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Evaluation of a magnetic polysulfone microcapsule containing organic modified montmorillonite as a novel solid-phase extraction sorbent with chlorophenols as model compounds

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ABSTRACT

A porous polysulfone microcapsule containing organic modified montmorillonite and magnetic nanoparticles (OMMT-Fe_3O_4@PSF) has been successfully prepared by a phase-inversion method and evaluated as a magnetic solid-phase extraction (MSPE) sorbent for clean-up and enrichment of 4-chlorophenol (4-CP) and 2-chlorophenol (2-CP) in aqueous samples. Compared with a microcapsule containing the conventional extraction sorbent C18 (C18-Fe_3O_4@PSF), OMMT-Fe_3O_4@PSF had much lower cost, a faster adsorption rate, and superior uptake amounts for the investigated analytes. The proposed microcapsule has been developed for the extraction of 4-CP and 2-CP from environmental water samples and their analysis by high-performance liquid chromatography with UV detection (HPLC-UV). Various parameters, such as pH, extraction time, the mass of sorbent, and the desorption conditions, have been evaluated and the calibration curves of the chlorophenols were linear ($R^2 \geq 0.9985$) in the range from 1.01 to 104.5 ng mL^{-1}. The limits of detection at a signal-to-noise (S/N) ratio of 3 were 0.22 and 0.17 ng mL^{-1} and the limits of quantification calculated at S/N = 10 were 1.52 and 1.07 ng mL^{-1} for 2-CP and 4-CP, respectively. The recoveries of 2-CP and 4-CP from natural water and the treated wastewater samples were in the range of 84.4–115% with relative standard deviations (RSDs) lower than 7.0%. The results have demonstrated the suitability of the MSPE approach for the analysis of trace chlorophenols in aqueous samples.

1. Introduction

Environmental pollutants pose great threat to human health or animals even if present in the environment at very low level. Especially the pollution of water resource has become a growing environmental problem. Chlorophenols are important pollutants in water owing to the use of some bactericides, herbicides, antiseptics, dyes, and wood preservatives [1–3].

To determine trace CPs in aquatic environments by instrumental analysis, a pre-concentration technique is usually required. Some sample pre-treatment methods, including solvent extraction [4,5], membrane extraction [6–8], steam distillation extraction (SDE) [9,10], solid-phase extraction (SPE) [11–13], solid-phase microextraction (SPME) [14–19], stir bar sorptive extraction (SBSE) [20], and liquid-phase microextraction (LPME) [21–23], have been developed for the pre-concentration of trace CPs in natural water samples. Nowadays, SPE is a well-established technique and has been applied for the pre-concentration and cleaning-up of numerous different classes of compounds in a variety of matrices [24–28] by virtue of its high enrichment factor, high recovery, rapid phase separation, low consumption of organic solvents, and compatibility with different detection techniques [29,30]. It is commonly acknowledged that the sorbent plays a very important role in the SPE technique, which is related to the analytical sensitivity, precision, and selectivity. Recently, various types of solid-phase sorbent have been developed. Besides the commercial SPE sorbents C18 [31,32] and C8 [33], other custom-made sorbents, including polystyrene–divinylbenzene-based polymer [34], molecularly imprinted SPE sorbent [12], pyrrole-based polymer [35], and various forms of carbon [13,36–38], have been employed for different analysis purposes. Among them, C18 or C8 sorbent can easily concentrate apolar compounds, but they have low breakthrough volume for the most polar compounds. In addition, silica-based materials are associated with some problems such as pH instability or inconsistent results, which are due to the presence of free silanol groups, the amount of which cannot be controlled or reproduced in the synthesis process [39]. In our previous work [40], a porous polysulfone (PSF) microcapsule containing both tributyl phosphate

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(TBP) as sorbent and Fe_3O_4 as magnetic separation nanoparticles was successfully prepared. The results demonstrated that the proposed microcapsule could be used as an ideal sorbent for the rapid removal of phenols from aqueous solution. However, it could not be used as an SPE sorbent due to the solubility of TBP in some organic solvents. Herein, we propose another solid powder sorbent wrapped within polysulfone for use as an SPE sorbent with potential application in the removal or trace analysis of CPs in environmental water samples.

