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ARTICLE

Preparation of ionic liquid-modified magnetic nanoparticles based on thiol-ene click chemistry for the analysis of polycyclic aromatic hydrocarbons in water and smoked meat samples

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In the present study, ionic liquid (IL)-modified Fe_3O_4 magnetic nanoparticles (Fe_3O_4) were synthesized by the thiol-ene click reaction for magnetic solid-phase extraction (MSPE) of polycyclic aromatic hydrocarbons (PAHs) in water and smoked meat samples. An IL 1-vinyl-3-butylimidazolium bromide was firstly synthesized, and then immobilized on the surface of thiol group-functionalized Fe_3O_4 via a thiol-ene click reaction. The as-synthesized Fe_3O_4@ILs were characterized using Fourier transform infrared spectroscopy, X-ray diffraction, and transmission electron microscopy. Various parameters (including the amount of adsorbent, extraction time, sample volume, and desorption conditions) affecting MSPE were optimized. Under the optimum conditions, the limits of detection of four PAHs in the range of 0.6–7.2 ng/L were obtained using high-performance liquid chromatography–ultraviolet detection. The accuracy of the method was assessed by recovery measurements on spiked real samples and good recovery of 80–108% with relative standard deviations lower than 8.16% was achieved. The enrichment factors ranging from 699 to 858 were obtained for the analytes. This result indicated that the proposed method had great potential for sample preparation.

KEYWORDS

ionic liquids, magnetic solid-phase extraction, polycyclic aromatic hydrocarbons, smoked meat, thiol-ene click chemistry, water samples

1 | INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent pollutants widely distributed in the natural environment and existed in soil, sediments, water, atmosphere, and animals.[1,2] These organic pollutants are commonly generated by human activities, mainly the incomplete burning of organic materials such as coal, petrol, gas, tobacco, and garbage.[3] In the last few decades, scientists have made great efforts to monitor and determine PAHs due to their high toxicity, carcinogenicity, teratogenicity, and mutagenicity.[4,5] PAHs have been considered hazardous to human beings by migrating through the food chain and accumulating in living organisms. Therefore, it was of great importance to develop sensitive, reliable, and easily operating analytical methods for the determination of PAHs in environmental samples. Several routine methods for analyzing PAHs are chromatographic techniques, including high-performance liquid chromatography coupled with UV,[6] diode array detection,[7,8] fluorescence detection,[9,10] and gas chromatography coupled with mass spectrometry (GC–MS).[11,12] However, the direct determination of PAHs in environmental samples is a difficult task due to the complex matrices and a very low concentration level. Consequently, prior to chromatographic analysis, a sample preparation step, which aims to concentrate the target analytes and eliminate matrix interference, is, therefore, indispensable.

Ionic liquids (ILs) are a class of molten salts containing organic cation and inorganic or organic anions with unique and fascinating properties, including low volatility, good thermal stability, miscibility, and tunable viscosity.[13,14] These fascinating properties have made significant contributions in the field of analytical chemistry.[15] Especially, ILs have been widely used for sample pretreatment, such as liquid–liquid extraction,[16,17] liquid-phase micro-extraction,[18,19] mixed hemimicelles solid-phase extraction,[20,21] and solid-phase micro-extraction.[22,23] In recent years, IL-modified Fe_3O_4 as an adsorbent for mixed hemimicelle solid-phase extraction has been studied by the research group of Yao.[24] Cheng et al.[25] utilized IL-coated Fe_3O_4 as an adsorbent for the preconcentration of two chlorophenols in water samples. Liu et al.[26] prepared Fe_3O_4@ILs@methyl orange nanoadsorbent through self-assembly for the extraction of target analytes. Cao et al.[27] have synthesized IL-coated Fe_3O_4@ grapheme nanocomposites and used to extract nitrobenzene compounds in environmental water samples. The application of IL-functionalized Fe_3O_4 has become an important separation technology in sample preparation. However, preparation of IL-modified Fe_3O_4 in solid-phase extraction is still at an early stage.

Nowadays, magnetic solid-phase extraction (MSPE) has attracted increasing attention attributing to its great potential application in different areas.[28] A distinct advantage of this technology is that magnetic materials can be readily isolated from sample solutions by the application of an external magnetic field, which makes the method environmentally friendly and economical.[29,30] Consequently, there have been several methods developed to introduce desired functionalities onto the surfaces of Fe_3O_4. Yao's group utilized the triphenylamine-functionalized magnetic microspheres as sorbents for the enrichment of PAHs in water samples.[31] Li et al.[32] described surface-exchangeable core@shell Fe_3O_4@Au nanoparticles for MSPE. Zhu et al.[33] prepared a magnetic graphene oxide composite and applied for the determination of PAH metabolites in human urine. Wang et al.[34] developed a method for the extraction of five PAHs from water samples using magnetic microsphere-confined grapheme as a sorbent. Meng et al.[7] synthesized polydopamine-coated Fe_3O_4 for enrichment of PAHs from environmental water samples. Recently, great interest was aroused in the use of the thiol-ene reaction in materials science, synthesis, and modification.[35] To date, the thiol-ene reaction has been widely used in the materials arena, great efforts have been made to fabricate surface functional Fe_3O_4 via thiol-ene click reaction. Zhang et al.[36] prepared boronic acid-functionalized Fe_3O_4 via a thiol-ene click reaction, and for preconcentration of proteins in complex biosamples. Liang et al.[37] reported the introduction of ferrocene onto the surface of Fe_3O_4 via a UV-induced thiol-ene reaction. These studies indicate that thiol-ene reaction has the potential to modify Fe_3O_4 nanoparticles (NPs) with mild reaction conditions at room temperature. These important research studies inspire us to explore novel functionalized materials to be used as MSPE adsorbents for enrichment of organic pollutants from environmental water samples. However, preparation of IL-modified Fe_3O_4 through thiol-ene reaction for enriching PAHs has not been reported.

