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Preparation of a hollow porous molecularly imprinted polymer using tetrabromobisphenol A as a dummy template and its application as SPE sorbent for determination of bisphenol A in tap water

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ABSTRACT

In this paper, a highly selective sample cleanup procedure combing dummy molecular imprinting and solid-phase extraction (DMIP–SPE) was developed for the isolation and determination of bisphenol A (BPA) in tap water. The novel hollow porous dummy molecularly imprinted polymer (HPDMIP) was prepared adopting a sacrificial support approach, using tetrabromobisphenol A (TBBPA), whose structure was similar to that of BPA, as the dummy template and mesoporous MCM-48 nanospheres as the support. Owing to a very short distance between the binding sites and the surface, a large surface area and a good steric structure to match its imprint molecules, the maximum adsorption capacities (Q_{max}) of the dummy-imprinted and non-imprinted sorbents for BPA were as high as 445 and 340 μmol g^{-1}, respectively, and the adsorption reached about 73% of Q_{max} in 10 min. Meanwhile, a method was developed for the determination of BPA using HPDMIP as a solid-phase extraction enrichment sorbent coupled with HPLC. Under the optimum experimental conditions, HPDMIP exhibited satisfactory results in the enrichment and determination of BPA in tap water with a recovery rate of 95–105%, and relative standard deviations of below 6%, and it can achieve a limit of detection as low as 3 ng mL^{-1}. The developed extraction protocol eliminated the effect of template leakage on quantitative analysis and could be applied for the determination of BPA in complicated functional samples.

1. Introduction

Phenolic compounds are environmental pollutants and their sources can be as different as industrial effluents, reaction products, degradation of some pesticides, etc. BPA, as one of the typical phenolic estrogens, has been used in industries worldwide for the production of polycarbonate plastics and epoxy resins ranging from plastic bottles to inner coating of food packages to even feeding-bottles [1]. Hence, it is often found in environmental samples. Many researchers have found that BPA shows oestrogenic activity in in vitro experiments, sometimes, even though BPA concentration is as low as 1 ng L^{-1}, it can affect endocrine systems and cause adverse effects such as endocrine dyscrasia, precocity and even cancer [2,3]. Furthermore, it is expected to be more persistent in water and soil than in air [4]. Therefore, there has been a rising international concern over the monitoring of BPA released into our environment especially by trace amount in water samples.

Different analytical methods have been developed for the determination of BPA at the ng L^{-1} and μg L^{-1} concentration levels in various samples. Most of the methods are based on high-performance liquid chromatography (HPLC) or gas-chromatography (GC) techniques, and usually require a preliminary liquid–liquid or solid-phase extraction (SPE) step [5]. To achieve high selectivity and good recovery of pre-concentrating BPA by SPE, multifarious materials such as C18, surfactant-modified zeolite, microporous bamboo charcoal, and imprinted molecular polymers (MIPs), have been adopted as sorbents [6–9]. The traditional sorbents are to some extent limited in their applications in SPE owing to their inefficient selectivity, which can be improved by the use of MIPs. Although a variety of MIPs have so far been synthesised and used as affinity chromatography supports by different methods such as suspension polymerization, emulsion polymerisation and surface imprinting technology, the use of MIPs still faces challenges such as template leakage, low binding capacity and slow mass transfer [10–17]. To address the existing problems, new strategies such as dummy molecularly imprinted polymers, porous molecular imprinting and hollow molecular imprinting have been developed [18–21]. The MIPs mentioned above possess a high density of effective recognition

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sites because of their specific structures, narrow hole size and a large specific surface area, which contribute to their high adsorption capacity and fast kinetics to uptake target molecules. Meanwhile, some MIPs have been able to eliminate the undesired template leakage using analogues of the target molecule as the template [22–27].

In this paper, the new hollow porous dummy molecularly imprinted polymer(HPDMIP) was synthesized by using tetrabromobisphenol A (TBBPA), whose structure was similar to that of BPA, as the dummy template and mesoporous MCM-48 nanospheres as the support. The TBBPA-imprinted polymer was evaluated and applied as an sorbents for SPE combined with HPLC to detect BPA. The selectivity of the imprinted sorbent and cross-sensitivity affecting the preconcentration and separation of analytes were discussed in detail to build a simple and sensitive method as a potential analytical strategy to monitor BPA in the environment samples.

