



Preparation of polypyrrole-coated magnetic particles for micro solid-phase extraction of phthalates in water by gas chromatography–mass spectrometry analysis

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ABSTRACT

In this work, polypyrrole (PPy)-coated Fe₃O₄ magnetic microsphere were successfully synthesized, and applied as a magnetic sorbent to extract and concentrate phthalates from water samples. The PPy-coated Fe₃O₄ magnetic microspheres had the advantages of large surface area, convenient and fast separation ability. The PPy coating of magnetic microspheres contributed to preconcentration of phthalates from water sample, due to the π - π bonding between PPy coating and the analytes. Also, the coating could prevent aggregation of the microspheres, and improve their dispersibility. In this study, seven kinds of phthalates were selected as model analytes, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*iso*-butyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), benzylbutyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DNOP), and gas chromatography–mass spectrometry (GC–MS) was introduced to detect the phthalates after sample pretreatment. Important parameters of the extraction procedure were investigated, and optimized including eluting solvent, the amount of Fe₃O₄@PPy particles, and extraction time. After optimization, the procedure took only 15 min to extract and concentrate analytes with high efficiency. Validation experiments showed that the optimized method had good linearity (0.985–0.998), precision (3.4–11.7%), high recovery (91.1–113.4%), and the limits of detection were from 0.006 to 0.068 μ g/L. The results indicated that the novel method had advantages of convenience, good sensitivity, high efficiency, and it could also be applied successfully to analyze phthalates in real water sample.

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1. Introduction

In the past decades, solid-phase based sample preparation has received intensive attraction such as solid-phase microextraction (SPME) [1,2]. These sorbent based extraction techniques reduce the use of hazardous organic solvents, simplify the tedious clean-up procedures and achieve high preconcentration factor. On the other side, due to the limited rate of diffusion and mass transfer, the extraction equilibration time of solid-phase extraction is usually long [3–5]. In order to overcome the limitations, magnetic micro-/nano-particles have been introduced into sample preparation. Unlike the conventional solid-phase extraction (SPE), the micro-/nano-sorbents are capable to expose completely in water, so that little amount of sorbents and short extraction time are required to extract analytes from large volume system. Also, magnetic particles can be collected and separated from liquid phase simply under a magnetic field, which avoids the tedious filtration

or centrifugation procedure [5–7], and makes the particles easy to retrieve with low cost. These intriguing features of magnetic separation have led to its numerous applications in many research fields such as bio-separation [8–12]. While, due to the dipole–dipole interactions, the particles are easy to aggregate, which restricts the application of magnetic particles. Therefore, surface modification is very important, and it can not only disperse magnetic particles in matrix but also provide an active surface to interact with certain molecules such as aromatic compounds, heavy metals, biomolecules, etc. [13,14].

Coated with different functional groups, magnetic particles have been applied extendedly to sample preparation in a lot of research fields including proteomics, environmental monitoring and so on [5,15–18]. In our group, magnetic core–shell microspheres have been synthesized, and successfully applied to selective extraction and enrichment of phosphopeptides and glycopeptides [19–23]. More recently, magnetic particles which are used as sorbents to separate and preconcentrate analytes from environmental water samples arouse more and more attraction. Due to the great merits of magnetic micro-/nano-particles, many magnetic materials bounded with different functional groups have been synthesized

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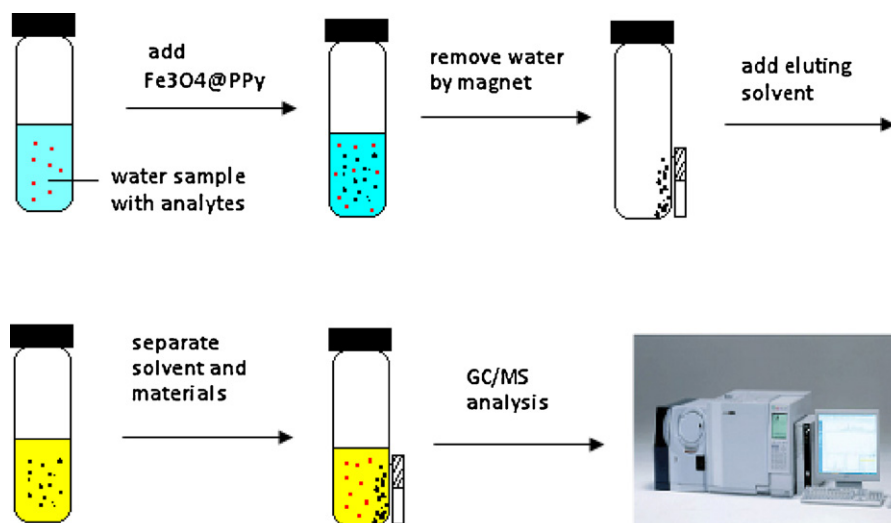