In this study, a novel thiol-ene click chemistry strategy was proposed for the preparation of IL-modified Fe_3O_4 (Fe_3O_4@ILs) for MSPE, which are used as adsorbents for the enrichment of PAHs. Fe_3O_4@ILs were facilely synthesized based on the thiol-ene click reaction between 1-vinyl-3-butylimidazolium bromide and thiol-functionalized Fe_3O_4. Four PAHs, including fluorene (Flu), anthracene (Ant), pyrene (Pyr), and fluoranthene (Fla), were selected as model analytes to evaluate the extraction performance of the prepared nanoadsorbent. The significant experimental factors affecting the extraction recoveries were examined. The results of analyzing four PAHs in water and smoked meat samples were proven to be applicable.

2 | EXPERIMENTAL

2.1 | Chemicals and materials

(3-Mercaptopropyl) trimethoxysilane (MPTMS) (98%), tetraethoxysilane (TEOS) (98%), vinylimidazole (98%), 1-bromobutane (98%), dimethyl sulphoxide (DMSO) and azobisisobutyronitrile (AIBN) were purchased from Alfa Aesar (Ward Hill, MA, USA). Potassium hexacyanoferrate (II) trihydrate, zinc sulfate heptahydrate, fluorene, anthracene, pyrene, and fluoranthene were obtained from Sigma-Aldrich (St. Louis, MO, USA). All the iron (III) chloride hexahydrate, sodium acetate trihydrate, ethylene glycol, absolute alcohol, isopropanol, glacial acetic acid, triethylamine, ammonium hydroxide, toluene, hydrochloric acid, potassium hydroxide, and sodium hydroxide, etc., were of analytical grade. High-performance liquid chromatography (HPLC)-grade methanol and acetonitrile were purchased from Shanghai Chemical Reagents Corporation (Shanghai, China). The ultrapure water used for the preparation of solutions was produced by a Yue Chun water system (Chengdu, China). All samples were filtered (MFS-25, 0.22 μm, Shanghai, China) before being injected into the HPLC system.

2.2 | Apparatus

The morphology and sizes of the Fe_3O_4@ILs were characterized by transmission electron microscopy (TEM, FEI Tecnai G20). The characterization of the crystalline phase was performed on a Rigaku D/max 2500/PC (Japan) X-ray diffraction (XRD) with a Cu Kα source. Fourier transform infrared (FT-IR) spectroscopy was conducted on a Thermo Nicolet 6700 FT-IR spectrometer over the range of

500–4,000 cm^{-1}. The electrospray ionization mass spectra (ESI-MS) were recorded using the Bruerhct (Bruker, Germany) operated in the positive ion mode. ^{1}H-NMR spectra were recorded using a Bruker Avance AV 500 spectrometer.

A KQ2200DE ultrasonic bath with temperature control (Kunshan Shumei Ultrasonic Instrument, Suzhou, China) was used to disperse the nanoparticles in the solution. A microwave extraction lab station (MDS-10 Sineo, Shanghai, China) was employed to extract target analytes from solid matrices. The reported pH of solution was carefully measured using a PHS-3B pH-meter (Shanghai, China). An Nd–Fe–B magnet (8.0 × 6.0 × 1.6 mm) was used for magnetic separation.

2.3 | Synthesis of IL

The IL (1-vinyl-3-butylimidazolium bromide) was synthesized according to the procedures as described in our previous work.[38] 1-Bromobutane (4.11 g, 0.03 mol) and 1-vinylimidazole (2.82 g, 0.03 mol) were added to a dry three-necked round-bottomed flask, then ethanol (50 mL) was added into the bottle as a solvent. The mixture was refluxed for 48 hr under nitrogen with stirring at 60°C. The obtained red-brown viscous product of the IL was washed several times with ethyl acetate and dried under vacuum. Yield: 96%. The obtained product was characterized by FT-IR (Figure S1), ESI-MS (Figure S2) and ^{1}H-NMR (Figure S3), and spectral data for IL were as follows: FT-IR (KBr, ν, cm-1), 3,428.4, 3,060.2, 2,962.2, 2,868.3, 1,648.2, 1,569.5, 1,456.9, 1,374.9, 1,172.5, 1,116.3, 1,022.3, 957.3, and 751.2. ESI-MS, m/z at 152.12 $[M\text{-}Br]^+$ ions. ^{1}H-NMR (500 MHz, DMSO), 9.64 (1H, s), 8.26 (1H, d), 7.98 (1H, d), 7.31 (1H, dd), 5.99 (1H, dd), 5.42 (1H, dd), 4.22 (2H, t), 1.81 (2H, m), 1.28 (2H, m), and 0.90 (3H, t).