Montmorillonite (OMMT), a class of natural clay that possesses a large surface area and high cation-exchange capacity, has been demonstrated to serve as an effective sorbent for phenols [41–44]. However, there are some drawbacks associated with OMMT as a stationary phase in traditional SPE, such as a tedious column-packing procedure, high back-pressure, and a low flow rate. On the other hand, because of the small diameter of OMMT particles, it would be hard to remove or separate this sorbent from samples. To address these deficiencies, OMMT powder and magnetic nanoparticles have been wrapped within polysulfone (PSF) to form magnetic OMMT-PSF microcapsules. As an SPE sorbent, these microcapsules should easily achieve extraction and magnetic separation.

In this work, a novel and simple magnetic OMMT-PSF (OMMT-Fe_3O_4@PSF) microcapsule has been prepared and evaluated as a magnetic solid-phase extraction (MSPE) sorbent for clean-up and enrichment of 4-CP and 2-CP. The determination of 4-CP and 2-CP in water samples has been achieved by HPLC-UV. Compared with C18-Fe_3O_4@PSF microcapsule, the proposed microcapsule provides a rapid, sensitive, and reliable method for analysis of trace amounts of 4-CP and 2-CP in water samples.

2. Experimental

2.1. Materials

Polysulfone (PSF) with intrinsic viscosity of 0.56 was purchased from Dalian Polysulfone plastic Co. (Dalian, China). Ferrous chloride ($FeCl_2{\cdot}4H_2O$) and ferric chloride ($FeCl_3{\cdot}6H_2O$) were obtained from Tianjin Chemical Regent Co. (Tianjin, China). N, N-Dimethylformamide (DMF) and methanol were purchased from Tianjin Guangfu Chemical Regent Co. (Tianjin, China). 2-CP, 4-CP, and Sodium dodecyl sulfate (SDS) were obtained from Shanghai Chemical Regent Co. (Shanghai, China). Montmorillonite with a cation exchange capacity (CEC) of 110 mol kg^{-1} was obtained from Zhejiang Fenghong Clay Chemical Regent Co. (Huzhou, China).

Acetonitrile (ACN) and methanol of HPLC grade were purchased from Dima Technology (Richmond Hill, VA, USA). Purified water by a Milli-Q (Millipore, Billerica, MA, USA) system was used throughout the experiments. Stock solutions of 4-CP and 2-CP (1.0 mg mL^{-1}) in methanol were stored at 4 °C and diluted with ultrapure water to give the required concentration.

2.2. Instrumentation

The chromatographic system consisted of Varian 210 high performance liquid chromatographic pump (CA, USA), 325 UV–vis detector and Varian Star Chromatographic workstation.

Chromatographic conditions included C 18 column (5 μm, 4.6 mm × 250 mm, Dima Technology) and gradient elution (A: 1% (v/v) acetic acid and 0.5 g L^{-1} of KCl aqueous solution, B: ACN; 0 min $A = 75\%$, $B = 25\%$; 25 min $A = 50\%$, $B = 50\%$; 30 min $A = 0\%$, $B = 100\%$; 32 min stop) with a flow-rate of 1.0 mL min^{-1} and detection wavelength was 280 nm. Both mobile phase and analysis solutions were filtered through a 0.22-μm nylon membrane filter. The target compounds were identified by the relative retention time and diode array detection.

2.3. Procedures

2.3.1. Preparation of the OMMT-Fe_3O_4@PSF microcapsule sorbent

Magnetic microspheres were prepared by the co-precipitation method [45], and were used to prepare OMMT-Fe_3O_4@PSF microcapsules by the phase-inversion precipitation technique [41]. The microcapsule synthesis process was as follows: PSF (1.2 g) was dissolved in DMF (16 mL) to obtain the PSF solution. OMMT (or C18) (1.2 g) and Fe_3O_4 magnetic nanoparticles (0.1 g) were dispersed in DMF (4 mL) by ultrasonication, and then this suspension was added to the above PSF solution and the mixture was stirred for 2 h at room temperature. In this way, a dispersed phase of OMMT (or C18), Fe_3O_4 magnetic nanoparticles, and PSF was obtained. At the same time, another continuous phase composed of SDS solution (0.5 wt.% Sodium dodecyl sulfate in aqueous solution) and ethanol (1:1, v/v) was prepared. The dispersed phase was then injected into the continuous phase using a 0.45 mm diameter syringe needle to obtain the OMMT (or C18)-Fe_3O_4@PSF microcapsules. The magnetic microcapsules were separated from the resulting solution by a magnet, rinsed several times with deionized water, and kept in deionized water for the extraction process overnight. Finally, the microcapsules were air-dried at room temperature. The preparation procedure of the OMMT-Fe_3O_4@PSF microcapsules was shown in Fig. 1.

