph), fluorene (Flu), anthracene (Anth) was bought from Merck (Darmstadt, Germany). A stock solution of PAHs (500 mg L^{-1}) was prepared in the methanol and kept in a refrigerator at 4 °C. Fresh working solutions were prepared daily by diluting of the stock solution in deionized water. Analytical-grade ammonia, acetonitrile, ferric chloride ($FeCl_3.6H_2O$), ferrous sulfate ($FeSO_4.7H_2O$), methanol, acetone, isopropyl alcohol, dichloromethane and NaCl were all purchased from Merck (Darmstadt, Germany).

2. 2. Instrumentation

Gas chromatographic analysis was carried out using a Chrompack CP9001 (Middelburg, the Netherlands) fitted with a split/splitless injector and flame ionization detector (Middelburg, the Netherlands). Helium (99.999%, Sabalan Co., Tehran, Iran) was used as the carrier gas and was set at 1 mL min^{-1}. The separation was performed with a CP-Sil 24CB (50% phenyl, 50% dimethylsiloxane) capillary column, WCOT Fused silica, 30 m × 0.25 mm ID with 0.25 μm stationary film thickness (Chrompack, Middelburg, The Netherlands). The column temperature was programmed as follows: initial oven temperature 70 °C for 2 min, increasing to 220 °C at 40 °C min^{-1} and holding for 15 min. The injector and detector temperature were set at 250 and 280 °C, respectively. A VELP Scientifica heating magnetic stirrer, model ARE (Milano, Italy) was employed for stirring and heating samples during the extraction. To mix various solution ingredients, a ultrasonic bath (Branson 1510, Branson Ultrasonics Co., Danbury, CT), was employed at a frequency of 42 kHz. Also the surface characteristics of the created coating were studied by scanning electron microscopy (SEM) (LEO, model 1450VP, Germany).

2.3. Procedure of magnetic solid-phase extraction

Extraction was performed by adding 10 mg of CNFs-Fe_3O_4 sorbent to 50 mL of a standard sample solution containing 100 ng/mL of the analytes in a glass vial. The suspension was stirred for 10 min to facilitate adsorption of the PAHs on the surface of sorbents. After the extraction, the magnetic adsorbents were collected by a strong magnet with 1.2 Tesla magnetic field (5.0 cm × 3.0 cm × 2.0 cm) and the supernatant was decanted. The preconcentrated target analytes were desorbed from the surface of the sorbent by addition of 1 mL dichloromethane during 2 min sonication. Finally, the magnet was used again to settle the nanoparticles, and the desorbed solution was

evaporated under a gentle nitrogen flow. The residue was re-dissolved in 50 µL methanol, and 1 µL of this solution was injected into the GC system for analysis.

3. Results and discussion

3.1. Preparation of CNFs-Fe_3O_4

3.1.1. Synthesis of branched carbon nanofiber

Commercially available, unsized, polyacrylonitrile (PAN)-based carbon fibers (Toho Tenax America, Inc.) were utilized as the base fiber. The carbon fibers (CFs) were immersed into an iron nitrate nonahydrate solution (100 mM) and followed by ultrasonic agitation for 2h. Then, they were dried and calcinated at 200°C under air flow for 2h to remove the nitrate components and make the desired catalyst coating on the surface of the CF. Chemical vapour deposition (CVD) was applied to grow the CNFs on the CF at atmospheric pressure and the temperature at 600°C for 30min. This process was fulfilled by a catalytic reaction of an acetylene flow rate of 50 standard cubic centimeters per minute (sccm) over Fe/CF in the reactor under a flow rate of H_2/N_2 (100, 100 sccm). At the end of the run time, the C_2H_2 flow stopped, the heater turned off and then the reactor cooled under the flow of N_2.

