Green Process Synth 2019; 8: 54–61 **DE GRUYTER**

Abdulhadi Muftah Faraj Benrabha and Kheng Soo Tay*

Room temperature silanization of Fe_3O_4 for the preparation of phenyl functionalized magnetic adsorbent for dispersive solid phase extraction for the extraction of phthalates in water

https://doi.org/10.1515/gps-2017-0171
Received November 19, 2017; accepted March 6, 2018; previously published online April 14, 2018

Abstract: The preparation of magnetic solid adsorbents for solid phase extraction often involved time-consuming stepwise reaction and high-temperature reaction. In this study, the coating of silica and the functionalization of magnetite were performed in a single step at room temperature. The prepared solid adsorbent was phenyl functionalized magnetic adsorbent (Fe_3O_4@SiO_2-Ph). The Fe_3O_4@SiO_2-Ph was used for the determination of phthalates (butyl phthalate, butyl benzyl phthalate, di-ethylhexyl phthalate and di-n-octyl phthalate) in water. Under optimized conditions, this developed magnetic solid phase extraction method achieved the pre-concentration factor of 100, low method detection limit (0.62–1.02 μg/l) and limit of quantitation (1.98–3.25 μg/l), wide linear dynamic range (0.5–100 μg/l) with good coefficient of determination (>0.9980) and good repeatability (relative standard deviation <5%) during the extraction of the selected phthalates. The developed method was also successfully applied to analyze drinking water, mineral water and lake water with good extraction efficiency (70%–102%) and a high degree of precision (≤5%).

Keywords: butyl phthalate; di-ethylhexyl phthalate; di-n-octyl phthalate; water analysis.

1 Introduction

Phthalate esters (PEs) are synthetic chemicals that have been utilized since the 1930s as plasticizers in polymers and as additives to various products [1, 2]. These compounds act as the additive to promote the plasticity and flexibility of plastic materials. Phthalates have also been used to improve the property of personal-care items, such as perfumes, fragrances, nail polishes, hair sprays, etc. [3]. Due to their wide range of uses, the occurrence of PEs in the environment has been widely reported [4]. PEs are released into the environment through the disposal of PEs-containing products as well as through the migration from plastic products as these compounds are not chemically bonded to the polymeric matrix [5]. The toxicity of PEs is known for decades [6]. Studies have shown that PEs elicit reproductive and developmental toxicities in laboratory animals [7]. Some of the PEs have been reported as carcinogens, and it has also been classified as endocrine-disrupting chemicals with the potential to disrupt the human endocrine system [8]. A recent study also showed that one of the PEs, dibutyl phthalate, is toxic to aquatic plants [4]. For these reasons, several developed countries, such as the United States, Japan, China and those in the European Union have restricted the use of PEs in industrial products. Environmental and drinking water quality standards have also been developed for environmental and human health protection purposes [9].

The United States Environmental Protection Agency (US EPA) proposed the standard analytical procedure for PEs analysis in 1996. The proposed method for water matrices involved the combination of the pre-concentration method [e.g. liquid-liquid extraction (LLE) and solid phase extraction (SPE)] with gas chromatographic-based detection [10]. LLE is not an environmentally friendly method as it requires the substantial volume of organic solvents. On the other hand, SPE has been extensively used in water analysis due to its high enrichment factor and possible automation. However, this method has several deficiencies in that it requires high operational cost and complex equipment, is time consuming, and generates massive secondary wastes [11].

Recently, magnetic dispersive micro-solid phase extraction (MDSPE) has been introduced to overcome the disadvantages of the conventional extraction methods [12]. MDSPE is an improved technique of conventional dispersive micro-solid phase extraction (D-μ-SPE) wherein the solid adsorbent is replaced with magnetic particles. During MDSPE, the magnetic particle is first dispersed in water samples for the extraction of analytes. Then, the magnetic particles are separated from the water matrices after extraction by using the external magnetic field, replacing the centrifugation required by D-μ-SPE [13].

***Corresponding author: Kheng Soo Tay,** Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia, e-mail: khengsoo@um.edu.my
Abdulhadi Muftah Faraj Benrabha: Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

So far, most of these magnetic adsorbents with specific properties were produced through a series of reactions, including the synthesis of magnetic particles (Fe_3O_4), the coating of Fe_3O_4 with the silica layer and the functionalization of silica-coated Fe_3O_4. The functionalization of silica-coated Fe_3O_4 is often achieved via the condensation reaction with the organosilane containing various functional groups [14]. Functionalized silica-coated Fe_3O_4 is often further modified via various reactions to obtain the magnetic particles with specific properties [12, 15]. Therefore, the process by which to obtain the magnetic adsorbents can be time-consuming and involve high-temperature reactions.

