A hierarchical porous composite magnetic sorbent of reduced graphene oxide embedded in polyvinyl alcohol cryogel for solvent assisted-solid phase extraction of polycyclic aromatic hydrocarbons

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Abbreviations: **SPE,** solid-phase extraction; **PAHs,** polycyclic aromatic hydrocarbons; **rGOx,** reduced graphene oxide; **PVA,** polyvinyl alcohol; **$CaCO_3$,** calcium carbonate; **Phe,** Phenanthrene; **Pyr,** Pyrene; **BaA**, Benzo(a)anthracene; **BbF**, Benzo(b)fluoranthene; **BaP**, Benzo(a)pyrene

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Abstract

A hierarchical porous composite magnetic sorbent was fabricated and applied to the dispersive solvent assisted-solid phase extraction of five polycyclic aromatic hydrocarbons. A sorbent was first prepared by incorporating graphene oxide, calcium carbonate and magnetite nanoparticles into a polyvinyl alcohol cryogel. The graphene oxide was converted to reduced graphene oxide using ascorbic acid and a hierarchical porous structure was produced by reacting hydrochloric acid with incorporated calcium carbonate to generate carbon dioxide bubbles which created a second network. Before extracting the target analytes, extraction solvent was introduced into the hierarchical pore network of the sorbent. The extraction was based on the partition between the analytes and introduced extraction solvent and the adsorption of analytes on reduced graphene oxide. The extraction efficiency was enhanced through π-π and hydrophobic interactions between polycyclic aromatic hydrocarbons and reduced graphene oxide and extraction solvent. The extracted polycyclic aromatic hydrocarbons were determined using HPLC coupled with fluorescence detector. The developed method was applied to extract polycyclic aromatic hydrocarbons in disposable diaper, coffee and tea samples and recoveries from 84.5 to 99.4% were achieved with relative standard deviations below 7%. The developed sorbent exhibited good reproducibility and can be reused for ten cycles.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic environmental pollutants, generally produced by the incomplete combustion of organic matter or by high temperature pyrolysis during manufacturing processes [1]. PAHs are frequently found in industrial products and foods. Some PAHs have been classified as potential human carcinogens and the World Health Organization (WHO) has set the maximum permissible concentration of some PAHs in drinking water at 0.2 μg L^{-1}. For this reason, the quantitative analysis of PAHs in certain matrices is of great importance. The determination of PAHs is normally performed with high performance liquid chromatography (HPLC) since the separation column used in this technique enables the simultaneous detection of several target PAHs with high sensitivity and good precision [2, 3]. However, target PAHs usually exist at trace concentrations in complex matrices and before chromatographic analysis can be performed, an appropriate extraction and enrichment process is normally required to reduce matrix interferences and increase the sensitivity of the response [4].

The extraction and enrichment of PAHs in various matrix samples can be accomplished with liquid-liquid extraction (LLE) [5], solid phase extraction (SPE) [4, 6], solid phase microextraction (SPME) [7], stir bar sorptive extraction (SBSE) [8] and magnetic solid phase extraction (MSPE) [9-11]. SPE is a widely used technique because it can be modified to improve extraction efficiency and the enrichment factor. Efficient analyte extraction with SPE requires a suitable adsorbent material and the choice of adsorbent material depends on the target molecule and the anticipated interactions between the target analyte and the adsorbent [12, 13]. Solid sorbents for the adsorption of PAHs have been fabricated using multiwalled carbon nanotubes [14], polyaniline [11], graphene [15], molecularly imprinted polymer [16] and covalent organic frameworks [17] but commercial packed-particle SPE sorbents for the extraction of PAHs normally generate high back pressure, resulting in clogging of the cartridge. The use of a porous composite SPE sorbent is a more convenient approach that is able to overcome this drawback and improve extraction performance [18].