For increasing the dispersibility of CNFs into various solvents, the partially ionizable carboxylic acid groups created during the oxidation of CNFs. For this reason, the functionalization of CNFs was performed as follows: predetermined quantities of raw CNFs (0.3 g) and 50 mL nitric acid were added into a round-bottomed glass flask, and the CNFs mixture sonicated for 30 min in an ultrasonic bath. Next the mixture was refluxed at 120 °C and maximum stirrer rate for 24 h. After having been cooled to the room temperature, the mixture was filtered on a 0.22 µm filter (Millipore, Bedford, MA, USA),

washed with excess distilled water to neutral pH, and dried under vacuum at 60°C for 12 h.[20]

3.1.2. Preparation of surface-modified CNFs with Fe_3O_4 (CNFs-Fe_3O_4)

CNFs-Fe_3O_4 NPs were prepared by a chemical co-precipitation method. In this case, 0.1 g of functionalized CNFs was added to 60 mL of deionized water by ultrasonic irradiation for 20 min. Then, 150 mg of $FeCl_3.6H_2O$ and 80 mg of $FeSO_4.7H_2O$ were added under nitrogen gas with vigorous stirring for 30 min. After that, 18 mL of 25% NH_3 was added to the solution until the pH of the solution reached to 11. The mixture was stirring at 80 $^{\circ}$C for 1 hour. During the process, the solution temperature was maintained at 80 °C and nitrogen gas was purged to prevent the intrusion of oxygen. After the reaction, the obtained NPs precipitate were separated from the reaction medium by the magnetic decantation, and then washed several times with deionized water until the pH became neutral and finally dried.

The same above experiment obtained functionalized CNFs and pure Fe_3O_4 nanoparticles without using ferric chloride, ferric sulphate and ammonia. Changing the feeding weight ratios of Fe_3O_4 to CNFs (m Fe_3O_4: m CNFs = 0.1:0.1, 0.2:0.1, 0.4:0.1, 0.6:0.1, 0.8:0.1 and 1:0.1), gave six samples of CNFs/Fe_3O_4 nanocomposites.

3.2. Structural Characterization of sorbent

The morphology of the prepared products were investigated through a scanning electron microscope (SEM) and transmission electron microscope (TEM). The SEM image of synthesized CNFs on CF was shown in Fig. 1. The morphology of the fiber surface

showed a rough and highly porous structure which greatly increases the surface area for CNF and further provide enhanced stationary phase loading and the extraction capacity.