The obtained products were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Hitachi, Japan) and Fourier-transform infrared spectrometry (FT-IR, Nicolet Nexus 670, USA). Magnetic properties were measured using a vibrating sample magnetometer (VSM, Lakeshore 7304, USA).

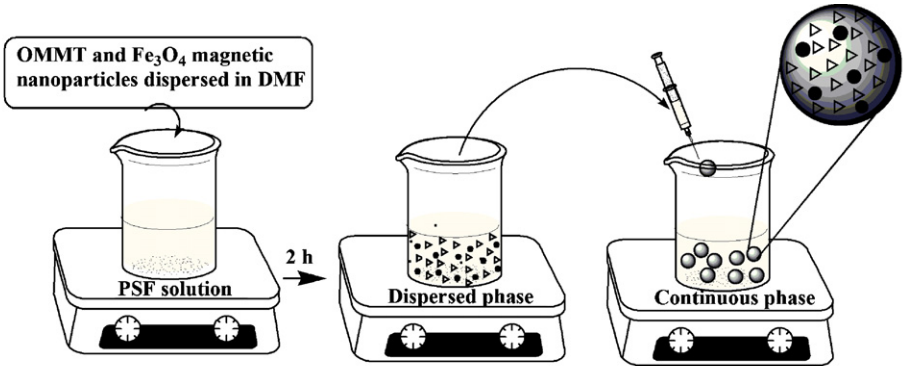

Fig. 1. Preparation protocol of OMMT-Fe_3O_4@PSF microcapsules. ●, Fe_3O_4; □,-OMMT.

2.3.2. *Magnetic solid-phase extraction*

Adsorption experiments were carried out by adding OMMT-Fe_3O_4@PSF (or C18-Fe_3O_4-@PSF) microcapsules (25 mg) to 25 mL flasks containing 1.0 mg mL^{-1} of 4-CP or 2-CP solution (10 mL). The microcapsules and CP solution were shaken in an SHA-C constant-temperature shaker (Guohua Co., Jiangsu) at 20 °C. After adsorption, the microcapsules were isolated by an external magnetic field, and the supernatants were determined by UV/Vis spectrophotometry at 280 nm (TU-1800, Beijing, China). The amounts of 4-CP and 2-CP adsorbed were calculated from the absorbances measured before and after adsorption. In addition, the effects of pH (2.0–12.0), extraction time (5–160 min), and initial CPs concentration (∼100–1100 mg L^{-1}) on adsorption amounts were evaluated.

2.3.3. *MSPE procedure of 4-CP and 2-CP in real water samples*

A river water sample was collected from the Yellow River (Lanzhou, China). The treated wastewater samples were obtained from rubber plant and oil refinery. The MSPE procedure was carried out by adding OMMT-Fe_3O_4@PSF microcapsules (80 mg) to 150 mL of the above filtered water sample. The mixture was shaken in a constant-temperature shaker at 20 °C for 30 min. After extraction, the magnetic microcapsules were isolated from the suspension with a magnet (Nd–Fe–B, 60 mm × 60 mm × 30 mm). Subsequently, the concentrated target analytes were eluted from the isolated particles with ACN (3.0 mL). The solvent was removed from the eluent with a stream of nitrogen at 40 °C and the residue was redissolved in ACN (0.1 mL). An aliquot (20 μL) of the filtered eluent was then injected into the HPLC system for analysis.

3. Results and discussion

3.1. *Characterization of OMMT-Fe_3O_4@PSF microcapsule*

Typical SEM images of the general view and outer surface of the microcapsule are shown in Fig. 2. It can be seen from Fig. 2a that the microcapsules had good and regular shape. Fig. 2b show that uniform meshes could be observed on the surface of the microcapsules, which reduced mass-transfer resistance and allowed compounds to readily access the microcapsule.

In order to examine the magnetic properties of the OMMT–Fe_3O_4@PSF, VSM analysis was employed. The magnetization curve from VSM analysis is shown in Fig. 3. The curve has a typical shape, being symmetrical about the origin. This feature is characteristic of the superparamagnetic property, showing that the materials responded magnetically to an external magnetic field and that this response vanished upon removal of the field (at the origin). The key parameter to note is the saturation magnetization (S), which is a measure of the maximum magnetic strength of a material. The saturation magnetization of the microcapsule could be calculated as 1.5 emu g^{-1} from the experimental data. Fig. 4 displays the magnetism of the microcapsules, in that they were attracted by a conventional magnet.