The current study demonstrated a method that simplified the preparation of magnetically retrievable adsorbents. In this method, the coating of the silica layer and functionalization were performed in a single step at room temperature. The phenyl group functionalized adsorbent ($Fe_3O_4@SiO_2$-Ph) was prepared for the extraction of phthalates in water through the MDSPE. The efficiency of the $Fe_3O_4@SiO_2$-Ph in the extraction of phthalates was also evaluated. The phenyl group-modified adsorbents have been used as one of the solid phases in solid phase extraction (SPE) for the extraction of nonpolar to moderately polar aromatic compounds [16–18]. However, this functional group is seldom used to modify the adsorbents for dispersive solid phase extraction. The phenyl group was found to provide active sites for the adsorption of pesticides via the π-π interaction between aromatic rings in addition to the hydrophobic interaction [19, 20]. Phthalates are slightly polar compounds with the aromatic ring [21]. Therefore, the $Fe_3O4@SiO_2$-Ph was selected to carry out the selective extraction of phthalates in water.

2 Materials and methods

2.1 Chemicals and reagents

Analytical grade ferric chloride anhydrous, ferrous chloride tetrahydrate, ammonium hydroxide solution (25%), tetraethyl orthosilicate (TEOS, purity of 98%), phenyltriethoxysilane (PTES, purity of 98%), sodium dihydrogen phosphate monohydrate, di-sodium hydrogen phosphate, dichloromethane and methanol were purchased from Merck (Darmstadt, Germany). Acetone, acetonitrile and 2-propanol were obtained from RCI Labscan (Bangkok, Thailand). Di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di-(2-ethylhexyl) phthalate, (DEHP) and di-*n*-octyl phthalate (DNOP) were purchased from Sigma Aldrich (Munich, Germany). Ultrapure water was produced by using an Elga water purification system (Buckinghamshire, UK). The Neodymium disc magnet (20 mm diameter × 3 mm height) was purchased from Eclipse Magnetics (Sheffield, UK). The stock solutions of 2000 mg/l of PEs standard were prepared by dissolving the appropriate amounts of selected phthalates in methanol. The working standard solutions were prepared daily by diluting the stock standard solution to the required concentrations. For the real water samples, surface water was collected from a local lake and stored in the glass bottle, whereas drinking water and mineral water were obtained from the local market. The water samples were filtered through a cellulose nitrate membrane filter (pore size 0.45 mm) and kept at 4°C before used.

2.2 Instrumental analysis

Fourier-transform infrared (FTIR) spectra were recorded using a Perkin-Elmer FTIR (Waltham, USA). The FTIR spectra of the synthesized adsorbents were collected in the transmission mode by pressing the sample with potassium bromide powder to form pellets. For the collection of the FTIR spectra, a resolution of 2 cm^{-1} and 16 scans were both applied. Hitachi Energy dispersive X-ray spectroscopy (EDX) SU8200 (Tokyo, Japan) was used for the elemental analysis. The morphologies of the synthesized Fe_3O_4 and $Fe_3O_4@SiO_2$-Ph were obtained by scanning electron microscopy (SEM). The SEM micrographs were taken in a Hitachi SU8220 (Tokyo, Japan). The separation and detection of PEs were performed using the Agilent Model 7890A Gas Chromatograph (Santa Clara, USA), which was equipped with a split/splitless injector and a flame ionization detector (FID). SPB™-5 fused-silica capillary column (Agilent, Santa Clara, USA) (30 m length, 0.25 mm I.D. and 0.25 µm film thickness) was selected for the separation of the analytes. Nitrogen gas (with 99.999% purity) was used as the carrier gas at a constant flow rate of 10 ml/min. The GC temperature program was 100°C–310°C at 10°C/min. The injection port was operated at the splitless mode. The detector temperature was set at 320°C. The air and hydrogen flow for the detector were 400 and 30 ml/min, respectively. The flow rate of the makeup gas (nitrogen) was 18 ml/min.

2.3 Synthesis of the Fe_3O_4 nanoparticles

The Fe_3O_4 was prepared by using the co-precipitation method [22]. Briefly, $FeCl_2.4H_2O$ (3.2 g) and $FeCl_3$ (3.9 g) with the molar ratio of 2:3 were first dissolved in 50 ml deionized water. Then, 50 ml of ammonium hydroxide (25%) was added, and the mixture was stirred under vigorous mechanical stirring for 30 min at room temperature. We selected the Fe^{2+}:Fe^{3+} ratio of 2:3 because it enables the synthesis of Fe_3O_4 in the air atmosphere [22]. After the reaction, the Fe_3O_4 was precipitated using the external magnet field. The obtained Fe_3O_4 was washed with deionized water and then vacuum dried.