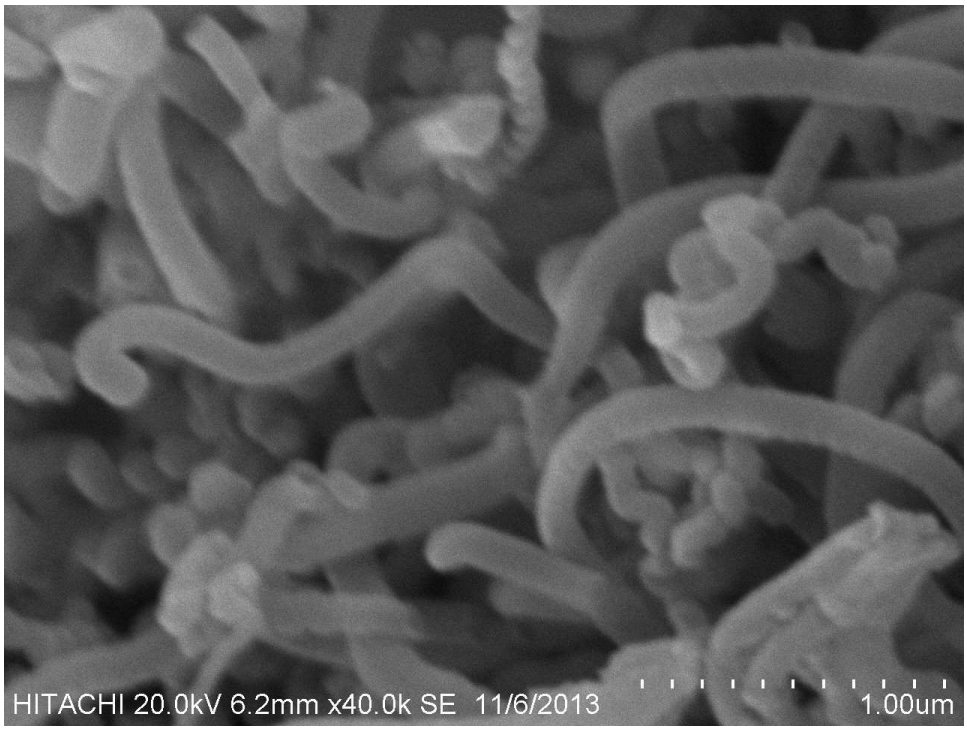
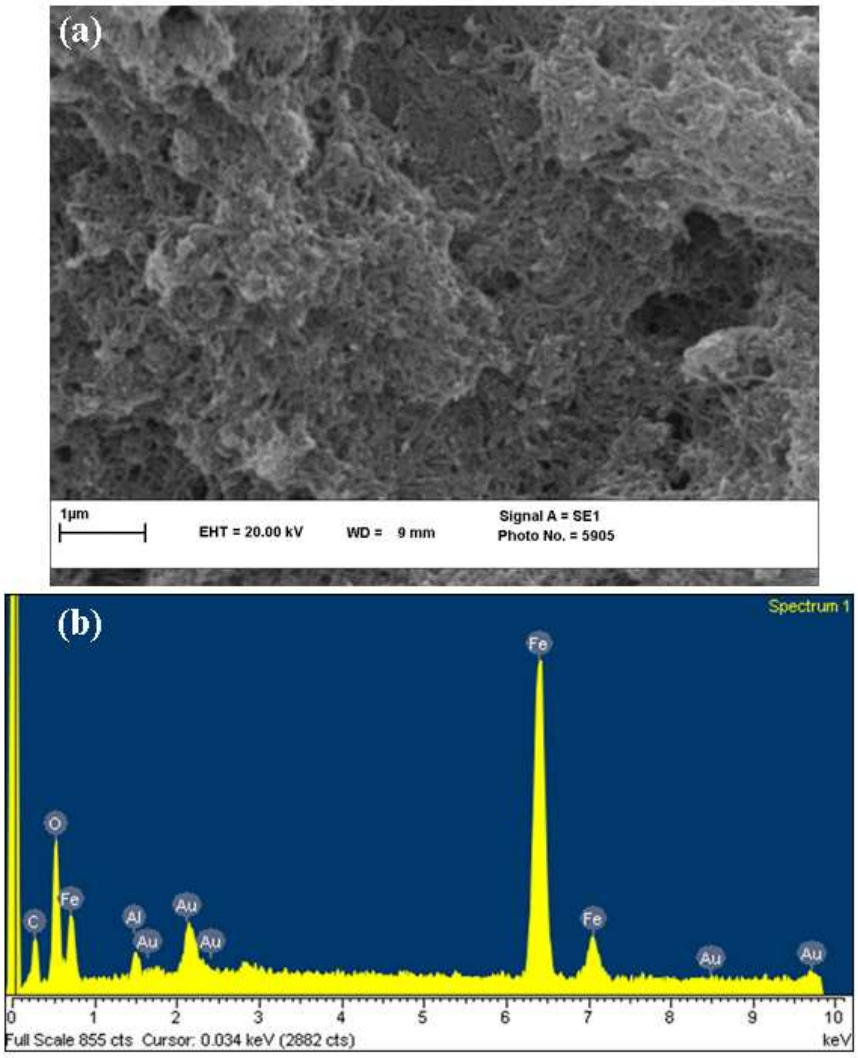


Fig. 1. SEM images of CNFs.

Also Fig. 2a display the SEM image of CNFs-Fe_3O_4, which illustrate the surface morphology and uniform size distribution of Fe_3O_4 nanoparticles. One of the instruments most commonly used in conjunction with the SEM is the Energy Dispersive X-ray Spectrometer (EDX). Combining the EDX with the SEM allows the identification, at microstructural level, of compositional gradients at grain boundaries, second phases, impurities, inclusions, and small amounts of materials. In the scanning mode, the SEM/EDS unit can be used to produce maps of element location, concentration, and distribution. The locations of the peaks are directly related to the particular x-ray "fingerprint" of the elements present. Consequently, the presence of a peak, its height, and several other factors, allow the analyst to identify the elements within a sample. The

196 EDX spectra of CNFs-Fe_3O_4 nanoparticles is shown in Fig. 2b. The results confirmed the
197 existence of Fe_3O_4 nanoparticles on the CNF surface.



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199 **Fig. 2.** (a) SEM image of CNFs-Fe_3O_4 nanoparticles, (b) EDX spectrum of CNFs-Fe_3O_4
200 nanoparticles.

201 Also, the size and morphological features of CNFs-Fe_3O_4 nanoparticles were visualized
202 with TEM. As you can see from Fig.3, the nanoparticles are spherical and have an
203 average diameter of 20 nm.