To ascertain the presence of OMMT in the microcapsules, the infrared spectra of OMMT, Fe_3O_4–PSF microcapsules, and OMMT–Fe_3O_4@PSF microcapsules were recorded and are shown in Fig. 5a–c, respectively. As can be seen in Fig. 5a, the features at 3624.65, 519.49, and 466.34 cm^{-1} are the characteristic peaks of OMMT. The spectrum in Fig. 5b exhibits two characteristic peaks at 1322.54 and 1103.64 cm^{-1} attributable to the antisymmetric and symmetric stretching vibrations of O=S=O of the PSF. Exhilaratingly, all of these features could be discerned in the spectrum in Fig. 5c, which indicated that OMMT had been successfully encapsulated in the microcapsules.

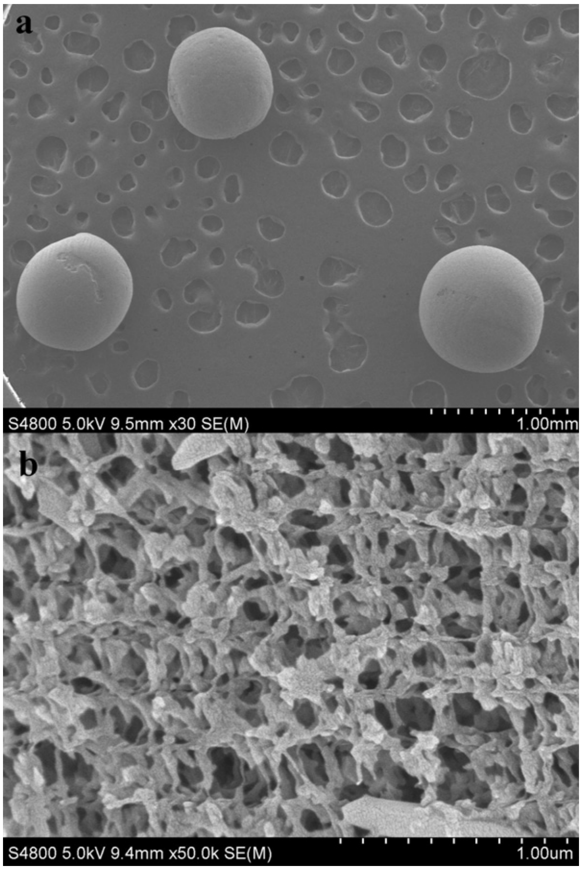

Fig. 2. General view of OMMT-Fe_3O_4@PSF microcapsules (a), outer surface of OMMT-Fe_3O_4@PSF microcapsules (b).

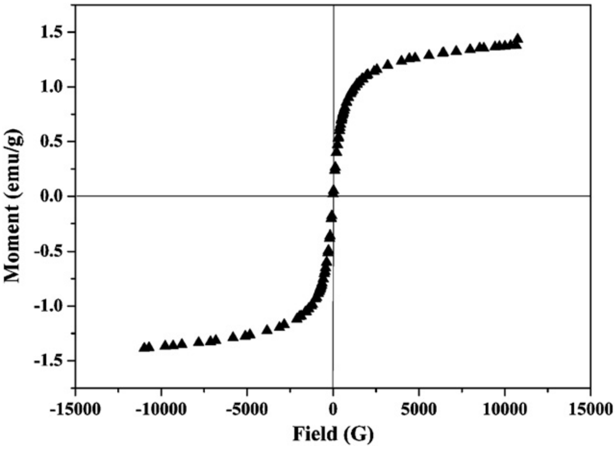

Fig. 3. VSM magnetization curve of OMMT-Fe_3O_4@PSF microcapsules.

3.2. *Optimization of the operating conditions*

3.2.1. *Effect of solution pH*

In general, adsorption capacity strongly depends on solution pH. It can be seen from Fig. 6 that the amounts of the investigated CPs adsorbed onto the two kinds of microcapsules drastically decreased when the pH was higher than 8.0. This might be attributed to formation of the negative anionic forms of the CPs ($pK_a \approx 9.41$ for 4-CP and 8.56 for 2-CP) by deprotonation in alkaline solution. However, for the investigated microcapsules, C18-Fe_3O_4@PSF relied on hydrophobic interaction for adsorption of the target compounds

Fig. 4. Photograph of OMMT-Fe_3O_4@PSF microcapsules attracted by a conventional magnet.