2. Experimental

2.1. Material and Reagents

Tetrabromobisphenol A (TBBPA,USA Sigma-Aldrich), Bisphenol A (BPA, purity > 95%), phenol, 4,4′-Dihydroxybiphenyl (BIP, purity > 99%) and p-tert-butylphenol (PTBP, purity > 99%) were purchased from Aladdin Reagent (Shanghai, China) Co, Ltd. 4-Vinylpyridine (4-VP, Alfa Aesar, 96%) and ethylene glycol dimethacrylate (EGDMA, Alfa Aesar, 98%) were purified by distillation under vacuum. Azobisisobutyronitrile (AIBN, chemical grade) was purchased from Shanghai no. 4 Reagent & H.V. Chemical Company (Shanghai, China), which was recrystallized with ethanol and then dried at room temperature in a vacuum condition prior to be used. HPLC grade methanol was purchased from Tedia (Fairfield OH, USA). Cetyltrimethylammonium bromide (CTAB, 99.8 wt %), tetraethyl orthosilicate (TEOS), ammonium hydroxide (28 wt % NH_3 in water), HF solution (40%), toluene and ethanol were purchased from Shanghai Chemical Reagent Co, Ltd. (China) and were used without any further purification. Doubly distilled water was used in all experiments.

2.2. Equipments and conditions

Infrared spectras of the polymer were collected using a Tensor-27 Fourier transform infrared FT-IR spectrometer (Bruker, Germany) with the resolution of 2 cm^{-1} and the spectral range of 4000–400 cm^{-1}. The micrographs of the sorbents were obtained by a SIRION200 scanning electron microscopy (FEI, Holland) and a JEM-2011 transmission electron microscope (JEOL, Japan) with measurements operating at 5 KV and 200 KV, respectively. Nitrogen sorption isotherms were measured at 77 K with a Micromertics ASAP 3020 analyzer (Micromertics, USA), before measurements, the samples were degassed in a vacuum at 200 °C for at least 15 h. The Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) model were utilized to calculate the specific surface areas (BET). Thermo-gravimetric analysis of the samples were monitored using SDT Q600 thermal analyzer (TA, USA) from room temperature to 600 °C under air with a heating rate of 10 °C min^{-1}.

Chromatographic separation and detection of BPA was performed by a chromatographic system (Shimadzu, Japan) consisting of LC-15C pump, SIL-10AF injector with 50 μL loop and a SPD-15C dual wavelength absorbance detector. All separations were achieved on an analytical GL Sciences C18 column (5 μm, 150 mm × 4.6 mm) with a mobile flow rate of 1.0 mL min^{-1} at room temperature. The injection volume of sample was 10 μL. The photodiode array detector was operated between 210 and 400 nm. The Empower software was used to acquire and process the spectral and chromatographic data.

2.3. Procedures for the preparation of the hollow porous dummy template-imprinted polymer nanospheres

The MCM-48 spheres were prepared according to the literature method with some modifications [28]. A 2.6 g aliquot of CTAB was dissolved in 120 mL of doubly distilled water, and then 80 mL of ethanol and 4 mL of TEOS were added to the surfactant solution. The solution was stirred for 30 min at room temperature (600 r min^{-1}), and 12 mL of aqueous ammonia (28 wt%) was added to it. After stirring the mixture for 6 h, a solid was formed, which was filtered, washed with distilled water and ethanol, and dried at 60 °C for 12 h. The CTAB was removed by calcination at 823 K (2 °C min^{-1}) for 6 h.

Next, 0.140 g of tetra-bromobisphenol A (TBBPA) and 0.093 g of 4-VP were dissolved in 10 mL of toluene at room temperature and the solution was ultrasonicated for 5 min; 0.639 g of EGDMA and 80 mg AIBN were added to this solution and it was purged with N_2, sealed and stirred for 1 h at 40 °C. Subsequently, 0.8 g of MCM-48 spheres were added to the solution, and it was ultrasonicated, purged with N_2, sealed and stirred for 6 h at 40 °C, and then heated and maintained at 65 °C for 16 h and at 80 °C for 6 h. Then the materials were washed with ethanol and immersed in 10% HF ethanol solutions for 6 h to remove the silica matrix and the imprint molecule TBBPA. After recovering the resulting solid by filtration and washing it with ethanol, the final products obtained were HPDMIP. For comparison, the corresponding non-imprinted polymer (HPNIP) was also prepared in the same way in the absence of a dummy template.

2.4. Measurement of recognition properties of HPDMIP

To measure the adsorption capacity of the materials, 10 mg of dummy imprinted or non-imprinted sorbents were equilibrated with 10 mL of various concentrations of BPA dissolved in toluene. The mixtures were mechanically shaken overnight at room temperature. After the solution was filtered, concentrations of BPA in the vials were determined by HPLC at 228 nm. Binding kinetics can be obtained by monitoring the temporal residual BPA concentration in the solution formed by adding 10 mg of HPDMIP to 10 mL of toluene solution containing 0.5 mmol L^{-1} BPA at certain time intervals.