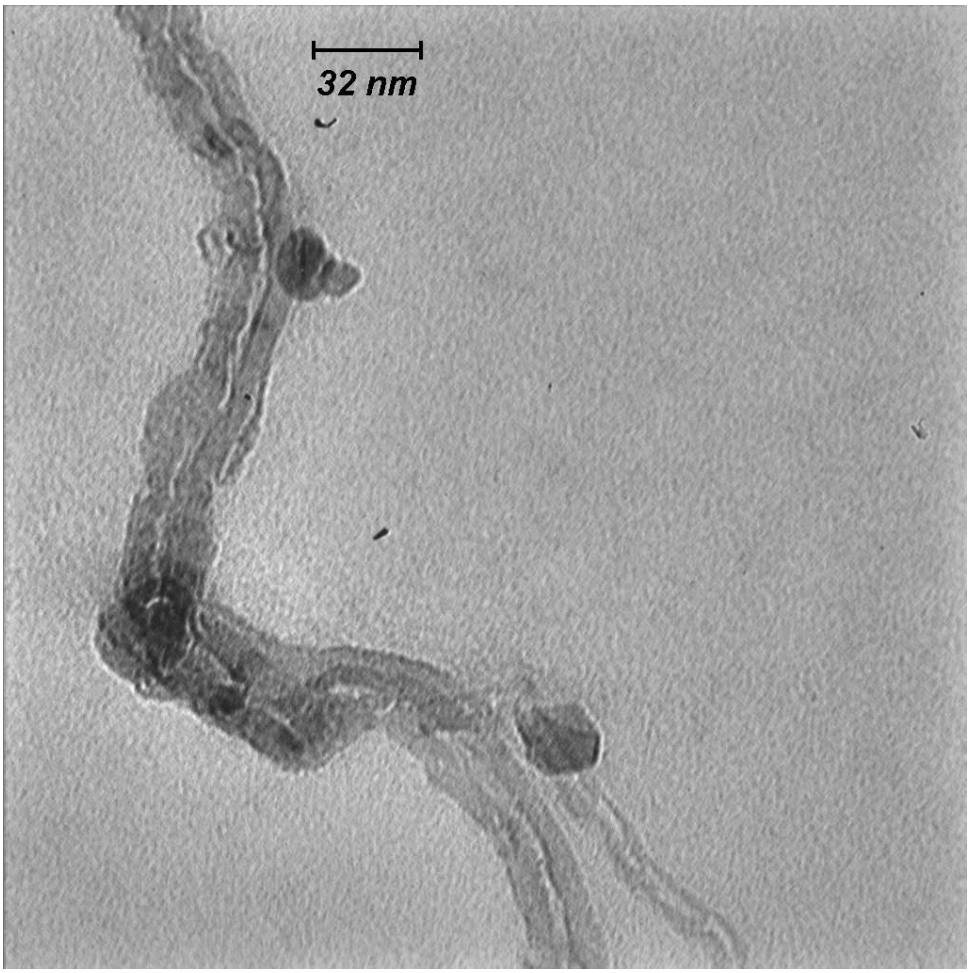

Fig. 3. TEM image of CNFs-Fe_3O_4 nanoparticles.

3.3. Optimization of magnetic solid-phase extraction conditions

In order to identify the responsible of the extraction, CNFs-Fe_3O_4 and Fe_3O_4 nanoparticles were used for the MSPE of target analytes. The chromatographic peak area at the same conditions and concentration for the CNFs-Fe_3O_4 and Fe_3O_4 nanoparticles were compared together and results shown that the peak area for CNFs-Fe_3O_4 nanoparticles is greater than Fe_3O_4 nanoparticles. This result was related to CNFs according to its special properties especially high surface area and ability to establish π–π interactions.

The adsorption of PAHs on different ratios of CNFs/Fe_3O_4 (m Fe_3O_4: m CNFs = 0.1:0.1, 0.2:0.1, 0.5:0.1, 0.6:0.1, 0.8:0.1 and 1:0.1) was recorded. The results shown that with the increasing the Fe_3O_4 nanoparticles on the surface of the CNFs the adsorption capacity decreased due to the surface of the CNFs was occupied by Fe_3O_4 nanoparticles. So the active sites of CNFs were blocked with Fe_3O_4 nanoparticles, so the adsorption capacity decreased. However, at a high amount ratios of Fe_3O_4/ CNFs, the magnetic properties of adsorbent enhanced and it can easily be separated in sample solution within short time under eternal magnetic field. Therefore, the Fe_3O_4/CNFs nanocamposite with the ratio 1:1 (m Fe_3O_4: m CNFs = 0.1:0.1) were selected for the following investigation.