Fig. 1. The scheme of micro solid-phase extraction procedure based on $\text{Fe}_3\text{O}_4@PPy$ microspheres.

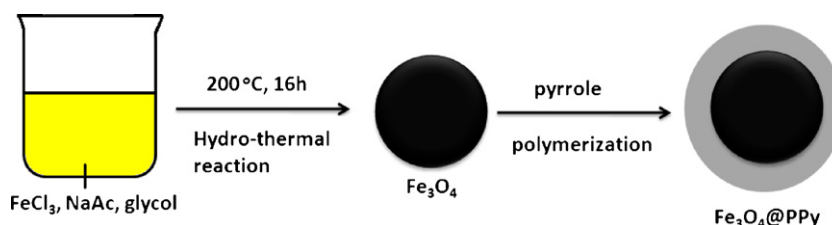


Fig. 2. The two-step procedure to synthesize $\text{Fe}_3\text{O}_4@PPy$ microspheres.

and applied to the extraction of various types of analytes from water sample [24–29].

Nowadays, magnetic particles coated with functional polymer have attracted tremendous interest, especially conducting polymers. Study on this kind of material has become one of the most promising research areas. These polymers are very attractive as they have great potential applications in batteries, molecular electronics, separation materials, ion exchangers and chemical sensors [30–32]. Many research achievements have published about synthesis of these functional polymer magnetic materials, including polystyrene, polyaniline, poly (*N*-isopropylacrylamide) and so on [33–36]. Recently, we successfully synthesized PMMA-coated Fe_3O_4 particles for the enrichment of low-abundance peptides [37].

Among these polymer materials, polypyrrole (PPy) and its derivatives are one of the widely used conducting polymers for the extraction of various different types of compounds. It has been demonstrated that PPy can be used to extract aromatic com-

pounds (e.g. PAHs), organometal compounds (e.g. organoarsenic) and anionic compounds (e.g. nitrite) with high efficiency [38–40]. This is probably because it has multifunctional properties, such as interactions among polar functional groups, π - π interactions and hydrogen bonds [30,31]. These properties help to grab and separate certain kind of compounds from different matrices. Up to now, PPy film has been successfully coated on the fiber of solid phase microextraction (SPME), and was widely used as sorbent to extract many compounds from water, plasma, and other systems [31,41–43]. However, to our best knowledge, there is no work published on synthesizing PPy-coated magnetic particle as the sorbent for extraction and analysis of contaminants in water. In this work, the phthalates were selected as targeted analytes because they are common pollutants in water and can interfere with human incrition, causing malformation and cancer [44–47]. A large number of methods have been developed to extract phthalates from different matrix, such as SPME,

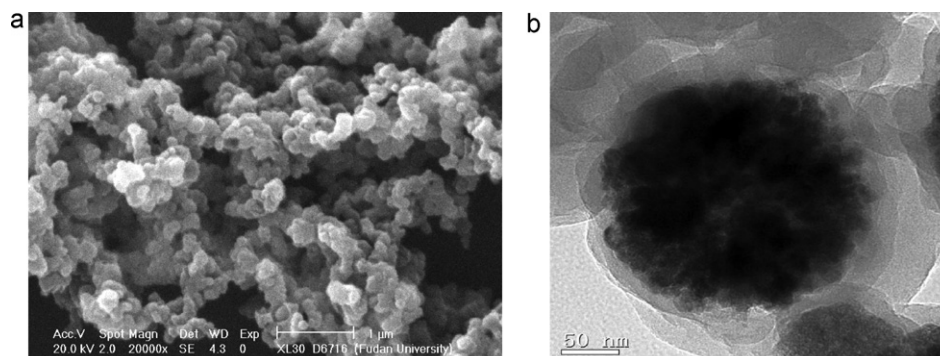


Fig. 3. SEM (a) and TEM (b) images of $\text{Fe}_3\text{O}_4@PPy$ microspheres.

