Novel Palm Fatty Acid Functionalized Magnetite Nanoparticles for Magnetic Solid-Phase Extraction of Trace Polycyclic Aromatic Hydrocarbons from Environmental Samples

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Abstract: A novel adsorbent, palm fatty acid coated magnetic Fe3O4 nanoparticles (MNP-FA) was successfully synthesized with immobilization of the palm fatty acid onto the surface of MNPs. The successful synthesis of MNP-FA was further confirmed by X-Ray diffraction (XRD), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and Energy dispersive X-Ray spectroscopy (EDX) analyses and water contact angle (WCA) measurement. This newly synthesized MNP-FA was applied as magnetic solid phase extraction (MSPE) adsorbent for the enrichment of polycyclic aromatic hydrocarbons (PAHs), namely fluoranthene (FLT), pyrene (Pyr), chrysene (Cry) and benzo(a)pyrene (BaP) from environmental samples prior to High Performance Liquid Chromatography- Diode Array Detector (HPLC-DAD) analysis. The MSPE method was optimized by several parameters such as amount of sorbent, desorption solvent, volume of desorption solvent, extraction time, desorption time, pH and sample volume. Under the optimized conditions, MSPE method provided a low detection limit (LOD) for FLT, Pyr, Cry and BaP in the range of 0.01-0.05 ng mL⁻¹. The PAHs recoveries of the spiked leachate samples ranged from 98.5% to 113.8% with the RSDs (n = 5) ranging from 3.5% to 12.2%, while for the spiked sludge samples, the recoveries ranged from 81.1% to 119.3% with the RSDs (n = 5) ranging from 3.1% to 13.6%. The recyclability study revealed that MNP-FA has excellent reusability up to five times. Chromatographic analysis demonstrated the suitability of MNP-FA as MSPE adsorbent for the efficient extraction of PAHs from environmental samples.

Key words: polycyclic aromatic hydrocarbons, magnetic solid phase extraction, palm fatty acid, magnetic nanoparticles

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) originate mainly from incomplete combustion of organic matters (e.g. wood, coal, garbage, tobacco and oil)1,2. During recent decades, PAHs have come into attention as a significant of pollutant contaminating our environment. The level of PAHs present in our environment depends on their composition, type and the degree of industrial pollution. PAHs are noxious, persistent and lipophilic in the environment3,4. Thus, they have high tendency to enrich in the food chain. PAHs are classified as carcinogenic, toxic and mutagenic, therefore, they are hazardous to the ecology and can cause a severe health hazard to human, mainly cancer5. Hence, the detection of PAHs from the environment has attracted worldwide concerns.

Since PAHs represent an emerging class of pollutants, it become necessary to develop a simple sample preparation technique to detect the trace residue in environmental matrices. There are numerous techniques for sample preparation that have been reported to isolate PAHs from complex matrices prior to instrumental analysis, including cloud point extraction (CPE)6, solid-phase micro extraction
(SPME)\(^7\), stir rod sorptive extraction (SRSE)\(^8\), micro-solid phase extraction (μ-SPE)\(^9\), dispersive liquid-liquid micro extraction combined micro solid phase extraction (DLLME/μ-SPE)\(^10\) and solid-phase extraction (SPE)\(^11, 12\). Among these, SPE is the most commonly used technique to pre-concentrate PAHs from environmental samples as this procedure requires only a small amount of organic solvents and the adsorbent can be recovered satisfactorily afterwards. However, this method is time and labour intensive especially when it involves a large volume of sample\(^13\). Hence, a rapid and simple SPE method for the extraction of PAHs from environmental samples is desirable.

In order to address these limitations, a new mode of SPE, magnetic solid phase extraction (MSPE) has gained a great consideration\(^14\) to isolate PAHs from complex matrices. This technique is based on the use of magnetic nanoparticles\(^15, 16\) which promises rapid extraction ability and excellent extraction efficiency\(^17-19\). Rapid separation of the analyte of interest from interference can be achieved by applying an external magnet to recover the saturated adsorbent. Currently, magnetite (Fe\(_3\)O\(_4\)) nanoparticles (MNPs) are widely used as a MSPE sorbent due to its super-paramagnetic property\(^20\), high surface area available for reaction, effective contact, and good uptake capacity\(^21, 22\).