The magnetic solid-phase extraction conditions involving the amount of sorbent, adsorption and desorption times, desorption solvent and also volume, and the salt effects were optimized to improve the extraction efficiency of the CNFs-Fe_3O_4. The chromatographic peak area was used to evaluate the influence of the factors on the extraction efficiency.

The selection of an appropriate desorption solvent is of major importance for the optimization of MSPE process. Five solvents were tested as desorption solvent in this study, including dichloromethane, acetone, isopropyl alcohol, methanol and acetonitrile. As shown in Fig. 4a, desorption ability of dichloromethane was found to be higher than the other solvents. Therefore, dichloromethane was used as desorption solvent throughout the experiments.

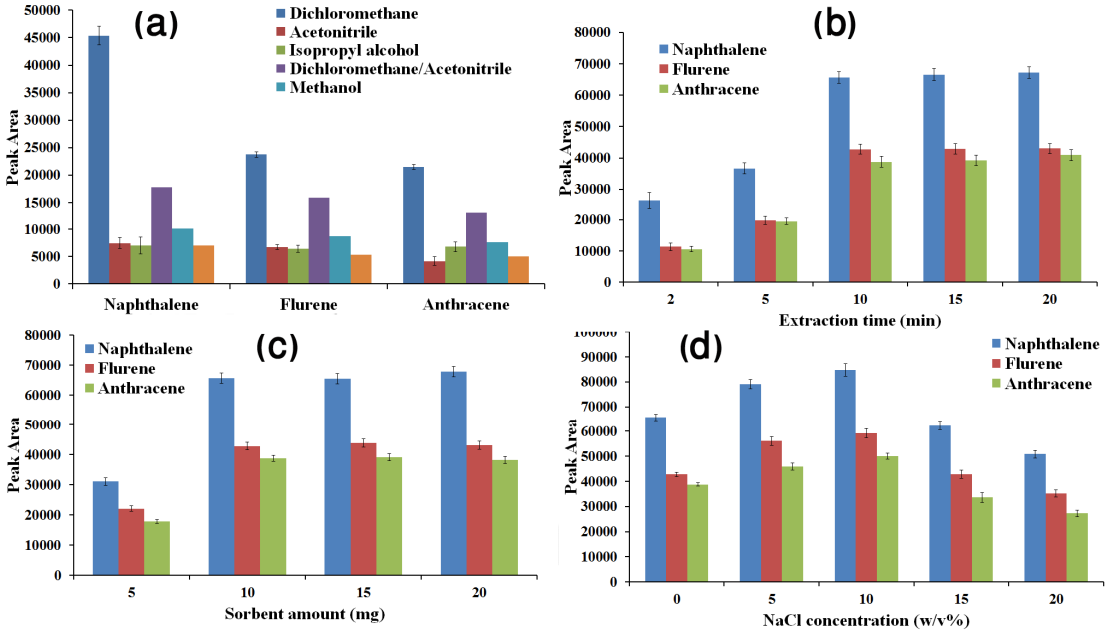

Fig. 4. (a) Effect of eluent type on the extraction efficiency of PAHs; (b) Effect of extraction time on the extraction efficiency of PAHs; (c) Effect of c sorbent amount on the extraction recovery of PAHs (d) Effect of salt on the extraction efficiency of PAHs.

The desorption time was studied in the range of 0.5 to 10 min. The results showed that the time of 5 min appeared to be the optimum value for the elution of the analytes. Additionally, the effect of the eluent solution volume on the desorption efficiency of the analytes was also investigated. It was found that all the analytes could be quantitatively desorbed from the sorbent by rinsing the nano-adsorbent with 1 mL of dichloromethane. Therefore, 1 mL of dichloromethane was selected for the elution of the analytes from the nano-adsorbent.

Large surface area and high extraction capacity are the main advantages of nanomaterial adsorbents. Therefore, compared to micro-sized sorbents, better extraction efficiency can

be achieved with a less amount of NPs. To study the effect of the amount of the sorbent on the extraction efficiency, the extraction was performed by varying the amounts of the sorbent from 5 to 20 mg (Fig. 4b). The results demonstrated that the extraction efficiency was enhanced by increasing the sorbent amount up to 10 mg. Further increase in the amount of sorbent did not change significantly the analytical signals. Therefore, 10 mg of the CNFs-Fe_3O_4 sorbent was used for further extractions.