Table 1
Validation for phthalates measured with Fe₃O₄@PPy based MSPE–GC–MS method.

Compound name	R _t (min)	Characteristic ion	Calibration curve	R ²	Linear range (μg/L)	RSD (%)	LOD (μg/L)	LOQ (μg/L)	Recovery (%)
dimethyl phthalate (DMP)	9.28	77, 163	y = 71.91x + 650.9	0.998	0.5–100	3.4	0.022	0.073	113.4
diethyl phthalate (DEP)	10.42	149, 177	y = 132.2x – 17.30	0.992	0.1–100	8.1	0.024	0.080	97.6
di-iso-butyl phthalate (DIBP)	12.43	149, 223	y = 630.3x + 19522	0.995	1.0–100	5.7	0.006	0.020	97.4
di-n-butyl phthalate (DBP)	13.06	149, 205	y = 251.0x + 6940.0	0.992	1.0–100	8.9	0.018	0.060	91.1
benzylbutyl phthalate (BBP)	15.46	91, 149	y = 62.02x – 13.67	0.995	0.1–100	8.8	0.068	0.230	108.2
di-(2-ethylhexyl) phthalate (DEHP)	16.53	149, 167	y = 76.21x + 1131.0	0.985	0.5–100	11.7	0.014	0.047	94.9
di-n-octyl phthalate (DNOP)	17.88	149, 279	y = 61.78x – 23.10	0.991	0.1–100	11.1	0.021	0.070	102.9

single-drop microextraction (SDME), liquid–liquid microextraction (LLME), monolith extraction, and so on [48,7,49–51]. In this study, we successfully synthesized Fe₃O₄@PPy microspheres, and applied them as the magnetic adsorbent to extract and analyze phthalates in water by gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Chemicals

The phthalate standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany), which contained dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DIBP), di-n-butyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP), benzylbutyl phthalate (BBP) and di-n-octyl phthalate (DNOP). Methanol, ethanol and glycol were prepared from Shanghai Lingfeng Chemical Reagent Ltd. Co. (Shanghai, China). Other chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China) if not mentioned.

The working phthalate standard solution was prepared by diluting the phthalates in acetone with a concentration of 1.0 mg/L. This working standard solution was stored at 4 °C, and ready for the following work.

2.2. Preparations of Fe₃O₄ microspheres

According to our previous method [52], Fe₃O₄ microspheres were prepared as followings. 1.35 g FeCl₃·6H₂O powder was dissolved with 75 mL glycol in a 100 mL dry vessel, followed by magnetic stirring until the mixture turned to be transparent. Then 3.6 g sodium acetate (NaAc) was added in the mixture with stirring till NaAc powder dissolved completely. The solution was dispersed under ultrasonic wave for 5 min, and then transferred to an autoclave, followed by heating at 200 °C for 16 h. After that the Fe₃O₄ microspheres were synthesized. The particles were then removed from autoclave, washed by ethanol for 5 times, and dried at 50 °C in vacuum for 24 h.

2.3. Preparation of PPy coated magnetic microspheres

The procedure of coating PPy on Fe₃O₄ microspheres was conducted according to the previous method [53,54]. 50 mL distilled water was firstly deaerated by bubbling nitrogen for 30 min and then added to a 100 mL three-necked round flask equipped with a mechanical stir. Then 0.066 g sodium dodecyl benzene sulfonate (NaDBS) was added and the solution was mixed under stirring. When NaDBS was dissolved, 0.025 g Fe₃O₄ was introduced in the flask and the solution was stirred for 15 min. Then 0.5 mL pyrrole was added and stirred for 1 h till all the compounds were dispersed entirely. Polymerization was started when FeCl₃ solution (0.28 g dissolved in 5.0 mL distilled water) was added dropwise, and the mixture was stirred for 12 h at room temperature. Finally, the synthesized Fe₃O₄@PPy microspheres were collected by a bar of magnet. The particles were obtained by washing with water and ethanol in sequence, and dried at 50 °C in vacuum for 24 h.