An alternative strategy that also improved the extraction efficiency of PAHs is a recently reported extraction technique that combined a liquid phase and a porous solid phase [19]. Using this technique, PAHs could be extracted from the sample solution based on the partition between the liquid phase, which is the extraction solvent, and the surface of the solid phase sorbent. Polyvinyl alcohol (PVA) cryogel is an interesting porous material since it can entrap other adsorption materials and also hold an extraction solvent [20, 21]. PVA cryogel can be easily prepared under cryogenic condition, and after thawing the ice crystals generated by freezing, the pores created can form the template for an interconnected hierarchical porous network [22]. A hierarchical porous PVA cryogel is a good choice for SPE and the extraction efficiency of PVA cryogel can be increased by incorporating hydrophobic material in a composite sorbent. A suitable hydrophobic material for this application is reduced graphene oxide (rGOx) which can adsorb PAHs via π-π interaction [23].

In this work, an extraction solvent was introduced into a hierarchical porous composite monolith sorbent for the extraction and enrichment of PAHs. The sorbent was fabricated by incorporating rGOx, magnetite nanoparticles and $CaCO_3$ into PVA cryogel (rGOx/Fe_3O_4-SiO_2/PVA cryogel). The incorporation of $CaCO_3$ enabled the creation of a porous network structure by reacting the $CaCO_3$ embedded in the PVA cryogel with HCl to produce CO_2 bubbles inside the sorbent. The porous composite sorbent was then soaked in extraction solvent. The developed solvent-assisted porous composite monolith sorbent was applied to extract and enrichment PAHs from samples of diaper material, tea and coffee. The extraction performance of the developed sorbent was compared with the performance of a commercial sorbent. The developed method was successfully applied to extract PAHs in disposable diaper, coffee and tea samples.

2. Materials and Methods

2.1 Chemicals and reagents

Phenanthrene (Phe), Pyrene (Pyr), Benzo(a)anthracene (BaA), Benzo(b)fluoranthene (BbF) and Benzo(a)pyrene (BaP) were purchased from Restek (Bellefonte, USA). Acetic acid, ascorbic acid, hydrochloric acid, toluene and poly (vinyl alcohol) (PVA) (≥ 98% hydrolyzed) were from Merck (Darmstadt, Germany). Glutaraldehyde, iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), acetonitrile, methanol, and graphene oxide (15 - 20 sheets, 4 -10 % edge-oxidized) were purchased from Sigma–Aldrich (Steinheim, Germany). Deionized water (DI) was produced from an ELGA Maxima ultrapure system (Buckinghamshire, England).

The individual stock standard solution of Phe, Pyr, BaA, BbF and BaP was prepared in acetonitrile at a concentration of 1000 mg L^{-1}. Working standard solutions of five PAHs were freshly prepared by serial dilution of the stock solutions with acetonitrile to the desired concentration.

2.2. Samples

Samples of disposable baby diapers (27), tea (5) and coffee (5) from many manufacturers typical for the specific type of sample were used for the analysis. The samples were stored in the original manufacturers' packaging at room temperature and protected from light.

2.3 Instrumentation

HPLC analysis of PAHs was performed on the Agilent 1100 series (Agilent Technologies Inc., Germany). PAHs were separated using a Fortis C_{18} column (5 μm, 150 mm × 4.6 mm i.d.). The mobile phase was water and acetonitrile (12:88 % v/v) passed at a constant flow rate of 1.0 mL min^{-1}. The injection volume was 20 μL and the column temperature was controlled at 30 °C. The responses of the target PAHs were measured by fluorescence detection. Excitation and emission wavelengths used are given in **Table S1**.

FTIR spectra were recorded by FTIR spectroscopy (PerkinElmer Waltham, MA, USA). Sorbent morphologies were determined by scanning electron microscopy (JSM-5200 JEOL Tokyo, Japan). Nitrogen adsorption and desorption isotherms, and surface areas were measured using the Quantachrome Autosorb 1 system (Quantachome Instruments, USA). CHN elemental analysis was performed on a MACRO CHNS Analyzer (LECO, USA). TGA analysis was carried out using the TGA8000 apparatus (Perkin Elmer, USA).