2.4 Synthesis of the $Fe_3O_4@SiO_2$-Ph

About 0.3 g of Fe_3O_4 was first dispersed in 50 ml of 2-propanol and 4 ml of deionized water through sonication for 30 min. Then, 1.9 ml of TEOS, 0.1 ml PTES and 5 ml of ammonium hydroxide solution (25%) were added. The mixture was stirred at room temperature for 12 h. The $Fe_3O_4@SiO_2$-Ph was precipitated using the external magnetic field and then washed thoroughly with deionized water. The $Fe_3O_4@SiO_2$-Ph was vacuum dried.

2.5 PE extraction using the optimized $Fe_3O_4@SiO_2$-Ph-based MDSPE

First, 20 mg of the $Fe_3O_4@SiO_2$-Ph was added to 20 ml of PEs standard solution. The vial was sealed and sonicated for 30 min. Then, the $Fe_3O_4@SiO_2$-Ph was separated from the solution using an external magnetic field. The solution was decanted while the $Fe_3O_4@SiO_2$-Ph was held inside the vial by an external magnet field. Then, 5 ml of water was added to the vial to rinse the $Fe_3O_4@SiO_2$-Ph. The $Fe_3O_4@SiO_2$-Ph was vacuum dried at room temperature. Then, 0.2 ml of methanol was used to desorb the PEs. The desorption process was performed through 1 min of sonication. The $Fe_3O_4@SiO_2$-Ph was again separated from the desorption solvent using an external magnet field. Finally, 2 µl of the solution was injected into the GC-FID.

3 Results and discussion

3.1 Characterization of the $Fe_3O_4@SiO_2$-Ph

The SEM images of Fe_3O_4 and $Fe_3O_4@SiO_2$-Ph were obtained to visualize the differences in surface morphology before and after surface modification (Figure 1). The $Fe_3O_4@SiO_2$-Ph exhibited smooth particle morphology with spherical shape compared with the Fe_3O_4. The size of the $Fe_3O_4@SiO_2$-Ph was significantly larger compared with the Fe_3O_4. These results showed the presence of silica coating on the $Fe_3O_4@SiO_2$-Ph. The FTIR analysis was carried out to verify the presence of the phenyl group and silica layer on the $Fe_3O_4@SiO_2$-Ph after the coating process of Fe_3O_4. The FTIR spectra of the Fe_3O_4 showed two significant peaks at 670 and 3445 cm^{-1}, which can be attributed to Fe-O and O-H stretching vibrations, respectively (Figure 2). After coating with the mixture of TEOS and PTES, the $Fe_3O_4@SiO_2$-Ph showed additional peaks at 1101, 1640 and 2960 cm^{-1}. The peak at 1101 cm^{-1} indicated the presence of Si-O bonding. The peaks at 1640 and 2960 cm^{-1} are attributed to the C-H and C-C stretching bands of the aromatic system, thus indicating the presence of phenyl groups in the $Fe_3O_4@SiO_2$-Ph. Using EDX, the elemental analysis was performed on the $Fe_3O_4@SiO_2$-Ph and $Fe_3O_4@SiO_2$ (silica-coated Fe_3O_4) to further confirm the presence of the phenyl groups. The $Fe_3O_4@SiO_2$-Ph showed the presence of 20% carbon element, whereas for the $Fe_3O_4@SiO_2$, carbon was not detected (Table 1). Therefore, the phenyl groups were successfully introduced into the $Fe_3O_4@SiO_2$-Ph with this simple coating method.

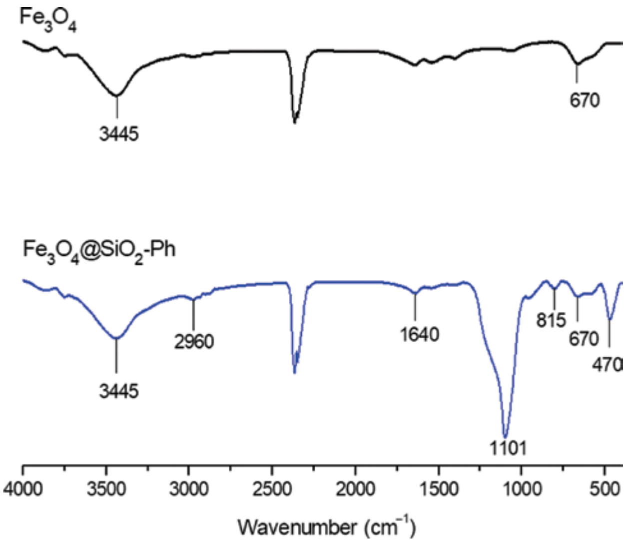

Figure 2: The FTIR spectra of Fe_3O_4 and $Fe_3O_4@SiO_2$-Ph (prepared using 5% of PTES in TEOS).