2.4 | Preparation of Fe_3O_4@ILs

Fe_3O_4 was prepared via a common solvothermal reaction.[39] After the reaction, the obtained Fe_3O_4 was dispersed into 150 mL of ethanol and sonicated for 10 min, then 10 mL of 26.5% aqueous ammonia and 4 mL TEOS were added successively. After that, the mixture was stirred for 24 hr. The resultant product was separated from the reaction medium by applying a magnetic field, followed by rinsing with ethanol four times and drying in a vacuum.

An amount of 0.6 g of the SiO_2-coated Fe_3O_4 was dispersed into 50 mL anhydrous toluene, then 4.0 mL MPTMS and 2 mL triethylamine were added. The mixture was stirred for 24 hr under reflux at 90°C. After cooling to room temperature, the resultant product was collected by applying a magnetic field, followed by rinsing with toluene, ethanol-water mixture (1:1, vol/vol), and ethanol in sequence. After drying under vacuum at 50°C for 12 hr, the as-prepared thiol-terminated Fe_3O_4 was dispersed in 50 mL ethanol, then 0.5 g ILs and 25 mg AIBN were added and the mixture was stirred for 6 hr at 50°C. The resultant product was collected by using a magnetic field and washed with deionized water, ethanol in turn. The obtained Fe_3O_4@ILs were dried in a vacuum for use. The preparation procedure is illustrated in Figure 1a.

2.5 | Sample collection

Three types of water samples were collected randomly, including river water collected from Longjiang River (Yi zhou, Guangxi), tap water collected from the local supply system (Yizhou, Guangxi), wastewater obtained from our laboratory. All water samples were filtered through a 0.22 μm membrane syringe filter to remove the suspended solids, and stored at 4°C before use.

The smoked meat sample was randomly purchased from a local market and stored at −20°C in the dark until further use. The smoked meat sample was minced in a meat grinder, and the extraction procedures were performed according to Kamankesh et al.[40]

2.6 | MSPE procedure

The MSPE procedure is illustrated in Figure 1b. First, Fe_3O_4@ILs were cleaned and activated with 5 mL acetonitrile and 5 mL water in order. Afterward, Fe_3O_4@ILs were incubated in a sample solution spiked with PAHs. To completely capture the target analytes, the mixture was sonicated for 3 min to suspend Fe_3O_4@ILs, and allowed to stand for 5 min. After that, the Fe_3O_4@ILs were collected using a magnetic field. After discarding the supernatant solution, 3 × 2 mL acetonitrile was added to the Fe_3O_4@ILs and sonicated for 1 min to release the PAHs. The eluate was collected and dried with a stream of nitrogen at 50°C. The

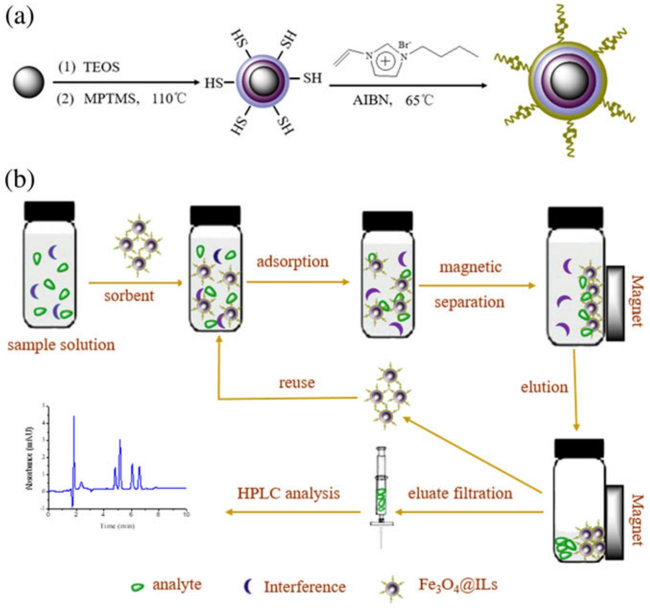

FIGURE 1 Schematic illustration of the synthesized Fe_3O_4@ILs (a). Procedure for MSPE of water sample using Fe_3O_4@ILs (b)

residue was redissolved in 100 μL acetonitrile and filtered through a 0.22 μm membrane syringe filter. Finally, 15 μL of this solution was injected for HPLC analysis.