2.4. Characterizations of Fe₃O₄@PPy microspheres

The morphology of Fe₃O₄@PPy microspheres was observed by transmission electron microscopy (JEM-2100F) and scanning electron microscopy (XL30). The surface modification of Fe₃O₄@PPy was investigated by Fourier-transform infrared (FTIR) spectroscopy (Nicolet Nexus 470).

2.5. The micro solid-phase extraction (MSPM) procedure by Fe₃O₄@PPy microspheres

Fig. 1 shows the procedure of sample preparation. First, 10 mL deionized water containing phthalates with a concentration of 100 μg/L was added in a 20 mL vial with PTFE-silicone septum. Then 30 mg Fe₃O₄@PPy microspheres were introduced in the vial to extract the analytes and the mixture was vibrated to make the particles contact entirely with water sample. After 15 min, a bar of magnet was placed beside the vial and it held the Fe₃O₄@PPy microspheres which had already extracted the analytes. And then water was removed from the vial with the sorbent remaining. The analytes were eluted by 800 μL ethyl acetate under ultrasonic wave,

and 1 μL solvent containing the extracted analytes was injected in GC–MS to analyze.

2.6. Instrument and chromatographic conditions

The determination of analytes was conducted on GC–MS instrument (6890GC/5973, Agilent Co.). The compounds were separated on an HP-5MS capillary column (30 m \times 0.25 mm, 0.25 μm), and the sample was injected in splitless mode. The column oven temperature was programmed with an initial temperature of 60 $^{\circ}\text{C}$ for 1 min, raised to 280 $^{\circ}\text{C}$ with a rate of 15 $^{\circ}\text{C}/\text{min}$, and then hold for 4 min. The injection temperature was 250 $^{\circ}\text{C}$. Helium (99.999%) was used as the carrier gas with a flow rate of 1 mL/min. All samples were analyzed in selected ion monitoring (SIM) mode. The ratio of mass-to-charge (m/z) of the characteristic ions and the retention time of each phthalate are tabulated in Table 1.

2.7. Analytical validations

The analytical validations of the proposed procedure were carried out with blank water sample spiked with phthalate standard solutions of certain concentrations. The linearity was evaluated by analyzing a series of concentrations (0.1–100 $\mu\text{g}/\text{L}$) of phthalate standard solutions. Calibration curve for each analyte was conducted by peak area of analyte (Y) versus corresponding concentration of the analyte (X).

To obtain the precision of the method, replicated analysis of spiked water samples were carried out for four times, and RSD values were calculated by the obtained peak area of each analyte. To determine the limit of detection (LOD) and limit of quantification (LOQ) of the method, water sample with a low concentration (0.05 $\mu\text{g}/\text{L}$) was analyzed for four times, and the LOD, LOQ values were calculated on the basis of $S/N = 3$ and $S/N = 10$, respectively. In addition, recoveries of the target compounds were also conducted by extracting spiked water sample (1 $\mu\text{g}/\text{mL}$) under the optimized condition for three times.