Furthermore, the surface of MNP can be easily functionalized to achieve selective sample extraction. For example, hydrophobic layers such as \(n\)-octadecylphosphonic acid (OPA)\(^23\), carbon\(^24\), octadecyl (C\(_{18}\))\(^25\), triphenylamine (TPA)\(^26\), graphene\(^27\), polymers\(^28\), and surfactants\(^29\) can be used to modify the surface of MNPs to enhance the selectivity of MSPE sorbent towards organic pollutants in environmental samples. However, preparations of the reported modified sorbents are tedious, time consuming and usually involve toxic reagents. Therefore, a novel magnetic adsorbent which is simple, eco-friendly, cost effective, and has a high selectivity towards organic pollutants is highly desirable in environmental analysis.

Fats and oil can be used as economical and eco-friendly hydrophobizing agents in modifying the surface of MNPs, turning it into a new highly hydrophobic MSPE adsorbent for the detection of lipophilic PAHs from the environmental samples. Herein, we highlight the facile synthesis of palm fatty acid functionalized magnetic nanoparticles (MNP-FA) as a new MSPE adsorbent for the extraction of PAHs from leachate and sludge samples. The presence of long alkyl chain in the mixture fatty acids; mainly C16 and C18 in palm olein, endowed the developed adsorbent with high extraction capabilities. This is because the hydrophobic alkyl chains can strongly interact with the organic PAHs pollutant in environmental samples. Additionally, this fabricated MSPE adsorbent showed a high resistance in corrosive media, suggesting the ability of this adsorbent to work in harsh environments.

### 2 Experimental section

#### 2.1 Chemicals and reagents

Iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate (Sigma Aldrich), N, N-dimethylformamide (DMF), (3-aminopropyl) triethoxysilane (APTES), aqueous ammonia, ethanol, ethyl acetate, acetonitrile, hydrochloric acid, potassium hydroxide (KOH), anhydrous sodium sulphate and hexane were purchased from Merck. PAHs standards, fluoranthene (FLT), pyrene (Pyr), chrysene (Cry) and benzo(a)pyrene (BaP) were obtained Supelco. The stock solutions were prepared in methanol at a concentration of 100 mg L\(^{-1}\). All stock solutions were kept at 4°C in the dark.

Palm olein was purchased from supermarket in Bangsar, Kuala Lumpur. Palm fatty acid was obtained from the hydrolysis of triacylglyceride (TAG) from palm olein. The fatty acid profile was analyzed and is shown in Table S1. The gas-liquid chromatography reference standard for fatty acid methyl esters was bought from Supelco.

#### 2.2 Instruments

The functional groups of the nanoparticles were first characterized using a FT-IR spectrometer (Spectrum 400 PerkinElmer) with a diamond ATR accessory, absorption mode with 4 scans at a resolution of \(\pm 4\) cm\(^{-1}\), and a wavenumber range of 4000 to 450 cm\(^{-1}\). Wettability analyses were performed using the TL 100 and TL 101 contact angle measurement instruments. The particle size and morphology were investigated by JEOL JEM-2100F transmission electron microscope (TEM). EDX analysis was performed using scanning electron microscopy (SEM HITACHI SU8220, OXFORD Instruments) equipped with an energy dispersive X-ray spectrometer. The crystal phase of the prepared nanoparticles was determined using a PANalytical EMPYREAN X-ray powder diffraction (XRD) diffractometer (Cu K\(_\alpha\), radiation, \(\lambda = 1.541874\) nm), at a scanning speed of 0.07° / min from 15° to 75° (2θ). The fatty acid methyl esters were prepared from palm fatty acid using an acid catalyst (sulphuric acid method)\(^29\). The fatty acid composition was analyzed using a Shimadzu 2010 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a split/ splitless injector and a flame ionization detector (FID). A BPX50 capillary column (SGE Analytical Science, Australia) (30 m x 0.25 mm i.d. 0.25 μm film thickness) was applied for the separation of fatty acids. Helium (with 99.999% purity) was the carrier gas and is fed at a constant flow rate of 59.2 mL min\(^{-1}\). The injection port was operated using split mode. The detector temperature was set at 260°C, injection temperature was set at 139°C, and the oven temperature was initially set at 139°C for 2 min, then increased by 8°C min\(^{-1}\) up to 165°C, then 3°C min\(^{-1}\) up to 192°C, 13.7°C min\(^{-1}\) up to 240°C and, finally for 11°C min\(^{-1}\) at 240°C.
2.3 Preparation of newly adsorbent (MNP-FA)