2.7 | HPLC analysis

HPLC was performed using an Agilent Technologies (Santa Clara, CA, USA) 1,200 liquid chromatograph equipped with a UV detector. An Agilent Zorbax SB-C18 column (100 × 4.6 mm) and a particle size of 3.5 μm were used for all analyses. The mobile phase consisted of methanol and 0.1% (vol/vol) aqueous acetic acid in a ratio of 85:15 (vol/vol), the flow rate was set at 0.6 mL/min, the column temperature was 30°C, the detection wavelength was set at 254 nm.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of Fe_3O_4@ILs

The morphology and size of the prepared Fe_3O_4@ILs were characterized by TEM. As can be seen from Figure 2, the Fe_3O_4 and Fe_3O_4@ILs were of spherical shape, and have relatively good monodispersity. After Fe_3O_4 was coated with silica and further modified with ILs, a dark Fe_3O_4 core was coated with a gray shell (Figure 2b). This result proves that Fe_3O_4-supported silica-IL nanoparticles were synthesized.

The synthesized Fe_3O_4@ILs were further characterized using FT-IR. Figure 3a describe the FT-IR spectra of different materials. As can be seen, the peaks at about 580 and 3,200 cm^{-1} appearing in all curves correspond to the Fe-O, O-H stretching vibrations, In addition, the peak at 1624 cm^{-1} corresponds to the O—H bending vibrations. In the spectra of Fe_3O_4@IL NPs, the Si-O absorption at 1100 cm^{-1} can also be observed, and the peaks at 2854.1 and 2,923.6 cm^{-1} were assigned to C—H stretches within the side alkyl chain of the imidazole ring, indicating that ILs were successfully bonded to the surface of Fe_3O_4.

The crystalline structures of different magnetic particles are investigated using XRD and the results are shown in Figure 3b. The special reflection peaks at 2θ = 30.2°, 35.5°, 43.3°, 56.6°, 57.2°, and 62.8° can be ascribed to the (220), (311), (400), (422), (511), and (440) planes of the Fe_3O_4 lattice, respectively. This result indicated that the crystalline structure of Fe_3O_4 was not changed during the coating process. In addition, the peak at 2θ = 25.1° can be attributed to the presence of amorphous silica.[41] The decline of the magnetic strength is likely attributed to the coating of nonmagnetic shells on magnetic particles. This phenomenon proves the successful preparation of Fe_3O_4@ILs.

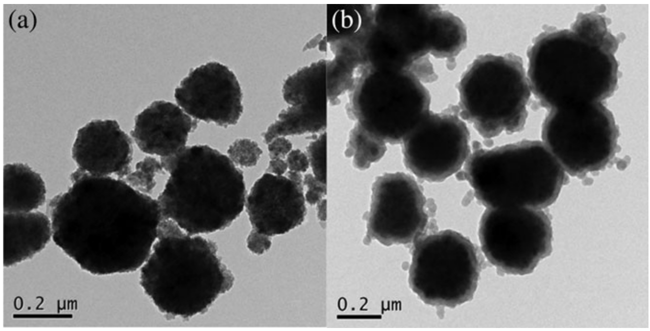

FIGURE 2 TEM images of Fe_3O_4 (a), Fe_3O_4@ILs (b)

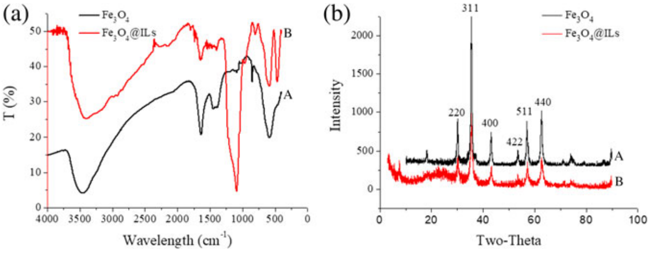

FIGURE 3 FT-IR spectra (a) and XRD patterns (b) of Fe_3O_4 (A), Fe_3O_4@ILs (B)

3.2 | Optimization of extraction conditions

To meet a satisfactory recovery rate, the parameters affecting the recovery of analytes including the amount of adsorbent, extraction time, sample volume, and desorption conditions were investigated and optimized. In this research, ultrapure water spiked with 1 μmol/L of each PAH was used for these optimization experiments.

3.3 | Effect of the amount of Fe_3O_4@ILs

The amount of Fe_3O_4@ILs necessary to afford quantitative concentration of target analytes is a vital parameter that determines the recovery rate of the MSPE method. Therefore, different amounts of Fe_3O_4@ILs ranging from 10 to 120 mg were tested. As can be seen in Figure 4, the recoveries of the PAHs increase with an increase in the amount of Fe_3O_4@ILs from 10 to 40 mg, but no obvious change with a

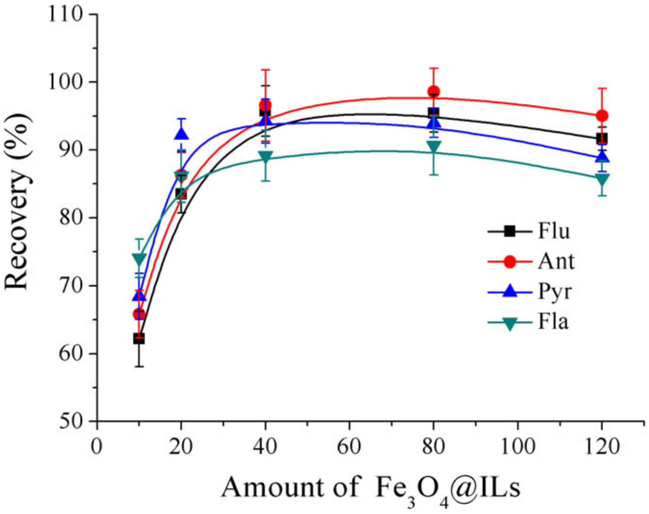

FIGURE 4 Effect of the amount of Fe_3O_4@ILs

further increase in the amount. Based on this result, 40 mg was selected for further experiments.