3.2 The effect of the TEOS to PTES ratio on the $Fe_3O_4@SiO_2$-Ph properties

In this study, the Fe_3O_4 was first coated with the mixture of TEOS and PTES with different ratios to obtain $Fe_3O_4@SiO_2$-Ph with the suitable properties for PEs extraction in

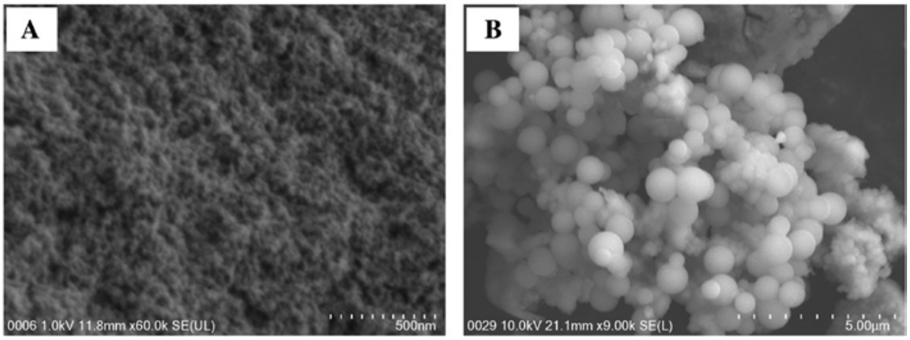

Figure 1: The SEM images of (A) Fe_3O_4 and (B) $Fe_3O_4@SiO_2$-Ph.

Table 1: Elemental compositions of $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-Ph.

Element	%	
	$Fe_3O_4@SiO_2$	$Fe_3O_4@SiO_2$-Ph
Fe	31.0	18.4
O	57.8	51.6
Si	11.0	10.0
C	0	20.0

water. These properties include the dispersibility of the $Fe_3O_4@SiO_2$-Ph in water during extraction and retrievability after extraction. The percentage of PTES in TEOS varied from 50, 12.5 and 5% (v/v). The total volume of the PTES and TEOS mixture was 2 ml. The $Fe_3O_4@SiO_2$-Ph were dispersed in water using sonication for 30 min. Then, the $Fe_3O_4@SiO_2$-Ph were retrieved using the external magnet field. The result showed that the $Fe_3O_4@SiO_2$-Ph prepared using 5% of PTES in TEOS showed good dispersibility (Figure 3A). This adsorbent showed a good property, which allows it to be retrieved entirely from water by using an external magnetic field (Figure 3B). The $Fe_3O_4@SiO_2$-Ph that were prepared using 12.5% and 50% of PTES in TEOS were poorly dispersed after 30 min of sonication; moreover, part of these particles were also found to be floated on the surface of water due to the high hydrophobic property after retrieval. Therefore, the $Fe_3O_4@SiO_2$-Ph that was prepared using 5% of PTES in TEOS was used as solid adsorbents for MDSPE. The selected PEs in this study were DBP, BBP, DEHP and DNOP.

3.3 Optimization of the operating parameters of the MDSPE

The effect of the amount of $Fe_3O_4@SiO_2$-Ph on the PEs extraction efficiency was assessed using 5–20 mg of the $Fe_3O_4@SiO_2$-Ph. The peak area of the selected phthalates was found to increase with the increasing amount of $Fe_3O_4@SiO_2$-Ph. This result was due to the increase in

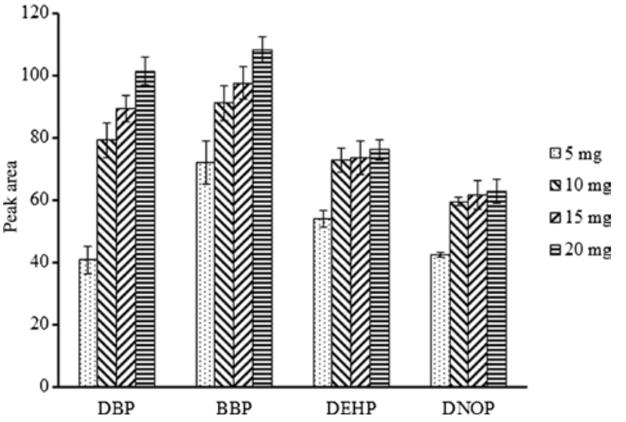

Figure 4: The effects of the amount of the $Fe_3O_4@SiO_2$-Ph on the extraction efficiency of selected PEs. (Sonication time = 30 min; desorption solvent = methanol; desorption time = 1 min; without pH adjustment).