3. Results and discussion

3.1. Synthesis and characterization of the $\text{Fe}_3\text{O}_4@PPy$ microspheres

The synthesis of $\text{Fe}_3\text{O}_4@PPy$ microspheres was performed by a two step reaction (Fig. 2), which was very simple and convenient. Fig. 3 is SEM and TEM images of $\text{Fe}_3\text{O}_4@PPy$, respectively. As seen from the SEM and TEM images, pyrrole was successfully polymerized on Fe_3O_4 microspheres. TEM image of $\text{Fe}_3\text{O}_4@PPy$ indicated that Fe_3O_4 particles (darker section in TEM) were coated totally by PPy (lighter section in TEM). Therefore, a distinct core-shell structure of the particles formed and the Fe_3O_4 cores were well coated with PPy. The diameter of Fe_3O_4 core was about 200 nm, and the thickness of PPy coating was about 25 nm. In addition, the successful connection between Fe_3O_4 microspheres and polypyrrole was also proved by FT-IR spectra of $\text{Fe}_3\text{O}_4@PPy$ microspheres (Fig. 4). The peaks of 1538 cm^{-1} and 1450 cm^{-1} were related to the characteristic absorption peaks of pyrrole rings. The bands at 1162, 887 and 775 cm^{-1} corresponded to =C–H in-plane and out-plane vibration of pyrrole. These peaks mentioned above were consistent with references reported [55], so these results indicated that polypyrrole was successfully coated on Fe_3O_4 microspheres.

3.2. PPy-coated Fe_3O_4 microspheres as the adsorbent for extraction and concentration of the analytes

In this work, core-shell $\text{Fe}_3\text{O}_4@PPy$ microspheres were developed as the adsorbent for micro solid-phase extraction of pollutants

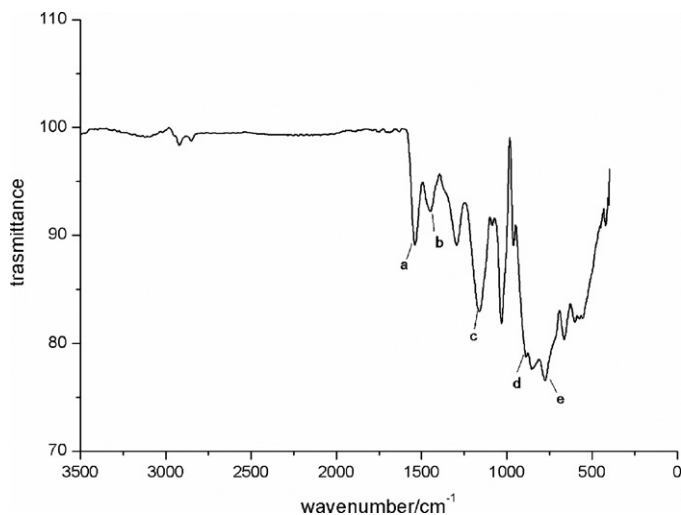


Fig. 4. The FT-IR spectra of $\text{Fe}_3\text{O}_4@PPy$ microspheres. The wavenumber of each characteristic peak is: a, 1538 cm^{-1} ; b, 1450 cm^{-1} ; c, 1162 cm^{-1} ; d, 887 cm^{-1} ; e, 775 cm^{-1} .

from water. The phthalates were selected as the model analytes to demonstrate the extraction capacity of the $\text{Fe}_3\text{O}_4@PPy$. Moreover, it is easy to interact with polypyrrole because of π – π interaction between phenyl groups of phthalates and pyrrole rings. In this method, large surface area of $\text{Fe}_3\text{O}_4@PPy$ microspheres contributed to extensive contact with analytes, and magnetic property of the sorbent could also simplify the extraction and isolation procedure. The major parameters affecting the extraction were investigated, and optimized, and the validation of the proposed method was also verified. In the extraction procedure, many parameters would affect the extraction efficiency, including particle properties (such as surface area and particles size), type of eluting solvent, extraction time and so on. Therefore, in the following work, we optimized some parameters of eluting solvent, extraction time and amount of particles.