3.4 | Effect of extraction time and sample volume

To achieve high recovery, an appropriate extraction time is necessary for Fe_3O_4@ILs to achieve adsorption equilibrium. Thus, the effect of extraction time on the recoveries of PAHs was examined in the range of 2–20 min and the experiment result is shown in Figure 5a. The recoveries of four PAHs increase with increasing extraction time for up to 10 min, the maximum recoveries for PAHs were obtained, indicating that equilibrium is achieved within 10 min. The efficient diffusion route of nanosized sorbents meets the rapid extraction dynamics of analytes on the sorbent surface. However, the recoveries of four PAHs showed a slight decrease when the extraction time increased to 20 min, this phenomenon may be attributed to the desorption of PAHs. Acceptable recovery of target analytes in as large volume of sample solutions as possible was achieved. In the present study, the investigation of sample volumes was studied by extracting target analytes, fixed quantities of 0.1 μmol of each PAHs were added to different sample volumes (50–300 mL). The obtained results are shown in Figure 5b, a decline of the recoveries was observed when the sample volume was above 150 mL. This phenomenon could be due to more loss of the Fe_3O_4@ILs sorbent in a large volume solution. Therefore, a sample volume of 150 mL was selected for further experiments.

3.5 | Effect of elution solvent and elution time

A suitable eluent should be used to elute PAHs from the Fe_3O_4@ILs. Different solvents including methanol, ethanol, acetonitrile, and isopropanol have been applied to elute all target analytes. Figure 6a shows that acetonitrile is more preferable than other organic solvents. Thereby, acetonitrile was selected as the eluent in this study. The effect of elution time from 1 to 10 min was studied to improve the recoveries. The result shown in Figure 6b indicates that the recoveries of all target analytes increased with increasing elution time for up to 5 min. However, the recoveries slightly decrease after 5 min. Consequently, an elution time of 5 min was enough.

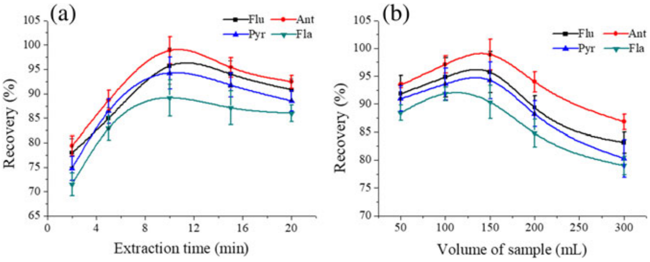

FIGURE 5 Effect of the extraction time (a) and sample volume (b) on the recovery of PAHs

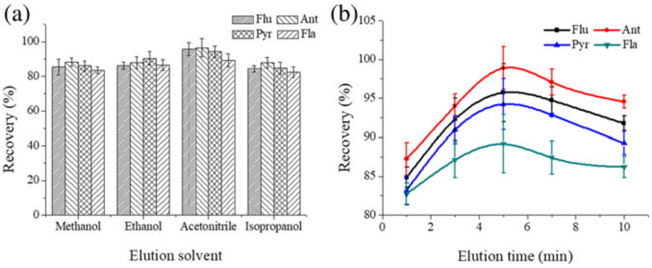

FIGURE 6 Effect of the elution solvent (a) and elution time (b) on the recovery of PAHs

3.6 | Reusability and regeneration

To assess the reusability and regeneration of the Fe_3O_4@ILs, reusability tests were carried out by extraction and desorption for seven consecutive cycles under optimal conditions. Figure 7 show that the Fe_3O_4@ILs can be reused up to seven times without obvious decrease in recoveries of the four PAHs. These results indicate the good reusability of the Fe_3O_4@ILs.

3.7 | Preconcentration performance

Under the optimal extraction conditions, the proposed method was validated by analyzing 100 mL ultrapure water samples spiked with PAH standard at the same concentration. Some quantitative parameters of the proposed method, such as linear range, correlation coefficients (R^2), limits of detection (LOD), and relative standard deviation (RSD), were tested and the experiment results are shown in Table 1. As can be seen, the proposed method has a wide linear range and good linearities with R^2 ranging from 0.9886 to 0.9912 for all analytes were obtained. The LOD, calculated on the basis of a signal-to-noise ratio (S/N) of 3 for Flu, Ant, Pyr, and Fla were 2.5, 0.6, 5.8, and 7.2 ng/L, respectively. The precision of the analytical method was evaluated with five parallel experiments, and the results indicated that the RSD (n = 5) for all analytes were less than 5.31%. At a sample