2.4 Synthesis of magnetite nanoparticles

Fe_3O_4-SiO_2 nanoparticles were synthesized following a reported procedure [14] with modification. The detail for the synthesis of Fe_3O_4-SiO_2 is provided in the Supporting Information.

2.5 Fabrication of hierarchical porous composite monolith sorbent

The fabrication procedure of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent is shown in **Fig. 1**. A homogenous PVA solution was obtained by stirring 2.0 g of PVA powder in 100 mL of DI water at 90°C for 20 min. The solution was allowed to cool down to room temperature and pH was adjusted to 1.0 with 0.5 M HCl. Subsequently, 0.2 g of the synthesized Fe_3O_4-SiO_2 nanoparticles, 5.0 mg of GOx, and 0.25 g of $CaCO_3$ were added to the PVA solution and stirred at 30 °C for 6 h. The composite cryogel sorbent was fabricated by dropping 0.20 mL of the mixture solution into the well of a 96-well plate, adding 5.0 μL of glutaraldehyde to the well, and freezing the solution at -20 °C for 12 h. The porous GOx/Fe_3O_4-SiO_2/$CaCO_3$ PVA cryogel sorbent was obtained by thawing the frozen sorbent at room temperature (29 ± 2 °C). The thawed sorbent was removed from the plate and washed with DI water until pH was neutral (~5.5-7.0). The GOx incorporated in the obtained cryogel sorbent was reduced to rGOx by heating the sorbent in 100 mL of 0.20% w/v ascorbic acid at 80 °C for 6 h. When the sorbent changed color from brown to black, a composite rGOx/Fe_3O_4-SiO_2/$CaCO_3$ PVA cryogel sorbent was obtained. The sorbent was removed from the acid, washed with 50 mL of DI water and dried. The dried cryogel sorbent was then placed in 100 mL of HCl (20% w/v). The $CaCO_3$ in the composite sorbent reacted with the HCl to produce CO_2 bubbles which created a second pore system in the cryogel. Finally, the fabricated hierarchical porous composite cryogel sorbent was washed with DI water until pH was nearly neutral (~5.5-7).

2.6 Solvent-assisted solid phase extraction

The solvent assisted-SPE of PAHs using the porous rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent is illustrated in **Fig. 1A**. First, porous composite sorbents are placed in a glass bottle containing the extraction solvent and stirred for 30 min to allow the extraction solvent to diffuse and fill the pores of the sorbents. The pores of the sorbents retain the solvent through hydrophobic interaction with the rGOx. The composite sorbents, now charged with extraction solvent, are isolated using a magnet, transferred to 10.0 mL of sample solution in a vial and stirred for 15 min at 1000 rpm to extract the target analytes. The sorbents are isolated from the sample solution using a magnet, soaked in 2.0 mL of eluting solvent, sonicated for 5 min to elute PAHs and again isolated with a magnet. The eluting solvent is evaporated to dryness at 50 °C using a rotary evaporator. The residue is reconstituted in 0.5 mL of mobile phase and 20.0 μL are injected into the HPLC-FLD. The quality control of the developed method was considered from the blank extraction. To ensure that there is no contamination which may occur during the extraction, blank extraction was performed with deionized water and the whole procedure was conducted as described above.

To achieve the highest extraction efficiency, the following parameters were optimized: the amount of $CaCO_3$ and GOx incorporated in the PVA solution, the extraction time, the stirring rate, the type of extraction solvent used, the volume of eluting solvent used, desorption time, sample volume and sample pH. Extraction performance was evaluated from extraction recovery (ER), which was determined according to the following equation:

$$ER\ (\%) = (CV/C_XV_X) \times 100$$

where C and Cx are the respective concentrations of PAHs in the reconstituted solvent (μg L^{-1}) and spiked sample, and V and V_X are the volumes of the reconstituted solvent (0.50 mL) and the spiked sample, respectively.