2.3.1 Hydrolysis of palm olein

Hydrolysis of palm olein (Fig. 1A) as stated in literature was applied to obtain palm fatty acid. Typically, 50 g of palm olein and 300 mL of 1.75 M of ethanolic KOH were heated at 65°C for 2 hours. The unsaponifiable products were extracted by 100 mL of hexane and then discarded. The obtained mixture was mixed with deionized water and acidified with 100 mL 6 N hydrochloric acid until the solution turned acidic (pH 1). The extraction of fatty acids was repeated three times by using 100 mL of hexane for each extraction. The extraction product, a fatty acids-hexane mixture was washed with deionized water and dried with anhydrous sodium sulphate. The solvent was removed by rotary evaporator at 35°C to obtain the palm fatty acid.

2.3.2 Synthesis of MNPs

The procedure for the preparation of the MNPs is shown in Fig. 1B. The magnetite nanoparticles (MNPs) were synthesized using a chemical co-precipitation method. Briefly, 3.1736 g of FeCl₃·4H₂O and 7.5709 g FeCl₂·6H₂O were dissolved in 320 mL deionized water. The mixed solution was then stirred under nitrogen at 80°C for 1 hour. Then, 40 mL of aqueous ammonia was added into the reaction mixture rapidly. The resulting mixture was stirred under nitrogen for another 1 hour and then cooled to room temperature. The precipitated magnetic particles were washed five times with hot water until the filtrate becomes neutral and separated by magnetic decantation.

2.3.3 Synthesis of MNP-APTES

MNP-APTES was prepared via a reported method (Fig. 1C). In this synthesis, hydrolyzed APTES was added to 100 ml magnetite fluid in a 250 ml round bottom flask. The mixture was stirred for 5 hours at 60°C under nitrogen protection. After the solution was cooled to room temperature, the resulting brownish product was separated by an external magnet and washed with ethanol and deionized water respectively several times. The final product was then dried in the vacuum at 70°C for 24 hours.

2.3.4 Synthesis of MNP-FA

Figure 1D illustrates the preparation route of MNP-FA. Freshly prepared 1.000 g MNP-APTES was dispersed in 10 ml of DMF, followed by the addition of 2.000 g palm fatty acid. The reaction mixture was stirred overnight at 60°C under nitrogen protection. Then, the solution was cooled to room temperature and the obtained brownish product (MNP-FA) was magnetically collected. The obtained MNP-FA was washed repeatedly with excess ethanol and deionized water respectively and finally vacuum dried at 70°C for 24 hours.

2.4 MSPE experiment

15 mg of MNP-FA was placed in a vial. Then 30 mL of the prepared spiked PAHs solution was transferred into the same vial. The solution was shaken for 15 minutes. The adsorbent was isolated from the sample solution using an external magnet and the sample solution was then decanted. The adsorbed PAHs on MNP-FA were eluted by shaking with 2.0 mL of desorption solvent (hexane) for 10 minutes. The collected eluate was dried under a flow of nitrogen gas and then dissolved in 0.5 mL acetonitrile. Finally, 10 μL of the eluate was injected into the HPLC system for analysis. The schematic process of MSPE method is shown in Fig. 2.

2.5 Real sample pre-treatment

Leachate and sludge samples were collected from a landfill in Jeram, Kuala Selangor and were chosen as representatives of real samples in this study. The leachate samples were filtered through a 0.22 μm membrane and stored at 4°C prior to use. 30 mL of the filtered leachate are used in each MSPE run.

The sludge samples were dried at room temperature, pulverized, and passed through a 1 mm sieve. Then, ultrasound-assisted extractions (UAE) of the sludge samples were performed. Briefly, 1.00 g of the sludge sample was mixed with 3 mL of methanol in a 50-mL centrifuge tube and then sonicated for 10 min. The mixed sludge solution was centrifuged at 3500 rpm for 5 min and the supernatant was filtered through a PTFE syringe filter (13 mm, 0.22μm pore size) into a sample vial. The total volume of sample in the vial was then made up to 30 mL with distilled water. The sample are then used in MSPE as described previously in Section 2.4.