3.2.1. Influence of eluting solvent

It is necessary to use solvent to elute the analytes from $\text{Fe}_3\text{O}_4@PPy$ particles before GC–MS analysis, so the suitable solvent is indispensable which can elute the adsorbed analytes as much as possible. In this work, we selected methanol, ethyl acetate and chloroform to be optimized, and then compared their efficiencies. The results are shown in Fig. 5. According to Fig. 5, CHCl_3 had rela-

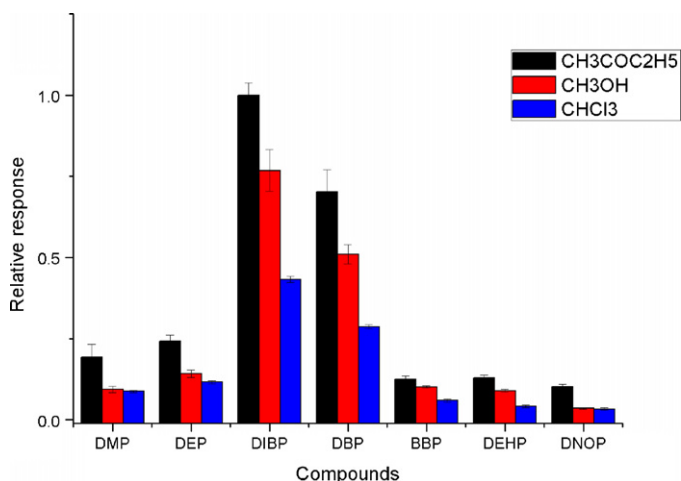


Fig. 5. The optimization of eluting solvent (chloroform, methanol and ethyl acetate).

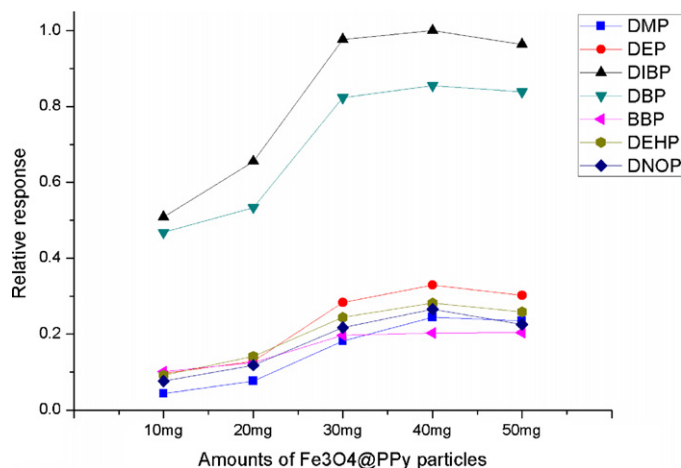


Fig. 6. The effect of amount of Fe₃O₄@PPy microspheres (10, 20, 30, 40 and 50 mg).

tive lower eluting ability for all phthalates than both methanol and ethyl acetate, and ethyl acetate had a highest efficiency. It could be explained by the theory of “like dissolve like”, and the solvent of ester could elute esters more easily than alcohol and chloride. So, ethyl acetate was selected as the optimized eluting solvent in the following work.

3.2.2. Effect of amount of Fe₃O₄@PPy microspheres

In order to enhance extraction efficiency, the amount of Fe₃O₄@PPy microspheres must be large enough to extract the analytes as completely as possible. So, we optimized the amount of particles, including 10, 20, 30, 40 and 50 mg. According to the results shown in Fig. 6, more analytes could be extracted as the amount of Fe₃O₄@PPy particles increases. When the amount reached to 30 mg, the curves turned out to be flat, and there was no distinct increase to extraction efficiency. When the amount increased over 50 mg, more than 500 μL solvent must be added to ensure all the materials submerge, and it might dilute the analytes in solvent correspondingly. So, we selected 30 mg Fe₃O₄@PPy as the optimized amount.

3.2.3. Effect of extraction time

Extraction time is also an important parameter which affects the efficiency to a large extent. In this work, different extraction time (5, 10, 15 and 30 min) was optimized. As is shown in Fig. 7, the extraction efficiency increased when extraction time