2.7 Preparation of diaper, coffee and tea samples

Three parts of each diaper, the top sheet, inside, and back sheet, were cut into small pieces (0.5 cm x 0.5 cm) and mixed together at an average weight of approximately 0.40 g in a 50 mL centrifuge tube. Then, 8.0 mL of acetonitrile were added and the samples were extracted with ultrasonication for 30 min. This step was repeated two times and the collected supernatants were combined and evaporated to dryness at 60 °C using a rotary evaporator. The residue was dissolved in 0.50 mL of acetonitrile and diluted with 10 mL of DI water ready for solvent assisted-SPE. Tea and coffee samples were prepared using hot water. In 100 mL of water at 95°C, 1.0 g of instant coffee was dissolved and stirred for 2 min. The solution was diluted 50 times before being extracted. Similarly, 1.0 g of dried tea leaves was soaked in 100 mL of hot water at 95°C for 2 min. Tea leaves were removed by filtering the infusion through a 15 μm filter paper. The liquid was allowed to cool to room temperature before being extracted by solvent assisted-SPE.

3. Results and Discussion

3.1 Characterization of porous composite monolith sorbent

The porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent was characterized using SEM, FTIR, TGA, CHN, BET and VSM techniques. SEM was used to investigate the surface morphology of the sorbent. SEM images (**Fig. 2A, B**) showed the high porosity of the

PVA cryogel which helps the sample solution pass through the sorbent easily. A photograph of the PVA cryogel is shown in **Fig. 2C**. The fabricated rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent exhibits a rough surface with a large surface area that aids analytes adsorption (**Fig. 2D, E**). A photograph of the porous rGOx/Fe_3O_4-SiO_2/PVA cryogel adsorbent is shown in **Fig. 2F**.

The PVA cryogel, different elements of the fabricated sorbent, and the sorbent itself were characterized by FTIR spectroscopy. The FTIR spectrum of PVA cryogel (**Fig. S1A a**) shows adsorption bands at 3458 cm^{-1} and 2948 cm^{-1} related to –OH and $-CH_2-$ asymmetric stretching, respectively. The adsorption band at 1436 cm^{-1} was assigned to C–H bending. The band at 1018 cm^{-1} corresponds to the C–O group. The FTIR spectrum of Fe_3O_4-SiO_2 (**Fig. S1A b**) shows bands at 3399 cm^{-1} and 1626 cm^{-1} that indicate the presence of –OH stretching vibrations due to the presence of hydroxyl. The adsorption bands at 592 cm^{-1} and 1088 cm^{-1} are due to the vibrations of Fe–O and Fe–O–Si stretching, respectively. In the spectrum of rGOx (**Fig. S1A c**), the bands at 1542 cm^{-1} and 1192 cm^{-1} correspond to C=C and C–OH, respectively. The FTIR spectrum of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent (**Fig. S1A d**) indicate that rGOx and Fe_3O_4-SiO_2 were successfully composited in the PVA cryogel.

CHN analysis was used to measure elemental carbon, nitrogen and hydrogen components of the porous composite sorbent. The results showed that the fabricated sorbent consisted of 58.87 % carbon, 0.02 % nitrogen and 7.76 % hydrogen.

The N_2 adsorption-desorption isotherm of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent is shown in **Fig. S1B**. The results showed that the sorbent exhibited a type IV isotherm and a clear hysteresis loop was obtained, implying a mesoporous structure. The BET surface area of the sorbent was calculated as 6.7650 m^2 g^{-1}.

To determine the thermal stability of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent, TGA analysis was performed from 25 to 900 °C. Since the TGA curve (**Fig. S1C**) indicated that no significant weight loss occurred up to 200 °C, the stability of the sorbent was considered sufficiently high for the intended extraction condition (27 ± 2°C).

The saturation magnetization of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent was determined using a vibrating sample magnetometer (VSM). As shown in **Fig. S1D**, the saturation magnetization was about 2.290 emu g^{-1} which is easily high enough for the sorbent to be separated from the solution with an applied magnet.