2.6 Liquid chromatographic condition

PAHs were separated and quantified using a high performance liquid chromatography (HPLC) system which consisted of a Shimadzu (Tokyo, Japan) LC-20AT pump, SPD-M20A diode array detector, SIL-20A HT auto sampler, and CTO-10AS VP column oven. The separation was conducted using a C-18 reverse phase column (250 mm × 4.6 mm; particle size 5 μm) hypersil gold, Thermo science USA. The mobile phase was acetonitrile-water (80:20, v/v) at a flow rate of 1.0 mL min⁻¹. The injection volume was 10 μL. The detections were set as follows: 6.77 min, 284 nm (for FLT); 7.22 min, 270 nm (for Pyr); 8.03 min, 266 nm (for Cry); and 10.82 min, 266 nm (for BaP).

3 Results and discussion

3.1 Characterizations of the newly MNP-FA

3.1.1 FT-IR spectra

In order to examine the functional groups of the synthesized MNPs, MNP-APTES and MNP-FA, all FT-IR spectra were recorded and are shown in Fig. 3A. In the FTIR spectrum of MNPs, the peak at 537 cm⁻¹ represents the vibration of the Fe-O band. The two absorption peaks at 3400 and 1604 cm⁻¹ correspond to the stretching and bending

Fig. 1  The preparation scheme of (A) Palm fatty acid (B) MNPs (C) MNP-APTES and (D) MNP-FA (R = the alkyl chain of the palm fatty acid).
of the O-H group on the surface of MNPs. The new peak at 981 cm\(^{-1}\) for MNP-APTES is attributed to the Si-O group from APTES confirming the presence of silane on the surface of MNPs. The bands at 3411 cm\(^{-1}\) and 1603 cm\(^{-1}\) are attributed to N-H stretching vibration and the NH\(_2\) group, respectively. The intense peak at 1626 cm\(^{-1}\) is associated with C=O stretching. In addition, new bands appeared at 2921 and 2853 cm\(^{-1}\) are assigned to the asymmetric and symmetric CH\(_2\) stretching, respectively. The new bands indicated that palm fatty acid has been successfully functionalized onto the surface of MNP-APTES.

3.1.2 Crystal phase analysis

The crystal phases of the prepared MNPs, MNP-APTES and MNP-FA were investigated by XRD (Fig. 3B). The spectrum of MNPs showed the presence of diffraction peaks at 2\(\theta\) = 30.42\(^\circ\), 35.59\(^\circ\), 43.42\(^\circ\), 53.63\(^\circ\), 57.35\(^\circ\), and
63.02° and are respectively assigned to the (220), (311), (400), (422), (511), and (440) planes of \( \text{Fe}_3\text{O}_4 \) (JCPDS 88-0866). These indicate that \( \text{Fe}_3\text{O}_4 \) nanoparticles has a cubic spinel structure. Similar diffraction peaks were also observed in the MNP-APTES and MNP-FA spectra revealing that the cubic spinel structure of \( \text{Fe}_3\text{O}_4 \) nanoparticles were not altered during the functionalization process. However, the intensity of the signals decreased for MNP-APTES and MNP-FA, suggesting the presence of APTES and palm fatty acid on the MNPs after modification.

3.1.3 Elemental analysis
Elemental analysis was employed to confirm the presence of elements of interests in MNPs, MNP-APTES, and MNP-FA. It was found that the elements present in MNPs are 75.5% Fe and 24.5% O (Fig. 4A). The result indicates that the magnetite (\( \text{Fe}_3\text{O}_4 \)) nanoparticles were successfully synthesized. In addition, APTES is confirmed to have coated the MNPs surface due to the presence of 5.0% C, 1.3% Si and 0.9% N in MNP-APTES (Fig. 4B). The high percentage of C (9.7%) and O (37.6%) in MNP-FA (Fig. 4C), proved that palm fatty acid has been successfully functionalized with MNP-APTES.