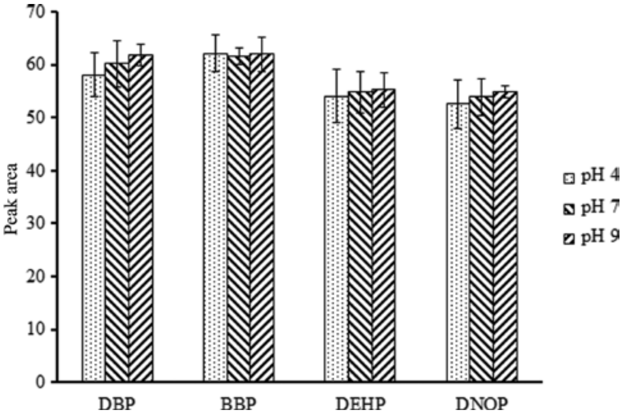

Figure 5: The effects of sample pH on the extraction efficiencies of PEs. (Amount of $Fe_3O_4@SiO_2$-Ph = 20 mg; sonication time = 30 min; desorption solvent = methanol; desorption time = 1 min).

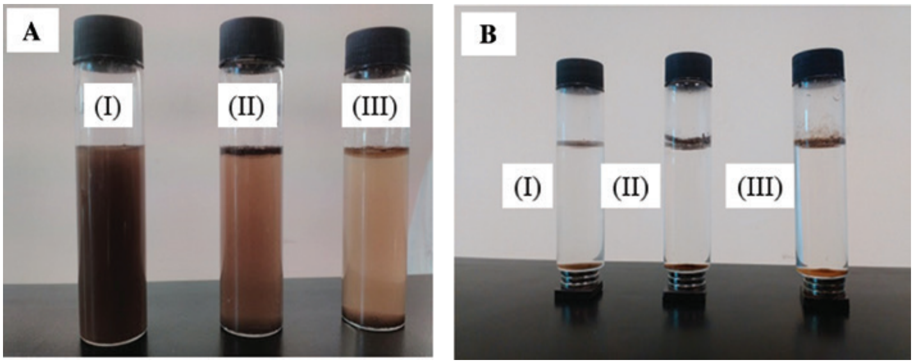

Figure 3: The (A) dispersibility and (B) retrievability tests for the $Fe_3O_4@SiO_2$-Ph prepared using (I) 5%, (II) 12.5% and (III) 50% of PTES in TEOS.

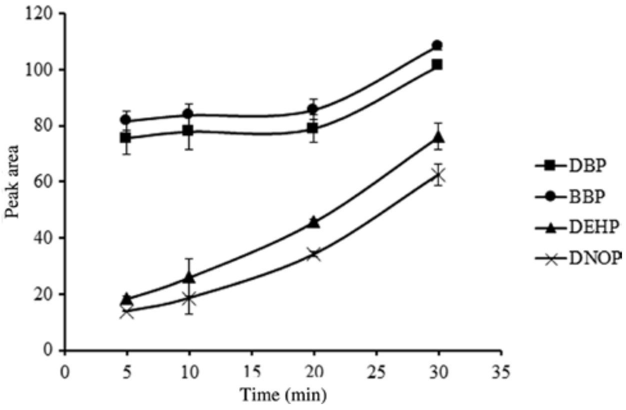

Figure 6: The effects of extraction time on the PE extraction efficiency. (Amount of Fe_3O_4@SiO_2-Ph = 20 mg; desorption solvent = methanol; desorption time = 1 min).