3.2 Optimization of the sorbent synthesis and extraction conditions

3.2.1 Effect of amount of calcium carbonate

Calcium carbonate ($CaCO_3$) was incorporated into the composite sorbent to produce the hierarchical porous structure by reacting with HCl to produce CO_2 bubbles. The optimization of incorporated $CaCO_3$ was studied from 0.0 to 0.75%w/v (**Fig. 3A**). Extraction recovery was the determining parameter and this increased with increments of $CaCO_3$ up to 0.25%w/v $CaCO_3$. Recovery decreased at greater loadings of $CaCO_3$ because the sorbent became unstable and began to break up during stirring. Thus, 0.25%w/v of $CaCO_3$ was used for the fabrication of the porous rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent.

3.2.2 Amount of graphene oxide

The GOx incorporated in the composite sorbent was reduced to rGOx, which can interact with PAHs via π-π interaction and can help to retain the extraction solvent in the pores of the sorbent through hydrophobic interaction. The optimization of the GOx loading was studied from 2 to 20 mg. The recoveries of PAHs increased with increments of GOx up to 5 mg and did not significantly change at larger loadings (**Fig. 3B**). Therefore, 5 mg of GOx was the optimal loading.

3.2.3 Extraction time

The duration of the solvent assisted-SPE of PAHs using the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent was varied from 10 to 30 min to obtain the highest recovery of PAHs. At 15 min, recoveries of all PAHs were higher than they were at 10 min, but remained constant after 15 min (**Fig. 3C**). Consequently, 15 min was selected as the optimal extraction time.

3.2.4 Effect of stirring rate

The stirring rate of the sample solution can affect the contact rate between the analytes and the sorbent, or the acceptor phase. In this work, the stirring rate of the sample solution was optimized between 500 and 1500 rpm. The highest extraction recoveries for all target PAHs was obtained at 1000 rpm (**Fig. 3D**). Lower recoveries were obtained at slower and faster stirring rates. At slower rates the low recoveries were perhaps due to insufficient contact rates between the analytes and liquid and solid acceptor phases. The lower recoveries at stirring rates above 1000 rpm may have been due to the reduced contact between the analytes and extraction phases. Also, too fast a stirring rate can cause extraction solvent to be discharged from the pores of the sorbent. Therefore, the optimal stirring rate of the sample solution was 1000 rpm.

3.2.5 Effect of type of extraction solvent

PAHs are non-polar compounds. The extraction solvent used to assist the extraction of PAHs from the sample solution, was selected after investigating the extraction performance achieved using acetonitrile, methanol, toluene, acetonitrile+toluene (1:1, v/v) and methanol+toluene (1:1, v/v) (**Fig. S2A**). The mixture of acetonitrile and toluene (1:1, v/v) provided the highest extraction recovery for all target PAHs, and therefore this was the solvent introduced into the pores of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent to assist extraction.

3.2.6 Volume of eluting solvent

At the end of the extraction cycle, the adsorbed PAHs were eluted from the pores of the sorbent using a mixture of acetonitrile and toluene (1:1, v/v). The volume of solvent used to elute the adsorbed PAHs was optimized from 1.0 to 4.0 mL (**Fig. S2B**) to obtain the lowest solvent consumption that could achieve a good extraction recovery. Recoveries of the five target PAHs increased with the increment of eluent volume from 1.0 to 2.0 mL and was unchanged above 2.0 mL. Thus, 2.0 mL of the mixture of acetonitrile and toluene (1:1, v/v) was selected to elute target PAHs from the fabricated sorbent.

3.2.7 Effect of desorption time

The optimization of the time required to desorb PAHs from the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent was studied under sonication from 1 to 20 min and the results are shown in **Fig. S2C**. The desorption of all target PAHs was completed after 5 min. The highest recoveries could therefore be obtained with a desorption time of 5 min.