3.1.4 Morphological analysis
Particle size and morphology of the prepared materials were studied using transmission electron microscopy (TEM). Figures 5A-C show the TEM images of all synthesized nanoparticles. It is clearly observed that all the particles are nano-sized, spherical in shape, and have uniform distribution of particle size. From the diameter distribution shown in Figs. 5A-C, it is observed that the average diameters of MNPs, MNP-APTES and MNP-FA are 4.90 ± 2.34 nm, 6.90 ± 2.51 nm, and 6.99 ± 2.81 nm, respectively. The increase of particle size after the functionalization process suggested that APTES and palm fatty acid were successfully introduced onto the surface of the MNPs.

3.1.5 Contact angle analysis
Water contact angle (WCA) analysis was used to characterize the wettability of MNPs and MNP-FA. From Fig. 6A, it can be observed that a water droplet on MNPs was dispersed on the MNPs substrate, suggesting that the MNPs were highly hydrophilic. In contrast, MNP-FA exhibited highly hydrophobic behaviour as the water droplet deposited on MNP-FA surface was nearly spherical. The contact angle (CA) measured was 123.6° (Fig. 6B). This confirms that the hydrophobizing agent, palm fatty acid was coated onto the surface of MNPs.

The relationship between pH and WCA on the hydrophobic surface of MNP-FA is shown in Fig. 6C. It can be clearly observed that the CA values always remain larger than 110° even when the pH of water droplet was varied from 2.0 to 14.0. This suggests that the pH of the aqueous solution has little effect on the wettability of the MNP-FA surface.

3.2 Comparison of extraction efficiency of MNPs, MNP-APTES and MNP-FA
Figure 7 shows the extraction efficiencies of bare MNPs,
MNP-APTES, and MNP-FA. It was found that MNP-FA was the best adsorbent for the extraction of PAHs as it had the highest extraction efficiency for all targeted PAHs. This result can be explained by considering that the long alkyl chains of the fatty acid form a hydrophobic framework which facilitates the adsorption of PAHs through hydrophobic interaction.

3.3 Optimization of the MSPE conditions

Several parameters such as dosage of adsorbent, type of desorption solvents, volumes of the desorption solvent, extraction time, desorption time, pH, and sample volume of the solution were optimized. Each experiment run was performed in triplicates. The optimization experiments were conducted using spiked standard aqueous solutions containing 100 ng mL⁻¹ PAHs each. Chromatography was used to evaluate the influence of these factors on the PAHs extraction efficiency.

3.3.1 Effect of the amounts of adsorbent

Various amounts of MNP-FA ranging from 3 – 25 mg sorbent were tested. As shown in Fig. 8A, the recoveries of PAHs increased when the adsorbent amount was increased from 3 mg to 15 mg. PAHs recovery plateaus after 15 mg due to the active sites on the PAHs being saturated after
the 15 mg point. Hence, 15 mg of MNP-FA appears to be the optimal amount of adsorbent for MSPE of PAHs and was set as the amount to use in further experiments.

3.3.2 Effect of desorption solvent and volume

To recover the sorbent after extraction, the PAHs must be desorbed from the sorbents. Four different common organic solvents (acetonitrile, toluene, hexane and ethyl acetate) were investigated as eluents. The desorption capabilities of these eluents are compared in Fig. 8B. As shown in the figure, hexane had a higher desorption capacity compared to other eluents. This fact can be attributed to the high solubility of the target analytes in this solvent. Thus, hexane was selected as the desorption solvent. Additionally, the effect of the volume of desorption solvent on the desorption efficiency was studied from 1 to 3 mL. It was found that the analytes could be completely desorbed from the sorbent by rinsing the sorbent with 2 mL of hexane.

3.3.3 Effect of the extraction and desorption time

Sufficient contact time is needed to attain maximum PAHs adsorption. The extraction time profiles were studied by varying the extraction time between 5 and 25 min. As shown in Fig. 8C, the extraction recoveries of all PAHs increased with extraction time up to 15 min, then plateaus after. It can be concluded that the extraction equilibrium between the aqueous phase and the sorbents was reached after 15 min. Similarly, the desorption time profiles were studied by varying the desorption time from 1 to 20 min. As shown in Fig. 8D, a desorption time of 10 min was sufficient to completely desorb PAHs from the sorbent. Hence, 15 min and 10 min were respectively selected as the best extraction and desorption times.