In order to explore the selectivity of HPDMIP towards BPA, a series of experiments were performed on HPDMIP and HPNIP, using 250 ml L^{-1} solution of BPA and its analogues BIP and PTBP.

2.5. Evaluation of HPDMIP used as the stationary phase of SPE

2.5.1. Cross-sensitivity between BPA and its Analogues

To determine the cross-sensitivity among BPA, BIP and PTBP, the HPDMIP sorbent (100 mg each) was placed into two empty SPE cartridges. After they were pre-treated with 10 mL of methanol and 10 mL of pure water, four solutions were prepared with different ratios of BPA/analogues. Then 10 mL of each of the mixture solutions was loaded onto the HPDMIP-SPE column and the column was eluted with 2 mL methanol–acetic acid–water (95:2.5:2.5, v/v/v) solution. The elution, after being filtered through a 0.45 μm nylon membrane, was analysed by HPLC with UV detection at 276 nm. at a speed of 0.5 mL min^{-1}.

2.5.2. Regeneration for reuse

Following a procedure similar to that described in Section 2.5.1, the HPDMIP-SPE was incubated with 10 mL of BPA solution

(BPA concentration 2.0 μg mL^{-1}). Afterwards, the HPDMIP-SPE was regenerated by washing four times with 5 mL of acetic acid/methanol (1:9, v/v), three times with 5 mL of methanol and three times with water. In accordance with the steps mentioned above, the HPDMIP-SPE column can be reused for at least six times.

2.5.3. *Application on water samples*

The calibration curve was established by analysing the elution of BPA standard solutions after carrying out the HPDMIP-SPE procedures using six different concentrations (5 ng mL^{-1}–100 μg mL^{-1}). The limit of detection (LOD) was defined as three times the signal-to-noise ratio (*S*/*N*).

The tap water sample came from our laboratory. The water was further adjusted to about pH 7.0 by adding NaOH (1 M), filtered through 0.45 μm nylon membranes in order to remove the suspended solids, and then stored under dark conditions at 4 °C.

An HPDMIP-SPE column was prepared for the determination of BPA following the procedure described in Section 2.5.1. If the samples were verified to be free of BPA, then they were spiked with BPA at three concentration levels—20.0, 2.0 and 0.1 μg mL^{-1}. Ten millilitres of each of these BPA solutions was introduced into the HPDMIP-SPE columns at a flow rate of 0.5 mL min^{-1}.

3. Results and discussion

3.1. *Preparation and characterisation of HPDMIP sorbent*

For the purpose of improving the selectivity and efficacy of the imprinted molecular material used for recognising BPA, a hollow porous dummy template MIP with a larger specific surface area and a higher speed of mass transfer was prepared using MCM-48 as the support and TBBPA as the virtual template. A schematic illustration of the routes for the preparation of these polymers is shown in Fig. 1. First, the molecularly imprinted precursor mixture was perfused into the inside of MCM-48 spheres by ultrasonic impregnation and was polymerised on their internal surfaces to form MCM-48–MIP composites. Finally, HPDMIP was obtained by removing SiO_2 and imprinted molecules with an ethanol solution containing HF. The aim of using TBBPA as the dummy template was to eliminate template leakage in trace-level determination of BPA, as the structural skeleton of TBBPA is similar to that of BPA (see Fig. 2), containing two hydroxy groups that can form strong hydrogen bonds with the amino group of the functional monomer of 4-vinylpyridine. It can be seen from Fig. 1 that TBBPA binds with two molecules of 4-vinylpyridine, which will lead to the formation of specific binding sites in the polymers.

The Fourier transform infra-red (FT-IR) diffuse reflectance spectra of MCM-48 and imprinted polymer are shown in Fig. 3. The observed features around 1091 indicated Si–O–Si and Si–O–H stretching vibrations, respectively. The bands around 800 and 465 cm^{-1} resulted from Si–O vibrations. [29]. Disappearance of the observed features around ~1091 cm^{-1} and formation of weak bands at 800 and 465 cm^{-1} indicated that MCM-48 had been removed. Simultaneously, existence of the bands of HPDMIP at ~1728 cm^{-1} and weak bands at ~1633 and 1160 cm^{-1} indicated that the molecularly imprinted polymer, which was prepared using 4-VP as the functional monomer and EGDMA as the cross-linking agent, had formed [30].