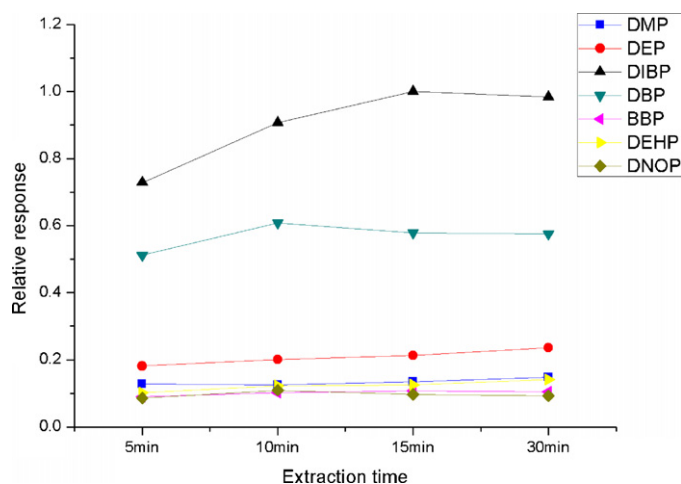


Fig. 7. The effect of different extraction time (5, 10, 15 and 30 min).

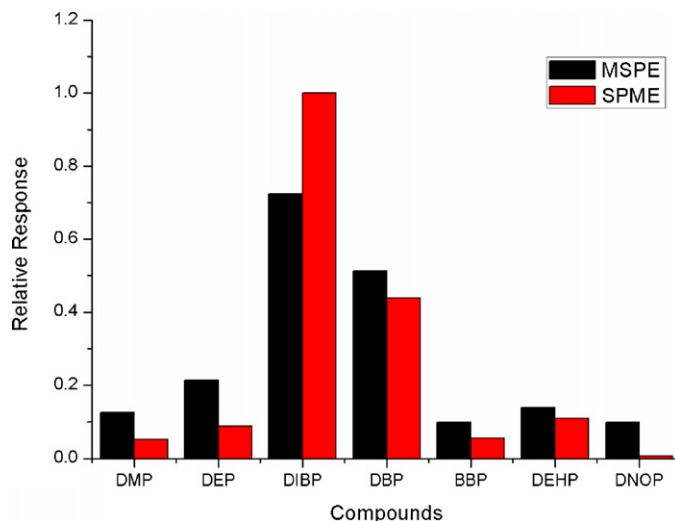


Fig. 8. The comparison of MSPE and SPME procedure in extraction efficiency

prolonged. For DIBP and DBP, the efficiency increased intensely before 15 min, and the curve flattened out from 15 min to 30 min. For other analytes, the increasing tendency was not as obvious as DBP and DIBP, but it could also be seen that the efficiency tended to be balanced after 15 min. It can be considered that extraction balance between water phases and sorbent was nearly reached after 15 min. Therefore the extraction balance can be attained in a very short time, and it would not affect the efficiency obviously when the extraction time was longer than 15 min. Hence, we selected 15 min as the best extraction time in the following work.

3.3. Validation of the method

To demonstrate the feasibility of the proposed method, analytical quality parameters were also investigated, including linearity, repeatability, limit of detection and limit of quantification. Good linearity was obtained, and the coefficient of determination (R^2) were more than 0.991, except for DEHP (0.985). Precision of the method varied from 3.4% to 11.7%. The LOD values were calculated on basis of $S/N=3$, and the values of all the analytes were from 0.006 to 0.068 μg/L. On the basis of $S/N=10$, the LOQ values of the analytes were from 0.020 to 0.230 μg/L. The recoveries of the analytes were from 91.1% to 113.4%. All the results were displayed in Table 1. The results illustrated that the proposed method based on magnetic micro solid-phase extraction technique is reliable.

3.4. Comparison with other microextraction methods

In order to further demonstrate the superiority of our proposed method, we compared our method with the conventional SPME method [49]. 3.5 mL spiked water sample with concentration of 100 μg/L was extracted by an 85 μm polyacrylate fiber. After an extraction of 90 min, the compounds were thermally desorbed in GC-MS injector at 250 °C. The results of both SPME and MSPE were shown in Fig. 8. In comparison with SPME procedure, MSPE method had higher extraction ability than SPME apart from DIBP, and thereby it illustrated our method not only had better extraction efficiency but also shortened extraction time to a great extent. Moreover, compared with liquid-phase microextraction (LPME) [50] and single-drop microextraction (SDME) [51] techniques, our method provided a relative wider linear range and a comparable detection limit. The results revealed that the proposed method for