3.3.4 Effect of pH

In this study, the effect of sample solution pH was studied in the range of 2.0 to 10.0. The sample solution pH was adjusted using volumes of 0.1 M HCl or NaOH. In Fig. 8E, it was observed that high recoveries of all selected PAHs were obtained at pH 6.5. In contrast, low recoveries were observed when the pH was higher or lower. This phenomenon can be explained by considering the charged species and charge density on the surface of the sorbent (MNP-FA). In acidic conditions, high amounts of protons are available, increasing the protonation of the hydroxyl groups on the MNPs surface. The sorbent sites saturates and the sorbent becomes more cationic. In basic conditions, the hydroxyl groups from MNPs deprotonates, causing the surface of the adsorbent to be more anionic.

Fig. 6 The water contact angle of (A) MNPs; (B) MNP-FA and (C) Relationship between pH of water droplet on water CA on the MNP-FA surface.

Fig. 7 Comparison of the extraction efficiencies of PAHs between MNPs, MNP-APTES and MNP-FA.
This reduces the hydrophobicity of MNP-FA affecting interaction with PAHs. Thus, pH 6.5 was selected as the best pH to use.

3.3.5 Effect of sample volume

The effect of the sample volume was examined by varying the sample solution volume between 15 mL to 100 mL. As shown in Fig. 8F, the extraction efficiency increased when the sample volume increases up to 30 mL and then plateaus above 30 mL. Hence, 30 mL of sample volume was selected as the best volume to use.

3.3.6 Reusability studies

In order to investigate the recyclability of the adsorbent, the spent adsorbent was washed twice with 5 mL of ethyl acetate and then dried before being used in the next MSPE.
cycle. The recoveries of PAHs are shown in Fig. 9. It was found that the sorbent can be reused five times without significant loss in the recoveries of all analytes.

3.4 Analytical performance

Various analytical parameters such as linearity, limit of detection (LOD), limit of quantification (LOQ), and precision were tested to evaluate the MSPE method performance. The results are listed in Table 1. The calibration curves are linear over a wide range with a correlation of 0.9998. Based on the results obtained, the LOD and LOQ values of the targeted PAHs ranged from 0.01 to 0.05 ng mL\(^{-1}\) and 0.03 to 0.16 ng mL\(^{-1}\), respectively. Intra- and inter-day relative standard deviations (RSDs) were assessed to evaluate the precision of the developed method. Satisfactory results were achieved with the intra- day RSD% being between 3.9% and 5.8% and inter-day RSD% being in the range of 1.1 to 3.1%. This demonstrates the good reproducibility of the current method.

3.5 Application to real samples

Under optimized conditions, the proposed method was successfully applied to the analysis of PAHs in real samples represented by leachate and sludge collected from Jeram Landfill, Kuala Selangor. To assess the accuracy of the method, the recoveries of the PAHs from leachate and sludge at spiking levels of 100, 10, and 5 ng mL\(^{-1}\) were measured. The results obtained are shown in Table 2. The PAHs recoveries from spiked leachate samples ranged from 98.5% to 113.8% with the RSDs \((n = 5)\) ranging from 3.5% to 12.2%, while PAHs recoveries from spiked sludge samples ranged from 81.1% to 119.3% with the RSDs \((n = 5)\) ranging from 3.1% to 13.6%. The results demonstrate the potential of MNP-FA in the application of environmental sample analysis. Figure 10 shows a typical HPLC-DAD chromatograms of the PAHs samples extracted from leachate samples using the developed method before and after spiking with 100 ng mL\(^{-1}\) of each PAHs.

3.6 Comparison with other reported MSPE adsorbents

Performance of the proposed method (MNP-FA-MSPE) was evaluated by comparing the obtained results with results from similar works reported in literature. The performance comparison is shown in Table 3. The performances were evaluated in terms of amount of sorbent used, extraction time, % recovery, and LOD. The proposed method (MNP-FA-MSPE) requires a lower amount of adsorbent compared to other MSPE adsorbents except g-C\(_3\)N\(_4\)/Fe\(_3\)O\(_4\) and Carbon-ferromagnetic nanocomposites. The LOD of our method is low, marking it as sensitive and comparable with others. Good % recoveries comparable to other works were also achieved.