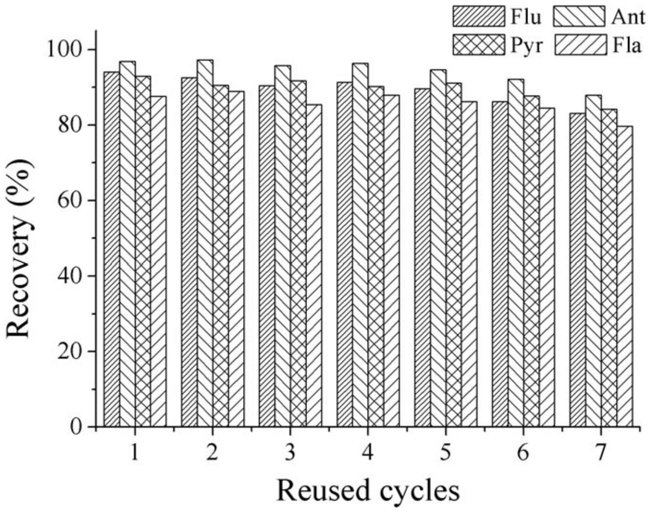

FIGURE 7 Reusability of Fe_3O_4@ILs

TABLE 1 Linear ranges of concentration and detection limits of the PAHs

Analyte	Linearity curve	Correlation coefficient R^2	Linear ranges (nmol/L)	LOD (ng/L)	RSD (%, $n = 5$)
Flu	$Y = 5.85X + 0.667$	0.9912	0.3–30	2.5	3.62
Ant	$Y = 31.59X - 2.554$	0.9907	0.25–25	0.6	5.31
Pyr	$Y = 5.52X - 0.441$	0.9891	0.35–35	5.8	2.85
Fla	$Y = 4.66X + 0.025$	0.9886	0.4–40	7.2	2.25

volume of 150 mL, the enrichment factors of the proposed method were about 817, 858, 768, and 699 for Flu, Ant, Pyr, and Fla, respectively. According to the Drinking Water Direction of the European Union (98/83/EC) and the Standards for Drinking Water Quality of China (GB 5749-2006), the total concentration of PAHs must be less than 100 ng/L[42] Thus, the method used in this study was sufficient for sensitive analysis of the real water samples.

The proposed method with Fe_3O_4@ILs as sorbents was also compared to other previous extraction methods that were used for the determination of PAHs,[10,24,43–45] the adsorbent amount, loading volume, RSD, LOD, and recoveries obtained with different materials are shown in Table 2. The present method provides that the LOD, RSD, and loading volume are lower or comparable with those previously reported in the literature.

3.8 | Analysis of the environmental water samples

To further validate the practical performance of the present method, the prepared Fe_3O_4@IL NPs were utilized for the determination of PAH concentration in environmental water and smoked meat samples including river, tap, wastewaters, and smoked meat. The results of the spiked real samples are shown in Table 3. These four PAHs were not detected in Longjiang river water, tap water, and wastewater. Figure 8a shows the HPLC chromatogram of the spiked water samples before and after MSPE using Fe_3O_4@ILs. As can be seem from Figure 8a-B,D,F, four peaks of the target analytes were observed in the chromatogram after extraction of PAHs from the spiked water sample. However, no peaks were observed before extraction of PAHs from the spiked water sample. This result indicated that the Fe_3O_4@ILs can act as sorbents for enrichment of PAHs in water samples. Figure 8b shows the HPLC chromatogram of the smoked meat sample and the spiked smoked meat sample with and without MSPE. As can be seem in Figure 8b-H, The Flu was detected in smoked meat, and the concentration was 0.27 μg/kg. Nevertheless, the tested samples were below the European Commission's maximum level for smoked meat.[46] The precision of the analytical method was assessed via the recovery test performed with spiked water and smoked meat samples. The recoveries of the spiked real sample were in the range of 80–108% with RSD less than 8.16%. These experimental results indicate that the present method provides acceptable recoveries and precisions for the determination of PAHs in environmental water and smoked meat samples.

4 | CONCLUSIONS

In the present study, a feasible method was developed to prepare Fe_3O_4@ILs via thiol-ene click reaction. The prepared Fe_3O_4@ILs were used as MSPE sorbents for pretreatment of four PAHs in environmental water and smoked meat samples before HPLC-UV detection. The result indicates that the Fe_3O_4@ILs sorbent offered high extraction efficiencies and good reusability. Under optimal conditions, the proposed method provides low LOD, good recoveries, high EFs, and easy operation. Thus, it is expected that the developed method can be used as a convenient and efficient extraction and enrichment technique for trace PAHs from environmental water and smoked meat samples.