3.2.8 Effect of sample volume

Sample volume normally affects the enrichment and extraction of analytes. Larger sample volumes provide higher enrichment factors which can help detect analytes at low concentrations. However, if the sample volume is too large, extraction recoveries can be low. Therefore, to achieve a high enrichment factor with satisfactory recoveries, the sample volume must be accurately optimized. In this work, sample volume was investigated from 5 to 20 mL. The optimal sample volume was 10 mL, which provided acceptable recoveries with a high enrichment factor (**Fig. S2D**).

3.2.9 Effect of sample pH

Sample pH can affect the extraction of analytes and the stability of the sorbent. Since PAHs are aromatic compounds, sample pH does not affect their structure but the stability and other properties of the sorbent may be affected. Therefore, the effect of sample solution pH was investigated between pH 3 and 11 and the results demonstrated that recoveries were not significantly changed within the studied range (**Fig. S3**). This finding confirmed that the fabricated composite sorbent can be used to extract PAHs in sample solutions within a wide pH range without the need to adjust the sample solution pH.

3. 3 Comparison of various polyvinyl alcohol cryogel sorbents

The PVA cryogel sorbent was evaluated at different stages of fabrication. The five target PAHs were extracted with hierarchically porous sorbents of Fe_3O_4-SiO_2/PVA, GOx/Fe_3O_4-SiO_2/PVA and rGOx/Fe_3O_4-SiO_2/PVA. The rGOx/Fe_3O_4-SiO_2/PVA sorbent exhibited the best extraction efficiency for all target PAHs (**Fig. S4**) due to the greater hydrophobicity of reduced graphene oxide compared to graphene oxide. The extraction efficiency of the Fe_3O_4-SiO_2/PVA sorbent was low due to its greater polarity, which inhibits interactions with less polar compounds.

3.4 Analytical performance

The developed porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent was coupled with HPLC analysis to determine the analytical performance of the system. The developed method demonstrated good linearity of BaA from 0.34-500.0 µg kg^{-1} of diaper material and from 1.7 -500.0 µg L^{-1} of coffee and tea. For the determination of Phe, BbF and BaP, the method showed linearity from 0.50-500.0 µg kg^{-1} of diaper material and from 3.4-500.0 µg L^{-1} of coffee and tea. For the determination of Pyr, the response was linear from 1.67-500.0 µg kg^{-1} of diaper material and from 5.0-500.0 µg L^{-1} of coffee and tea. The calculation of LODs was based on a signal-to-noise (S/N) ratio of 3. The LODs were 0.10-0.50 µg kg^{-1} for diaper material and 0.5-1.5 µg L^{-1} for both coffee and tea. The calculation of LOQs was based on an S/N of 10. The LOQs were 0.34-1.67 µg kg^{-1} for diaper and 1.7-5.0 µg L^{-1} for coffee and tea (**Table 1**).

3.5 Analysis of polycyclic aromatic hydrocarbons in disposable baby diapers, coffee and tea

The developed method was applied to extract and determine PAHs in samples of single-use diaper material (27 samples), coffee (5 samples) and tea (5 samples). The preparation of all samples was described in **Section 2.7.** The HPLC chromatograms of diaper material, coffee and tea are shown in **Fig. S5.** Five PAHs were found in baby diaper between 8.1 and 177.9 μg kg^{-1}, BaA, BbF and BaP were found in coffee and tea samples between 4.2 and 22.0 μg L^{-1}. The accuracy of the developed method was evaluated by determining the relative recoveries of PAHs from spiked samples at different concentrations and relative recoveries are summarized in **Table S2.** The relative recoveries of all target PAHs were in the range of 84.5 to 99.4% with RSDs of 0.9-6.5%. These results confirmed that the developed method has a good accuracy and can be applied to extract and determine PAHs in various sample matrices.