To increase the precision and sensitivity of the extraction method, it is necessary to provide an exposure time that guarantees the equilibrium between aqueous phase and sorbent. For studying the effect of sorption time on extraction efficiency, sorption times were varied in the range of 2.0–20 min (Fig. 4c). Due to the very high surface area to volume ratios in nano-adsorbents and their short diffusion routes which lead to a high rapid sorption process, the equilibrium between sample solution and sorbent surface can be reached in a shorter contact time in comparison with the conventional SPE sorbents. The results indicated that the extraction efficiency was enhanced by increasing the sorption time from 2.0 to 10.0 min, and then remained almost constant with further increase in time. Thus, the sorption time of 10.0 min was selected for further studies.

Addition of salt into the aqueous sample is usually causing improvement in the extraction of several analytes, because the increase in ionic strength brings a reduction on the solubility of the hydrophobic analytes in the water solution and forces more of these analytes into the extracting phase. The increase in the extraction extent can be explained by the engagement of water molecules in the hydration spheres around the ionic salt and hence in the reduction of the water concentration available to dissolve analytes. The salting-out effect was examined by monitoring the variation of peak areas in the presence

of different concentrations of NaCl (from saltless up to 20% *w/v*). Results show that the extraction efficiencies of the compounds under study increased with the salt content in the range tested, and in the 10% *w/v* salt concentration, maximum extraction efficiency was observed (Fig. 4d) and decreases, thereafter. The negative effect is attributed to the fact that the aqueous solution viscosity would increase with the addition of salt, which resulted in difficult mass transfer and low extraction efficiency.

3.4. Reusability of adsorbent

Reusability is another important factor for evaluating the performance of the magnetic nano-adsorbents. The adsorbent was regenerated by washing with 2 mL of methanol and then with 5 mL water before the next MSPE application. In such way, no carry-over of the analytes on the adsorbent was detected. The results showed that no obvious changes were observed in the extraction efficiency after ten successive extraction process. The good reusability indicates that this magnetic sorbent is stable and durable during the extraction procedure.

3.5. Evaluation of analytical performance

Under the optimal experimental conditions, different quality parameters were evaluated to assess the method performance. The results are summarized in Table 1. For the target analytes quantification, the external standard calibration at eight different concentration levels (for naphthalene: 0.025, 0.1, 0.5, 1, 10, 30, 50 and 100 ng mL^{-1}; fluorene: 0.04, 0.1, 0.5, 1, 10, 30, 50 and 100 ng mL^{-1}; anthracene: 0.08, 0.1, 0.5, 1, 10, 30, 50 and 100 ng mL^{-1}) was used. For each level, three replicate extractions were performed under optimal conditions. Good linear relationship between the corresponding peak areas and

the concentrations were obtained for all the analytes ($r > 0.9965$). The limits of detection (LODs) and quantification (LOQs), based on signal-to-noise ratio (S/N) of 3:1 and 10:1, were determined. LODs and LOQs were obtained in the range of 0.008–0.03 ng mL^{-1} and 0.025–0.08ng mL^{-1}, respectively. In order to assess the repeatability of the method, five replicate determinations were carried out at three concentration levels (0.1, 10 and 100 ng mL^{-1}) and the relative standard deviations (RSDs) were calculated. The observed repeatability ranged 3.2–11.2% depending of the compound considered.

Table 1. Figures of merit of the proposed method for the determination of PAHs

Analyte	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Linear range (ng mL^{-1})	Correlation coefficient (r)	RSD(%) at three concentration (ng mL^{-1})		
					0.1	10	100
Naphthalene	0.008	0.025	0.025–100	0.9980	9.8	5.7	4.8
Fluorene	0.01	0.04	0.04–100	0.9965	8.4	7.4	3.2
Anthracene	0.03	0.08	0.08–100	0.9965	11.2	4.6	4.5