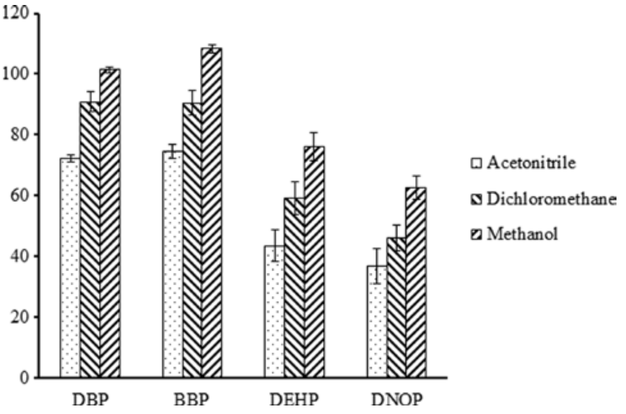

Figure 7: The effects of desorption solvents. (Amount of Fe_3O_4@SiO_2-Ph = 20 mg; sonication time = 30 min; desorption time = 1 min).

the number of adsorption sites for phthalates when the amount of Fe_3O_4@SiO_2-Ph increased. From 10–20 mg of Fe_3O_4@SiO_2-Ph, the peak areas of the DBP and BBP increased significantly (Figure 4). However, no significant increments in the peak areas were observed for DEHP and DNOP. Therefore, for further studies, 20 mg of Fe_3O_4@SiO_2-Ph was selected in order to reduce the operational cost of the developed extraction method.

The change of the solution's pH level may ionize both the analytes and the functional groups on the solid phase, which can then influence the efficiency of D-μ-SPE [17]. In this study, the effects of the solution's pH on PEs extraction efficiency were studied at pH 4, 7 and 9. As shown in Figure 5, no significant changes in the peak area of PEs were observed when the pH of the solution increased from 4 to 9. The PEs and phenyl group on the Fe_3O_4@SiO_2-Ph are not ionizable compounds nor functional groups. Therefore, the extraction efficiency was not influenced by the changes of the solution's pH. This result also indicated the versatility of the Fe_3O_4@SiO_2-Ph in extracting PEs at different pH conditions. Hence, the pH adjustment is not required by this developed MDSPE.

The dispersion of the Fe_3O_4@SiO_2-Ph was performed using sonication. Sonication time is an important factor that allows the complete dispersal of the Fe_3O_4@SiO_2-Ph in water for achieving the highest extraction efficiency. In this study, different sonication times ranging from 5 to 30 min were evaluated to obtain the most efficient extraction method. The peak areas, DBP, BBP, DEHP and DNOP, were found to increase from 5 to 30 min (Figure 6). In order to develop an efficient extraction method, 30 min was selected as the sonication time for the MDSPE.

The effectiveness of acetonitrile, dichloromethane (DCM) and methanol as desorption solvents for the selected PEs from Fe_3O_4@SiO_2-Ph was evaluated. The desorption process was performed using sonication for 1 min. The results showed that methanol had the highest efficiency in extracting PEs from the Fe_3O_4@SiO_2-Ph compared with acetonitrile and DCM (Figure 7). Therefore, methanol was selected as the desorption solvent.

3.4 The analytical performances of the developed MDSPE

The optimized operating parameters for the extraction of phthalate esters using the MDSPE were 20 mg of Fe_3O_4@SiO_2-Ph, 30 min of sonication time and the use of methanol as the desorption solvent.

The pre-concentration factor for the optimized method was calculated using the following equation [23]:

Table 2: Analytical performance of the developed method.

Analytes	Calibration curve	R^2	Linear range (μg/l)	MLD (μg/l)	LOQ (μg/l)	RSD (%) inter-day, n = 3	RSD (%) intra-day, n = 5
DBP	y = 23.6x − 0.50	0.9980	1–100	1.02	3.25	2.9	3.6
BBP	y = 13.6x + 1.95	0.9950	1–100	0.86	2.73	2.6	4.1
DEHP	y = 22.0x − 0.97	0.9997	1–100	0.62	1.98	1.9	2.0
DNOP	y = 19.0x − 1.83	0.9998	1–100	0.68	2.16	2.3	2.1