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TABLE 2 Comparison of the present method with other methods for determination of PAHs in water samples

Sorbent	Instrumental technique	Sorbent amount (mg)	Loading volume (mL)	RSD (%)	LOD (ng/L)	Recovery (%)	Reference
Cotton fiber	HPLC-FLD	—	50	4.73–8.09	0.1–2.00	70.69–110	[10]
Fe_3O_4@ C_{16}mimBr	HPLC-FLD	80	300	3.9–6.9	0.33–8.3	76–105	[24]
Fe_3O_4@ILs	GC–MS	30	100	4–8.9	40–1,110	75–102	[12]
Fe_3O_4@C_{18}	GC–MS	50	20	2–10	800–36,000	35–99	[43]
Fe_3O_4@graphene	HPLC-UV	40	50	1.7–11.7	90–190	77–103	[44]
Fe_3O_4@ag/b-TMPDTPA	HPLC-UV	50	100	2.6–8.3	20–100	82.4–109	[45]
Fe_3O_4@ILs	HPLC-UV	40	150	2.25–8.16	0.6–7.2	80–108	This work

TABLE 3 Recoveries of the PAHs in real samples ($n = 3$)

		Spiked concentration					
		2.5 nmol/L		**5.0 nmol/L**		**10.0 nmol/L**	
Matrix	**Analyte**	**Recovery (%)**	**RSD (%)**	**Recovery (%)**	**RSD (%)**	**Recovery (%)**	**RSD (%)**
Longjiang water	Flu	84	3.62	86	5.31	105	2.85
	Ant	80	3.77	87	4.29	102	3.91
	Pyr	89	2.25	83	3.86	106	5.33
	Fla	88	2.85	92	4.12	98	4.63
Tap water	Flu	80	6.1	92	5.57	89	5.05
	Ant	92	4.66	104	3.49	93	3.38
	Pyr	83	3.67	91	4.06	96	4.86
	Fla	81	3.73	90	4.95	95	3.51
Wastewater	Flu	104	5.07	88	4.19	96	6.75
	Ant	87	3.97	90	4.86	108	8.16
	Pyr	91	4.81	84	5.32	92	4.68
	Fla	89	5.43	94	7.76	105	6.95
Smoked meat	Flu	95	5.27	97	3.93	101	6.07
	Ant	98	4.97	92	5.54	107	6.25
	Pyr	87	4.81	102	4.11	93	6.73
	Fla	91	3.88	95	5.65	102	7.58

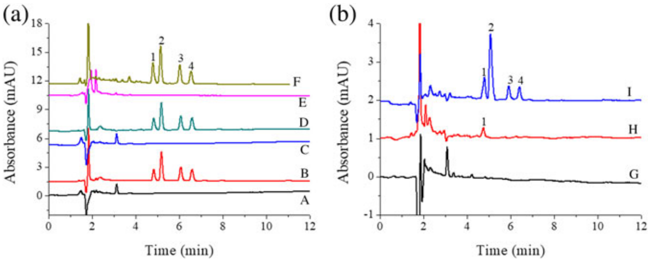

FIGURE 8 (a) HPLC chromatograms of water samples (spiked with 1 nmol/L ant, 5 nmol/L flu, Pyr and flu) without MSPE (A, C, E) and with MSPE (B, D, F). Longjiang River water sample (A, B); tap water (C, D); wastewater (E, F). (b) HPLC chromatograms of the smoked meat sample (G) no MSPE-treated smoked meat without spiked standards; (H) the MSPE-treated smoked meat without spiked standards; (I) the MSPE-treated smoked meat with spiked standards. Peak identifications: 1, Flu; 2, Ant; 3, Pyr; and 4, Fla