3.6. Real sample analysis

To evaluate the applicability of the proposed method, extraction and analysis was performed on different water matrices such as tap water, river water, well water and waste water samples. The quantitative results of this water samples are listed in Table 2. In order to investigate the performance of the established method, CNFs-Fe_3O_4 sorbents was applied to extract these water samples spiked at three concentration levels (0.1, 10 and 100 ng mL^{-1}) for each compound. The recoveries and determination precisions are listed in Table 2. The results showed that the mean recoveries of PAHs (n = 3) ranged

from 90.1 to 100.9% and the RSDs were between 3.2% and 9.8%. These results clearly demonstrated that the matrix effect did not have a significant role on the extraction efficiency. Fig. 5 shows the GC chromatograms obtained from spiked wastewater samples at concentration level of 10 ng mL^{-1} with the CNFs-Fe_3O_4. Downward shift in background of chromatogram may be due to some impurities in the background which are very volatile and coming up very soon in low temperature, and by increasing the temperature the baseline become stable.

Table 2. Content of PAHs in different water samples and the accuracy of the established proposed method.

Sample	Analyte	Mean (ng mL^{-1})	Spiked amount (ng mL^{-1})					
			0.1		**10**		**100**	
			Relative recovery (%)[a]	RSD (%)	Relative recovery (%)[a]	RSD (%)	Relative recovery (%)[a]	RSD (%)
Tap water	Naphthalene	ND	95.6	9.8	99.0	5.2	98.6	4.5
	Fluorene	ND	98.2	5.8	99.1	5.1	97.8	5.0
	Anthracene	ND	96.4	6.2	97.3	5.1	99.0	4.1
Well water	Naphthalene	ND	94.8	7.5	96.2	5.9	100.9	5.1
	Fluorene	ND	93.9	5.4	93.0	4.8	97.6	3.2
	Anthracene	ND	95.7	5.9	96.5	5.3	98.3	4.7
River water	Naphthalene	ND	93.7	7.5	96.9	6.3	98.1	6.5
	Fluorene	ND	96.3	8.9	98.6	5.6	95.8	4.9
	Anthracene	0.085	97.1	9.1	97.5	7.7	98.0	5.8
Wastewater	Naphthalene	0.038	92.3	8.6	93.9	6.0	93.5	6.5
	Fluorene	ND	93.7	5.5	95.0	4.5	95.9	4.6
	Anthracene	ND	90.1	7.1	91.6	5.9	92.1	6.4

ND: not detected

[a]: Relative recovery (%)= (The found amount in the spiked sample − The found amount in the sample/The added amount) × 100.

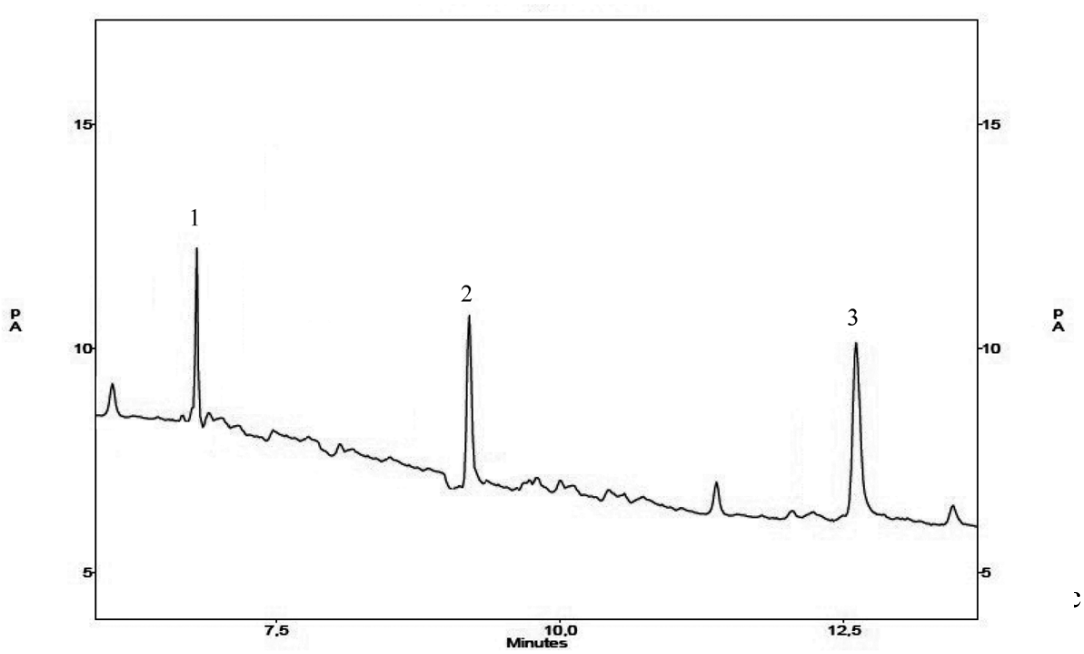

Fig. peaks: (1) Naphthalene, (2) Fluorene and (3) Anthracene.