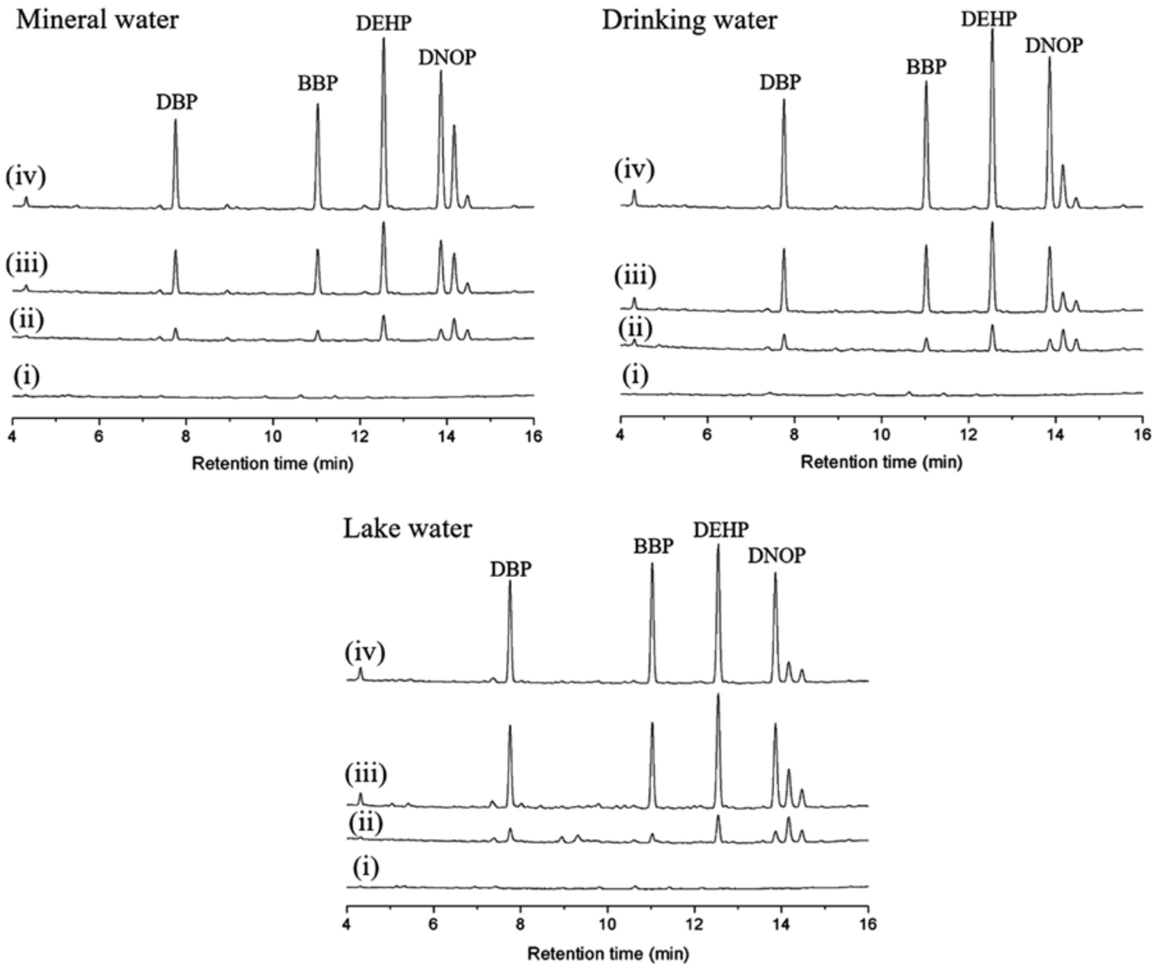

Figure 8: The GC-FID chromatograms of the PEs analysis in selected water samples with PEs spiked levels of (i) 0 µg/l, (ii) 10 µg/l, (iii) 50 µg/l and (iv) 100 µg/l.

$$\text{Pre-concentration factor} = \frac{V_0}{V_f},$$

where V_0 and V_f represent the initial volume of the water sample and the final volume of the PEs extract before the GC-FID analysis, respectively. This optimized method was used to pre-concentrate the 20 ml PEs standard solution. In this method, the final volume of the PEs extract before the GC-FID analysis was 200 µl, and the pre-concentration factor was 100. The analytical performance and the validation of the developed MDSPE method were evaluated using linearity, the method of detection limit (MDL), the limit of quantitation (LOQ) and the intra-day and inter-day precision (Table 2). The MDL and LOQ were obtained according to the guidelines set by the US EPA [24]. Briefly, a solvent blank and a method blank were first analyzed to determine the interference and contamination. The selected phthalates were not detected in both solvent blanks and method blanks. Then, the concentrations of phthalates in seven samples, which give rise to a peak with a signal-to-noise ratio of 3–5, was determined. This was followed by the calculation of the standard deviation (*s*). The MDL (at the 99% confident level) and LOQ were calculated using the following equations:

Table 3: Recoveries of PES in the real water samples.