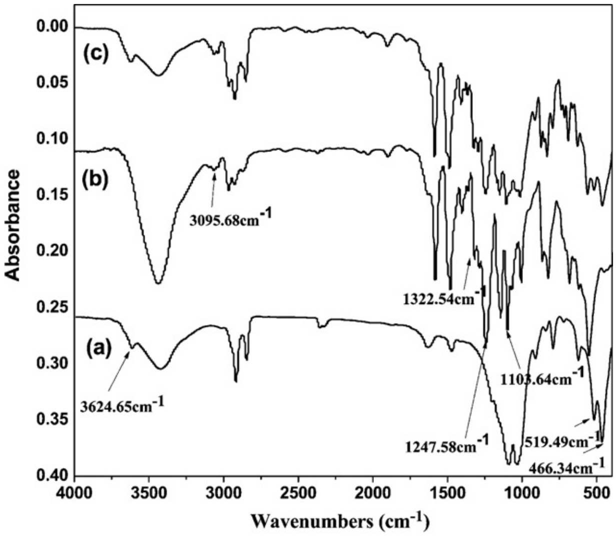

Fig. 5. Infrared spectra of (a) OMMT; (b) Fe_3O_4-PSF microcapsules; (c) OMMT-Fe_3O_4@PSF microcapsules.

and OMMT-Fe_3O_4@PSF showed cation-exchange properties. So, pH 6.0 was selected for further investigations.

3.2.2. Effect of adsorption time and initial concentration of CPs

Fig. 7 shows the effect of adsorption time on the adsorption of CPs at different initial concentrations. It can be seen that the amounts of CPs adsorbed on the two investigated microcapsules increased with increasing extraction time and initial CP concentration. It is also apparent from Fig. 7 that, as SPE sorbents, both the adsorption amount and the adsorption rate of OMMT-Fe_3O_4@PSF microcapsule were superior to those of C18-Fe_3O_4@PSF microcapsule. So, the OMMT-Fe_3O_4@PSF microcapsule was further investigated as an SPE sorbent for the enrichment and determination of 4-CP and 2-CP in water samples.

3.2.3. Effect of sorbent mass

In the extraction procedure, the OMMT-Fe_3O_4@PSF microcapsules were dispersed in a water sample to extract the analytes. Amounts of OMMT-Fe_3O_4@PSF microcapsules ranging from 20 to 150 mg were evaluated for 150 mL water samples containing 10 μg mL^{-1} 4-CP and 2-CP. It was found that 80 mg of microcapsules was sufficient for the extraction of the 2-CP and 4-CP (Fig. 8). Therefore, further experiments were performed with 80 mg portions of sorbent.

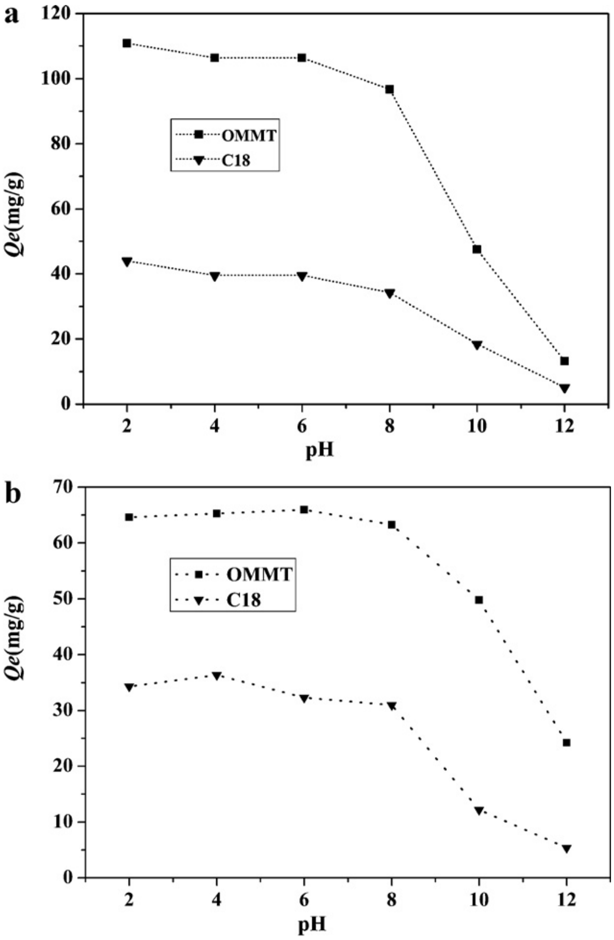

Fig. 6. Effect of pH on CPs uptake from aqueous solutions (initial CPs concentration, 550 mg L^{-1}; extraction time, 3 h, 20 °C): (a) 4-CP; (b) 2-CP. Qe is the maximum adsorption capacity (mg/g) under the experimental conditions.