3.7. Comparison with other related methods

A comparison between the figures of merit of the proposed method and some of the reported methods for the extraction and determination of PAHs water samples are summarized in Table 3.[19–23] The comparison of the results with other reported methods revealed that the proposed method has wider linear dynamic range and lower detection limit. Also, due to the large surface area and rapid extraction dynamics of the MNPs, this method has a very short extraction time using small amount of organic solvent. Hence, the analytical performance of the current method is acceptable.

Table 3. Comparison of the proposed method with other methods applied for the extraction and determination of PAHs.

Method	Analytes	Sample	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	RSD (%)	Reference
DLLME-SFO–HPLC	Naphthalene, acenaphthene , anthracene, fluoranthene	Water	0.045–1.10	0.1–50	1.3–4.4	21
LPME-SFO–GC-FID	Phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*ah*]anthracene, indeno[123-*cd*]pyrene, benzo[*ghi*]perylene	Water	0.07–1.67	0.25–300	<7	22
SPME–GC-FID	Acenaphthylene, fluoranthene, fluorene, naphthalene, phenanthrene, biphenyl	Water	0.04–0.06	0.1–100	4.1–6.7	23
SPME–GC-FID	Naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, biphenyl	Water	0.02–0.08	0.1–300	5.4–7.8	24
SPME–GC-FID	Naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, benzo(-ghi)perylene	Water	0.03–0.1	0.1–100	6–9	25
SPME–GC-FID	Naphthalene, phenanthrene, anthracene, fluoranthene, pyrene	Water and smoked rice	0.009-0.013	0.02–1000	1.33–3.61	26
SPE–HPLC-FD	Fluorene, anthracene, fluoranthene, pyrene, 1,2-benzanthracene, benzo(b)fluoranthene, benzo(k)fluoranthene	Water	0.0008–0.016	0.001–2.4	2.9–3.3	27
MSPE–GC-FID	Naphthalene, fluorene, anthracene.	Water	0.008–0.03	0.025–100	3.2–11.2	This study

Abbreviations: DLLME, Dispersive liquid–liquid microextraction; HPLC, High performance liquid chromatography; LPME-SFO, Liquid-phase microextraction method based on the solidification of a floating organic microdrop; SPME, Solid-phase microextraction.

4. Conclusion

In this work, for the first time, carbon nanofibers-Fe_3O_4 sorbents were prepared and then successfully applied for the analysis of some of polycyclic aromatic hydrocarbons in real water samples. Due to the unique properties of carbon nanofibers and the inherent advantageous features, this innovative sorbent exhibited porous surface structure, wide linearity, satisfactory relative recovery, good sensitivity and precision and short analysis

time. Additionally, this technique was successfully utilized to analyze of polycyclic aromatic hydrocarbons in real water samples with satisfactory accuracy and precision. On the basis of the obtained results, it is anticipated that the proposed method has a great analytical potential in the preconcentration of trace analytes from real sample in the same way.

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Figure Captions

Fig. 1. SEM images of CNFs.

Fig. 2. (a) SEM image of CNFs-Fe_3O_4 nanoparticles, (b) EDX spectrum of CNFs-Fe_3O_4 nanoparticles.

Fig. 3. TEM image of CNFs-Fe_3O_4 nanoparticles.

Fig. 4. (a) Effect of eluent type on the extraction efficiency of PAHs; (b) Effect of extraction time on the extraction efficiency of PAHs; (c) Effect of c sorbent amount on the extraction recovery of PAHs (d) Effect of salt on the extraction efficiency of PAHs.

Fig. 5. GC chromatogram of wastewater sample spiked at 10 ng mL^{-1}. Chromatographic peaks: (1) Naphthalene, (2) Fluorene and (3) Anthracene.

Table Captions

Table 1. Figures of merit of the proposed method for the determination of PAHs.

Table 2. Content of PAHs in different water samples and the accuracy of the established proposed method.

Table 3. Comparison of the proposed method with other methods applied for the extraction and determination of PAHs.