4 Conclusion

In this study, palm fatty acid functionalized Fe\(_3\)O\(_4\) nanoparticles (MNP-FA) was successfully synthesized, characterized and applied as a MSPE adsorbent coupled with HPLC- DAD for the enrichment of targeted PAHs in leachate and sludge samples. The LOD and LOQ of all selected PAHs using the proposed method were in the range of 0.01-0.05 ng mL\(^{-1}\) and 0.03-0.16 ng mL\(^{-1}\), respectively, with inter- and intra-day precisions being less than 6%. The recoveries for spiked leachate and sludge samples ranged from 98.5% to 113.8% and 81.1% to 119.3%, respectively. Owing to its hydrophobic framework, MNP-FA shows a great potential as a MSPE adsorbent for the enrichment of trace PAHs in environmental samples. The ex-

Table 1 Analytical performance for HPLC-DAD determination of PAHs using MNP-FA.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Linearity</th>
<th>LOD (ng mL(^{-1}))</th>
<th>LOQ (ng mL(^{-1}))</th>
<th>Precision</th>
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<td></td>
<td>LDR ((\text{ng mL}(^{-1})))</td>
<td>(R^2)</td>
<td>Intra-day (RSD% (n = 7))</td>
<td>Inter-day (RSD% (n = 3))</td>
</tr>
<tr>
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<td>0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>Pyr</td>
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<td>0.9998</td>
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<td>0.08</td>
</tr>
<tr>
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<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>BaP</td>
<td>0.1-100</td>
<td>0.9998</td>
<td>0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>
traction was rapid as the MNP-FA could be easily separated from the sample solution using an external magnet. It can be concluded that the proposed method is simple and efficient for the pre-concentration of trace PAHs pollutants from environmental samples.

### Table 2

The recoveries and standard deviations of PAHs in real environmental samples with a spiked concentration of 5 ng mL\(^{-1}\), 10 ng mL\(^{-1}\), and 100 ng mL\(^{-1}\) for each analyte.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Spiked (ng mL(^{-1}))</th>
<th>Leachate (n = 5)</th>
<th>Sludge (n = 5)</th>
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<tr>
<td></td>
<td>Recovery (%)</td>
<td>RSD (%)</td>
<td>Recovery (%)</td>
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<tr>
<td>FLT</td>
<td>5</td>
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<td>5</td>
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</tr>
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**Fig. 10** HPLC-DAD chromatograms of the PAHs after extraction using proposed MSPE: Non-spiked (A); and 100 ng mL\(^{-1}\) of each PAHs spiked leachate sample (B) (1) FLT, (2) Pyr, (3) Cry, and (4) BaP.
Table 3  Comparison of MNP-FA with other reported MSPE for extraction of PAHs.

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount of sorbent (mg)</th>
<th>Extraction time (min.)</th>
<th>% Recovery</th>
<th>LODs (ng mL⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNP-FA</td>
<td>15</td>
<td>15</td>
<td>81.1–119.3</td>
<td>0.01–0.05</td>
<td>This study</td>
</tr>
<tr>
<td>Fe₃O₄@Ag@b-TMP-DTPA NPs</td>
<td>50</td>
<td>20</td>
<td>82.4–109.0</td>
<td>0.02–0.1</td>
<td>33</td>
</tr>
<tr>
<td>Fe₃O₄/Graphene oxide</td>
<td>40</td>
<td>10</td>
<td>76.8–103.2</td>
<td>0.09–0.19</td>
<td>37</td>
</tr>
<tr>
<td>Ionic Liquid / Fe₃O₄</td>
<td>30</td>
<td>7</td>
<td>75.0–102.0</td>
<td>0.04–1.11</td>
<td>38</td>
</tr>
<tr>
<td>g-C₃N₄/Fe₃O₄</td>
<td>10</td>
<td>10</td>
<td>80.0–99.8</td>
<td>0.05–0.1</td>
<td>18</td>
</tr>
<tr>
<td>G/ Fe₃O₄@PT</td>
<td>20</td>
<td>4</td>
<td>83.0–107.0</td>
<td>0.03–80.0</td>
<td>39</td>
</tr>
<tr>
<td>Carbon-ferromagnetic nanocomposites</td>
<td>10</td>
<td>30</td>
<td>–</td>
<td>0.015–0.065</td>
<td>40</td>
</tr>
</tbody>
</table>

Supporting Information
This material is available free of charge via the Internet at http://dx.doi.org/jos.66.10.5650/jos.ess.17016

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