3.2.4. Optimization of desorption time

The effect of desorption time was studied over the range of 1–15 min. Fig. 9 indicates that 5 min was sufficient for the most effective extraction. Therefore, a desorption time of 5 min was selected for further studies.

3.3. Method validation and application to real samples

An analysis method based on MSPE coupled with HPLC-UV was investigated. As described in Section 2.3.3, analytical parameters including the linear range, the correlation coefficient, the limit of detection (LOD), and the limit of quantification (LOQ) were studied by extracting 4-CP and 2-CP from artificial water samples, and these parameters are listed in Table 1. As shown in Table 1, the proposed MSPE method showed 58 and 251 fold higher enrichment ratio than the direct injection (20 μL injection) of 2-CP and 4-CP, respectively. Furthermore, the results of the proposed method were compared with data obtained by other SPE sorbents [11–13], and other sample pretreatment processes such as SPME [15–19], SBSE [20], and LPME [21–23]. It can be seen that the proposed method showed lower LODs than SPE processes with polystyrene–divinylbenzene [11] and molecularly imprinted polymer [12] as sorbents. Compared with other methods, the LODs of the proposed method were also lower than those of SPME–LC–UV using PA fiber [15], molecularly imprinted polymer coating [19],

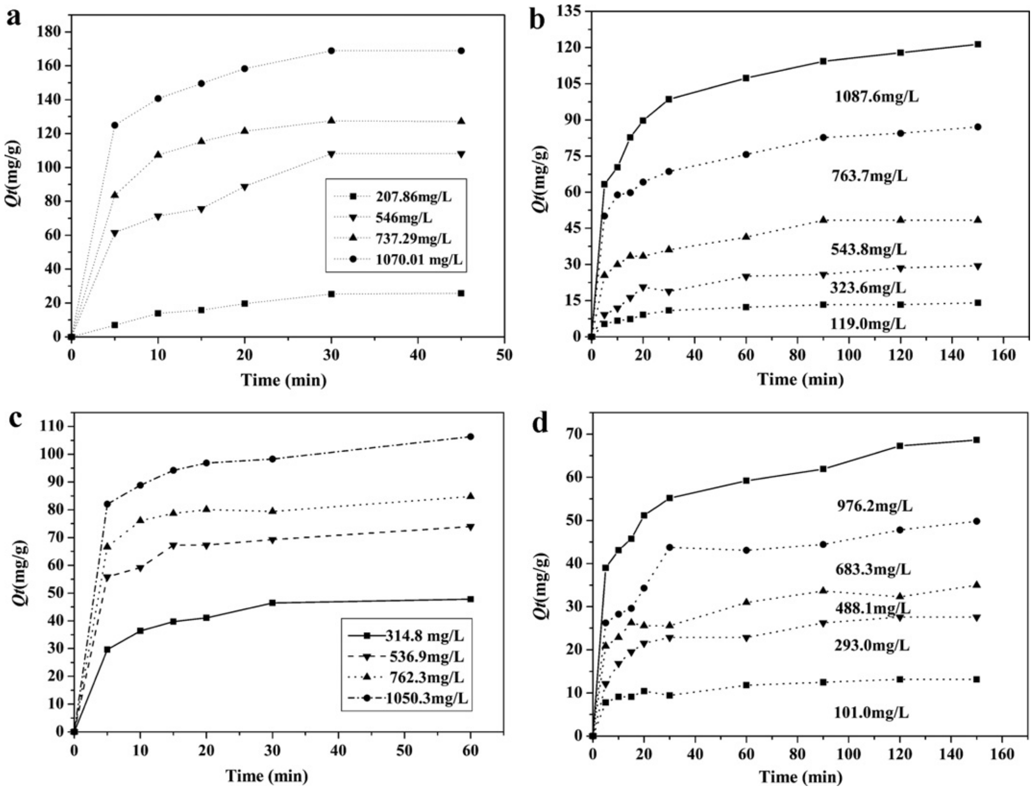

Fig. 7. Effect of extraction time and initial CPs concentration on CPs uptake from aqueous solutions (20 °C, pH 6.0): (a) the adsorption of 4-CP by OMMT-Fe_3O_4@PSF microcapsules; (b) the adsorption of 4-CP by C18-Fe_3O_4@PSF microcapsules; (c) the adsorption of 2-CP by OMMT-Fe_3O_4@PSF microcapsules; (d) the adsorption of 2-CP by C18-Fe_3O_4@PSF microcapsules. Qt is the quantity of CPs (mg/g) adsorbed on the microcapsules after various times.