3.6 Reproducibility and Reusability

The fabrication reproducibility of the porous composite rGOx/Fe_3O_4-SiO_2/PVA sorbent was evaluated by preparing six different lots of sorbent using the same procedure. The fabricated sorbents were used to extract the target PAHs and the results are presented in **Fig. S6**. The RSDs of all target PAHs were between 0.75 and 2.70 % which confirmed the good reproducibility of the fabrication process, which contributes to the good precision of the method.

The reusability of the fabricated sorbent was also evaluated to reduce fabrication time, material costs and chemicals used. After being applied to extract PAHs, the used sorbent was cleaned with 1.0 mL of the extraction solvent, rinsed with 5.0 mL of DI water and then used to extract PAHs for another extraction/desorption cycle. The extraction recovery of PAHs was better than 80% up to the tenth extraction cycle (**Fig. S7)**. The reduction in recovery after 10 extraction cycles may have been due to the loss of rGOx from the composite sorbent during desorption and washing. Perhaps some interfering species in the samples were adsorbed on the surfaces of the sorbent and reduced the number of active adsorption sites for target PAHs. We concluded that the developed porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent can be reused for 10 cycles of extraction and desorption.

3.7 Comparison with commercial sorbent and other works

The analytical performance and accuracy of the developed method were compared with the performance and accuracy of an octadecyl (C_{18}) modified silica sorbent and the results are presented in **Fig. S8.** Both the developed sorbent and the C_{18} modified silica sorbent achieved recoveries better than 80% for all target PAHs. These results confirm that the developed method is accurate and can be applied to extract PAHs in real samples. The advantages of the present method include simple preparation, convenience of use, reusability and high efficiency. The performance of the developed method was compared with the performance of other reported methods and the comparative study is summarized in **Table S3**. The LOD and extraction recovery of the developed method are better than or comparable with other methods. Therefore, the hierarchically porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent can be used to extract PAHs from complex samples for subsequent analysis.

4. Concluding remarks

A solvent assisted-solid phase extraction method was successfully developed and applied to extract, preconcentrate and determine polycyclic aromatic hydrocarbons. The developed method integrated solvent assisted and solid phase extraction strategies. A porous composite sorbent was prepared by incorporating graphene oxide into a PVA solution that was then subjected to cryogelization and thawing. The graphene oxide was converted to reduced graphene oxide with ascorbic acid. A hierarchical porous network was generated by incorporating $CaCO_3$ into the cryogel and then reacting it with HCl to create CO_2 bubbles that generated a second network of smaller pores. Magnetite nanoparticles were also caged into the PVA cryogel to produce a magnetic sorbent for simple and rapid isolation from sample solutions. The SPE was assisted by introducing an extraction solvent into the hierarchical porous network of the composite sorbent. The developed extraction method achieved recoveries of polycyclic aromatic hydrocarbons from 84.5 to 99.4%. This developed porous composite sorbent can be used to extract trace polycyclic aromatic hydrocarbons and can also be modified to extract less polar compounds.

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Conflict of interest

The authors declare that they have no competing interests.

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Figure captions

Fig. 1 Diagram (A) shows the procedures for the fabrication of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent and the dispersive solvent assisted-solid phase extraction of PAHs. Diagram (B) shows the formation of the hierarchically porous rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent.

Fig. 2 SEM images (A) and (B) are of PVA cryogel at magnifications of 100X and 10,000X and the photograph (C) is of the PVA cryogel monolith. SEM images (D) and (E) are of the porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent at magnifications of 100X and 10,000X, and the photograph (F) is of the porous rGOx/Fe_3O_4-SiO_2/PVA sorbent.

Fig. 3 Five polycyclic aromatic hydrocarbons in solution were extracted by solvent assisted-solid phase extraction using a porous composite rGOx/Fe_3O_4-SiO_2/PVA cryogel sorbent. Charts (A) and (B) show the effect on extraction recovery of the $CaCO_3$ and GOx loadings used in the sorbent fabrication. Charts (C) and (D) show the effect on recovery of extraction time and stirring rate used during the extraction procedure.