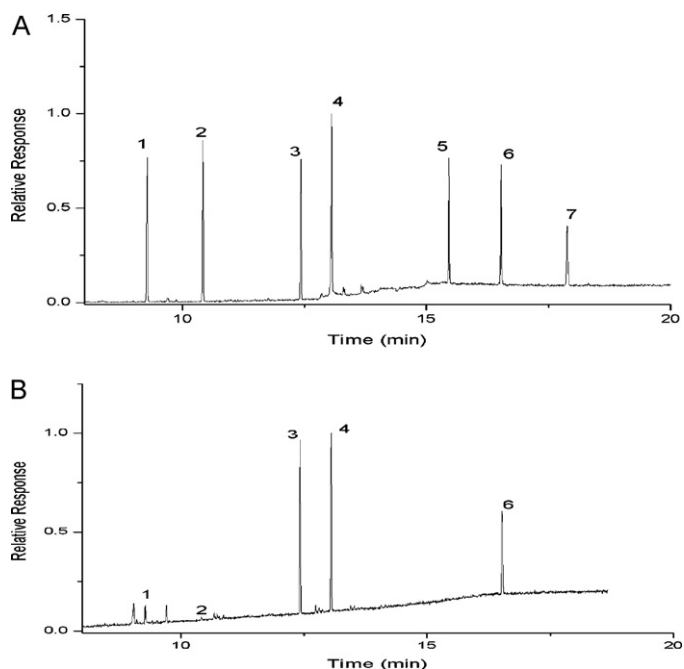


Fig. 9. The selected ion monitoring (SIM) chromatogram obtained from standard phthalates solution and tap water sample by the proposed method. The peaks marked from 1 to 7 indicate the compound of dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), benzyl-butyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DNOP), respectively. In tap water sample, DEP, DMP, DIBP, DBP and DEHP were detected.

the analysis of phthalates in water sample was simple, rapid and sensitive.

3.5. Application of the proposed method to the real water analysis

Furthermore, the proposed method was applied to the analysis of the real tap water samples. Tap water sample was directly collected from our laboratory and stored at 4 °C in glass bottles. The sample was analyzed within one day. According to the proposed method based on Fe₃O₄@PPy, the concentrations of phthalates in real water sample were analyzed. After a short extraction (15 min), the analytes-adsorbed Fe₃O₄@PPy particles were separated by magnetic field. The analytes on particles were eluted with solvent, and analyzed by GC–MS. The total ion chromatogram of the real water sample was shown as Fig. 9B, and was compared with the chromatogram of phthalates standard solution (Fig. 9A). As the results showed, in the tap water sample, none of BBP and DEHP was detected, while other five kinds of phthalates were detected. The calculated concentrations of the phthalates were listed in Table 2. This showed that the proposed method based on Fe₃O₄@PPy was feasible in the application of real water sample analysis.

Table 2

Concentrations of phthalates (ng/L) in real water sample.

Compound Name	Tap water (μg/L)
dimethyl phthalate (DMP)	3.4
diethyl phthalate (DEP)	2.1
di-iso-butyl phthalate (DIBP)	2.6
di- <i>n</i> -butyl phthalate (DBP)	7.4
benzylbutyl phthalate (BBP)	ND
di-(2-ethylhexyl) phthalate (DEHP)	5.8
di- <i>n</i> -octyl phthalate (DNOP)	ND

ND, not detected.

4. Conclusion

In the present study, PPy-coated Fe₃O₄ microspheres were successfully synthesized, and applied them as the absorbent to extract and concentrate phthalates in water sample. Due to the intense π–π bonding between polypyrrole and the analytes, the sorbent could extract and enrich phthalates from water sample in a short time of 15 min with a high efficiency. What's more, the magnetic property of the Fe₃O₄ core made the sorbent easy to remove from water sample and the eluant. The experiment results showed that the proposed procedure based on PPy-coated Fe₃O₄ microspheres was a fast, simple and convenient method to analyze phthalates from water sample, and it had a great potential in the application of detecting other compounds such as polycyclic aromatic hydrocarbons (PAHs) in water.

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