SPME–GC using an electropolymerized aniline-based fiber coating [16], SBSE [20], LPME [21,22], and gas chromatography–mass spectrometry (GC–MS) [18] methods. However, lower LODs were obtained by applying sensitive electrochemical detection (ED) [15], a derivatization process [17], SPE combined with headspace single-drop microextraction [11], SPE process with grapheme sorbent [13] and a liquid–liquid microextraction method [23].

The developed method was applied to determine 4-CP and 2-CP in real environmental water samples, and the experimental results were shown in Table 2. It can be seen from Table 2, 4-CP was found in the treated wastewater from rubber plant and oil refinery, 2-CP was found in the treated wastewater from oil refinery but cannot be quantified. However, the concentration of CPs in all water samples studied is lower than legislation limits of National Recommended Water Quality Criteria (4304T) of the United States Environmental Protection Agency (EPA) in 2006. In addition, recovery tests were carried out with standard CPs mixture-spiked water samples, and the results were also listed in Table 2. The recoveries of 2-CP and 4-CP from real samples were in the range 84.4–115% (the results of spiked with analytes at other concentration level were not shown in Table 2), with relative standard deviations (RSDs) lower than 7%, which indicated that the developed method was reliable for the determination of 2-CP and 4-CP in environmental water samples. The chromatograms of the wastewater and its spiked standard solution are shown in Fig. 10.

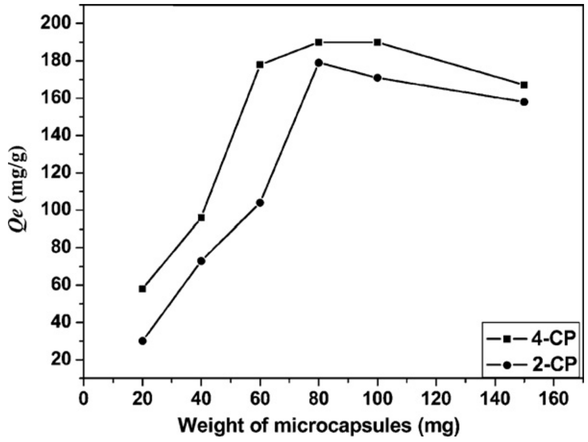

Fig. 8. Effect of microcapsules mass on the extraction efficiency. Experiments were carried out with 150 mL of an artificial water sample spiked with 10 $\mu g\,mL^{-1}$ 2-CP and 4-CP (pH of 6.0, extraction time for 30 min; extraction temperature, 20 °C).

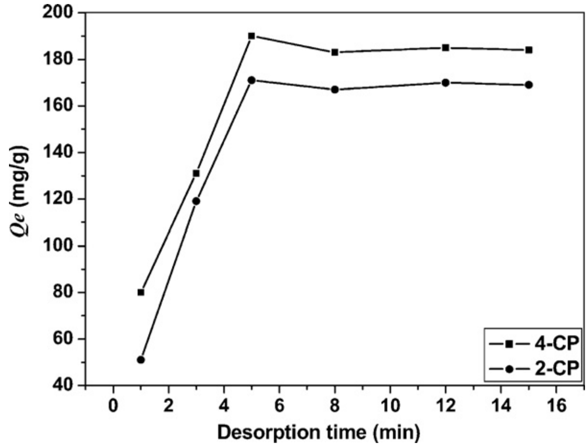

Fig. 9. Effects of desorption time on the extraction efficiency. Experimental conditions were the same as in Fig. 8.

Table 1
Analytical parameters of the proposed method for determination of 2-CP and 4-CP in water samples.