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REFERENCES

[1] A. Rubio-Clemente, R. A. Torres-Palma, G. A. Peñuela, *Sci. Total Environ.* **2014**, *478*, 201.
[2] P. Plaza-Bolaños, A. G. Frenich, J. L. Martínez Vidal, *J. Chromatogr. A* **2010**, *1217*, 6303.
[3] Y.-F. Chen, C.-L. Kao, J.-F. Yang, P.-C. Huang, C.-Y. Hsub, C.-H. Kuei, *J. Chin. Chem. Soc.* **2015**, *62*, 766.
[4] L.-B. Liu, Y. Liu, J.-M. Lin, N. Tang, K. Hayakawa, T. Maeda, *J. Environ. Sci.* **2007**, *19*, 1.
[5] J.-Z. Wang, C.-Z. Zhu, T.-H. Chen, *Environ. Sci.* **2013**, *15*, 1104.
[6] X. Zhang, S. Xie, M. Paau, B. Zheng, H. Yuan, D. Xiao, M. F. Choi, *J. Chromatogr. A* **2012**, *1247*, 1.
[7] Y. Wang, S. Wang, H. Niu, Y. Ma, T. Zeng, Y. Cai, Z. Meng, *J. Chromatogr. A* **2013**, *1283*, 20.
[8] W. B. Wilson, U. Hewitt, M. Miller, A. D. Campiglia, *J. Chromatogr. A* **2014**, *1345*, 1.
[9] S. Wu, W. Yu, *Food Chem.* **2012**, *134*, 597.
[10] J. Wang, S. Liu, C. Chen, Y. Zou, H. Hu, Q. Cai, S. Yao, *Analyst* **2014**, *139*, 3593.
[11] M. Moazzen, R. Ahmadkhaniha, M. E. Gorji, M. Yunesian, N. Rastkari, *Talanta* **2013**, *115*, 957.
[12] C. Perre, K. L. Ménach, F. Ibalot, E. Parlanti, H. Budzinski, *Anal. Chim. Acta* **2014**, *807*, 51.
[13] a) L. Vidal, M. L. Riekkola, A. Canals, *Anal. Chim. Acta* **2012**, *715*, 19; b) P. K. Mandal, A. Paul, A. Samanta, *J. Chin. Chem. Soc.* **2006**, *53*, 247.
[14] H. Yu, T. D. Ho, J. L. Anderson, *Trends Anal. Chem.* **2013**, *45*, 219.
[15] A. Mohammadi, R. Tavakoli, M. Kamankesh, H. Rashedi, A. Attaran, M. Delavar, *Anal. Chim. Acta* **2013**, *804*, 104.
[16] L. Liu, L. He, X. Jiang, W. Zhao, G. Xiang, J. L. Anderson, *J. Sep. Sci.* **2014**, *37*, 1004.
[17] H. Bai, Q. Zhou, G. Xie, J. Xiao, *Talanta* **2010**, *80*, 1638.
[18] Q. Zhou, Y. Gao, G. Xie, *Talanta* **2011**, *85*, 1598.
[19] H. Wu, J. Guo, L. Du, H. Tian, C. Hao, Z. Wang, J. Wang, *Food Chem.* **2013**, *141*, 182.
[20] H. He, D. Yuan, Z. Gao, D. Xiao, H. He, H. Dai, J. Peng, N. Li, *J. Chromatogr. A* **2014**, *1324*, 78.
[21] J. Wu, H. Zhao, D. Xiao, C. Pham-Huy, J. He, H. He, *J. Chromatogr. A* **2016**, *1454*, 1.
[22] H. Yan, M. Gao, J. Qiao, *J. Agric. Food Chem.* **2012**, *60*, 6907.
[23] M. L. Polo-Luque, B. M. Simonet, M. Valcárcel, *Electrophoresis* **2013**, *34*, 304.
[24] Q. Zhang, F. Yang, F. Tang, K. Zeng, K. Wu, Q. Cai, S. Yao, *Analyst* **2010**, *135*, 2426.
[25] Q. Cheng, F. Qu, N. Li, H. Luo, *Anal. Chim. Acta* **2012**, *715*, 113.
[26] X. Liu, X. Lu, Y. Huang, C. Liu, S. Zhao, *Talanta* **2014**, *119*, 341.
[27] X. Cao, L. Shen, X. Ye, F. Zhang, J. Chen, W. Mo, *Analyst* **2014**, *139*, 1938.
[28] M. Wierucka, M. Biziuk, *Trends Anal. Chem.* **2014**, *59*, 50.
[29] P. Liu, Y. Xu, P. Zheng, H. Tong, Y. Liu, Z. Zha, Q. Su, S. Liu, *J. Chin. Chem. Soc.* **2013**, *60*, 53.
[30] L. Chen, T. Wang, J. Tong, *Trends Anal. Chem.* **2011**, *30*, 1095.

[31] Y. Long, Y. Chen, F. Yang, C. Chen, D. Pan, Q. Cai, S. Yao, *Analyst* **2012**, *137*, 2716.

[32] Y. Li, L. Qi, Y. Shena, H. Ma, *Anal. Chim. Acta* **2014**, *811*, 36.

[33] L. Zhu, H. Xu, *J. Sep. Sci.* **2014**, *37*, 2591.

[34] W. Wang, R. Ma, Q. Wu, C. Wang, Z. Wang, *J. Chromatogr. A* **2013**, *1293*, 20.

[35] W. Xi, T. F. Scott, C. J. Kloxin, C. N. Bowman, *Adv. Funct. Mater.* **2014**, *24*, 2572.

[36] S. Zhang, X. He, L. Chen, Y. Zhang, *New J. Chem.* **2014**, *38*, 4212.

[37] C. Liang, L. Jing, X. Shi, Y. Zhang, Y. Xian, *Electrochim. Acta* **2012**, *69*, 167.

[38] J. Lu, F. Ye, A. Zhang, X. Chen, Y. Wei, S. Zhao, *Analyst* **2012**, *137*, 5860.

[39] Y. Xie, C. Deng, Y. Li, *J. Chromatogr. A* **2017**, *1508*, 1.

[40] M. Kamankesh, A. Mohammadi, H. Hosseini, Z. M. Tehrani, *Meat Sci.* **2015**, *103*, 61.

[41] F. Lan, H. Hu, W. Jiang, K. Liu, X. Zeng, Y. Wu, Z. Gu, *Nanoscale* **2012**, *4*, 2264.

[42] H. Hu, S. Liu, C. Chen, J. Wang, Y. Zou, L. Lin, S. Yao, *Analyst* **2014**, *139*, 5818.

[43] Y. Liu, H. Li, J. Lin, *Talanta* **2009**, *77*, 1037.

[44] Q. Han, Z. Wang, J. Xia, S. Chen, X. Zhang, M. Ding, *Talanta* **2012**, *101*, 388.

[45] E. Tahmasebi, Y. Yamini, *Anal. Chim. Acta* **2012**, *756*, 13.

[46] G. Purcaro, S. Moret, L. S. Conte, *Meat Sci.* **2009**, *81*, 275.

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