Water sample	Concentrations of spiked PES (µg/l)	Recovery ± SD (%)			
		DBP	BBP	DEHP	DNOP
Mineral water	10	70 ± 2	75 ± 1	100 ± 4	84 ± 1
	50	70 ± 1	83 ± 1	82 ± 3	81 ± 2
	100	74 ± 4	95 ± 4	99 ± 2	101 ± 3
Drinking water	10	70 ± 1	83 ± 1	96 ± 2	93 ± 1
	50	75 ± 3	81 ± 2	98 ± 1	98 ± 3
	100	72 ± 1	80 ± 1	100 ± 2	99 ± 3
Lake water	10	71 ± 1	95 ± 1	76 ± 1	74 ± 1
	50	87 ± 4	102 ± 5	101 ± 3	100 ± 3
	100	76 ± 3	92 ± 4	99 ± 4	99 ± 5

Table 4: Comparison of the developed method with other MDSPE methods in the determination of PEs.

Phthalates	Solid adsorbent	Detection method	Detection limits (µg/l)	Linear range (µg/l)	References
DBP, BBP, DEHP and DNOP	C18-Fe_3O_4@mSiO_2	GC-MS	31–77	50–2500	[25]
BBP, DEHP and DNOP	MNP@3TArH	GC-FID	0.054–0.080	0.1–50	[26]
DBP and DEHP	MWCNTs-PVA	GC-FID	26.3–36.4	25–10,000	[27]
DBP, BBP and DEHP	Magnetic MWCNT	GC-MS/MS	0.010–0.019	0.05–10	[28]
DBP, BBP, DEHP and DNOP	Fe_3O_4@SiO_2-Ph	GC-FID	0.62–1.02	0.5–100	This study

$$\mathrm{MDL} = s \times (\mathrm{t-value})$$

$$\mathrm{LOQ} = s \times 10$$

where student's *t*-value was equal to 3.143 for seven replicates and six degrees of freedom. The results showed that good linearity was obtained for the selected phthalates over the range of 0.1–100 µg/l ($R^2 > 0.9980$). The MDL and LOQ of the developed method ranged from 0.62–1.02 µg/l and 1.98–3.25 µg/l, respectively. The intra-day and inter-day reproducibility, expressed as relative standard deviation (RSD), were obtained by analyzing sets of three and five replicates of 50 µg/l of phthalate solution, respectively. The RSD values for intra-day and inter-day ranged from 1.9%–2.9% and from 2.0%–4.1%, respectively. The selected water samples were spiked with 10, 50 and 100 µg/l of PEs to investigate the effect of water matrices on the analytical performance of the developed method. The GC-FID chromatograms of the PEs analysis in selected water samples are presented in Figure 8. The recoveries of the PEs ranged from 70%–102% with the RSD < 5% (Table 3). This result indicated the water matrix does not influence the analytical performance of the developed method.

The performance of the developed Fe_3O_4@SiO_2-Ph-based MDSPE was compared with previously reported MDSPE methods for PE extraction (Table 4). These solid adsorbents were C18-Fe_3O_4@mSiO_2 (silica-coated Fe_3O_4 modified with *n*-octadecyltriethoxysilane), MNP@3TArH (polythiophene functionalized Fe_3O_4), MWCNT-PVA [magnetic multi-walled carbon nanotubes-poly (vinyl alcohol) cryogel] and magnetic MWCNTs (magnetic multi-walled carbon nanotubes). The Fe_3O_4@SiO_2-Ph showed wider linear range in the determination of PEs compared with the MNP@3TArH and the magnetic MWCNT. The detection limit of the developed method was also much lower than those of the C_{18}-Fe_3O_4@mSiO_2 and MWCNT-PVA based MDSPE.

4 Conclusion

The Fe_3O_4@SiO_2-Ph was successfully synthesized by coating phenyl group-containing silica gel onto the Fe_3O_4 at room temperature. The Fe_3O_4@SiO_2-Ph was employed as the solid adsorbent for the MDSPE. The Fe_3O_4@SiO_2-Ph-based MDSPE was used for the determination of PEs in water. Under optimized conditions, the developed MDSPE method provided a wide linear range with good coefficient of determination, good inter-day and intra-day repeatability and low method of detection. The developed method also showed high extraction efficiency and repeatability when it was used to determine the selected phthalates in drinking water, lake water and mineral water. In terms of performance, the Fe_3O_4@SiO_2-Ph prepared using the simplified method are comparable with the recently reported adsorbents in extracting selected phthalates in water.

Acknowledgments: This research was supported financially by the Ministry of Higher Education Malaysia (Fundamental Research Grant Scheme No. FP042-2016) and by the University of Malaya (Postgraduate Research Grant No. PG020-2016, Funder Id: 10.13039/501100004386).

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