Compounds	Linear range ($ng\,mL^{-1}$)	Correlation coefficient	Enrichment ratio	LODs[a] ($ng\,mL^{-1}$)	LOQs[b] ($ng\,mL^{-1}$)	LODs ($ng\,mL^{-1}$) [11]	LODs ($ng\,mL^{-1}$) [12]	LODs ($ng\,mL^{-1}$) [13]	LODs ($ng\,mL^{-1}$) [15]	LODs ($ng\,mL^{-1}$) [16]	LODs ($ng\,mL^{-1}$) [17]	LODs ($ng\,mL^{-1}$) [18]	LODs ($ng\,mL^{-1}$) [19]	LODs ($ng\,mL^{-1}$) [20]	LODs ($ng\,mL^{-1}$) [21]	LODs ($ng\,mL^{-1}$) [22]	LODs ($ng\,mL^{-1}$) [23]
2-CP	5.23–104.5	0.9990	58	0.22	1.52	1.6[c] 0.05[d]	1.08	0.1	–	58	0.031	0.27	4.5	–	–	–	
4-CP	1.01–101.2	0.9985	251	0.17	1.07	–	–	0.2	0.39[e] 0.06[f]	2.4	–	4.1	–	0.98	6	0.5	0.068

[a] LOD based on the signal being three times as large as the baseline noise (S/N = 3).
[b] LOQ based on the signal being ten times as large as the baseline noise (S/N = 10).
[c] Headspace single-drop microextraction of methyl ethers using 1-butanol as extraction solvent.
[d] Solid-phase extraction combined with headspace single-drop microextraction.
[e] Data were obtained by UV detection.
[f] Data were obtained by electrochemical detection (ED).

Table 2
Results of determination and recoveries of real samples spiked with target anaytes.

Samples compounds	Spiked ($ng\,mL^{-1}$)	Detected ($ng\,mL^{-1}$)[c]	Recoveries (%)[f]
River water			
2-CP	0	Nd[d]	97.1 ± 5.2%
	1.73	1.68	
4-CP	0	Nd	105.1 ± 1.5%
	0.99	1.04	
Wastewater 1[a]			
2-CP	0	Nd	108.1 ± 5.8%
	1.73	1.87	
4-CP	0	3.50	90.9 ± 6.7%
	0.99	4.41	
Wastewater 2[b]			
2-CP	0	Nq[e]	115 ± 4.2%
	1.73	1.99	
4-CP	0	1.02	109.1 ± 3.2%
	0.99	2.10	

[a] The treated wastewater from rubber plant.
[b] The treated wastewater from oil refinery.
[c] Mean for three determinations.
[d] Not detected.
[e] Found but cannot be quantified.
[f] Mean and standard deviation for three determinations.

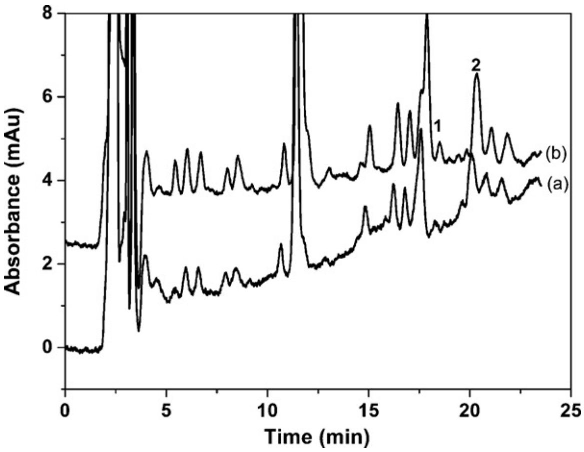

Fig. 10. Chromatograms of (a) the treated wastewater from oil refinery and (b) the treated wastewater spiked with 1.73 $ng\,mL^{-1}$ of 2-CP and 0.99 $ng\,mL^{-1}$ of 4-CP obtained by MSPE with OMMT-Fe_3O_4@PSF microcapsules. Peaks: (1) 2-CP; (2) 4-CP. MSPE conditions: extraction time, 30 min; extraction temperature, 20 °C; pH, 6.0; desorption time, 5 min; desorption solvent, acetonitrile; desorption temperature, 20 °C.

4. Conclusion

OMMT-Fe_3O_4@PSF and C18-Fe_3O_4@PSF microcapsules have been synthesized by a phase-inversion precipitation technique and applied for the enrichment of 4-CP and 2-CP in water samples. Comparative studies have shown that OMMT-Fe_3O_4@PSF had higher adsorption amounts and shorter adsorption equilibrium times than C18-Fe_3O_4@PSF for the investigated CPs. Subsequently, the OMMT-Fe_3O_4@PSF microcapsule was used as a magnetic SPE sorbent for analysis of 4-CP and 2-CP in water samples. The merits of the proposed microcapsule include its low cost, ease of synthesis, and applicability for rapid, sensitive, and reliable analysis. These characteristics suggest that OMMT-Fe_3O_4@PSF microcapsule as a sorbent has high potential for applications in the high-throughput removal of pollutants and the rapid analysis of trace pollutants in environmental aqueous samples.

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