The scanning electron and transmission electron micrographics of both MCM-48 and HPDMIP are shown in Fig. 4. It should be noted that the prepared MCM-48 spheres had an average diameter of 525 nm; the silica nanospheres were uniform and smooth and had good dispersity (see Fig. 4a and b). Meanwhile, as can be seen from Fig. 4c and d, the imprint precursor permeated into the matrix of MCM-48, leading to the formation of a porous structure that was very helpful for fast adsorption and desorption of the template molecules.

Nitrogen adsorption was used to measure the porosity of the obtained HPDMIP at −196 °C. The average pore size was 2.7 nm corresponding to the wall thickness of MCM-48. This also indicated that the prepared HPDMIP copied the template structure of MCM-48 [28]. As estimated by the standard BET method, specific surface area of the inside and outside section of the obtained HPDMIP was 512 $m^2\,g^{-1}$. The thermo-gravimetric analysis (TGA) curves of the MCM-48 and HPDMIP are given in Fig. 5. Thermogravimetric analysis revealed an obvious weight loss for HPDMIP in the temperature range 300–400 °C, and 95% of its quality was lost at 600 °C; this finding also confirmed the removal of the matrix MCM-48.

3.2. *Adsorption characteristic of BPA-imprinted Sorbents for BPA*

The static adsorption capacities of the HPDMIP and HPNIP sorbents for BPA were determined using various concentrations

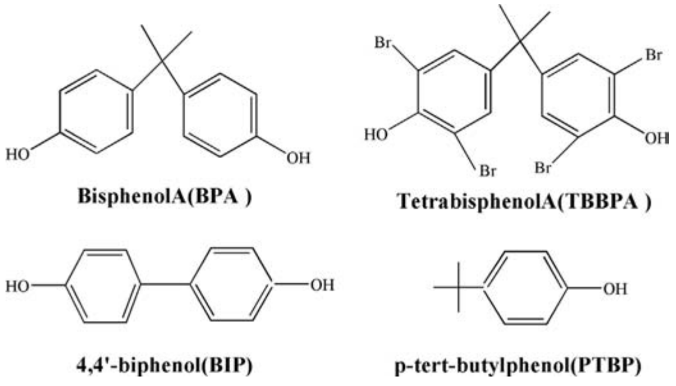

Fig. 2. The molecular structures of BPA, TBBPA, BIP and PTBP.

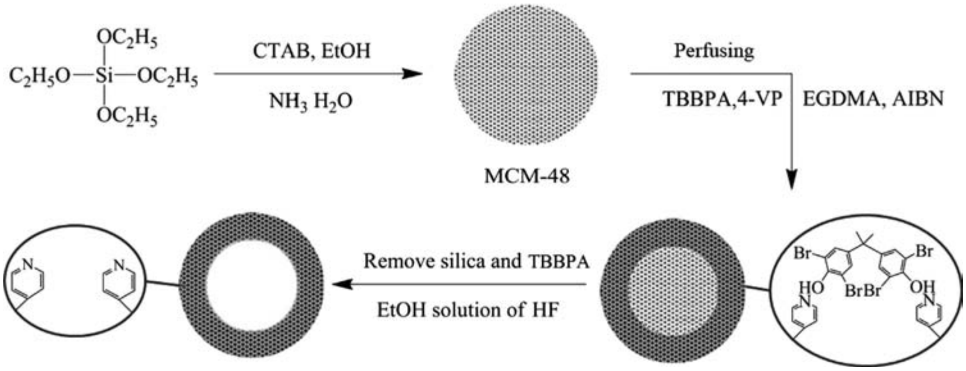

Fig. 1. Preparation protocol of the hollow porous dummy imprinted molecularly sorbent.

of BPA ranging from 0.1 to 3 mmol L^{-1} (see Fig. 6). It could be noted that the adsorption capacities of both HPDMIP and HPNIP increased with the increasing of the initial concentrations of BPA; the HPDMIP exhibits a higher capacity for BPA than the HPNIP. The weak adsorption of template on HPNIP is due to non-specific interaction with the polymer matrix. Meanwhile, the adsorption capacity of the HPDMIP-imprinted sorbent for BPA had been found to improve greatly compared with other ordinary sorbents [31,32]. Therefore, the BPA-imprinted sorbent would be more suitable for enriching trace BPA in water samples.

On the basis of the data of the static adsorption experiment, binding affinity of the imprinted polymer and its theoretical number of binding sites for the template could be estimated by Scatchard analysis; the Scatchard equation used in this analysis is as follows:

$$\frac{Q}{C_s} = \frac{Q_{\max} - Q}{K_d} \tag{1}$$

where Q (μmol g^{-1}) is the equilibrium adsorption capacity, C_s (μmol mL^{-1}) is the equilibrium concentration of BPA and $Q_{\max}$ is the apparent maximum number of binding sites. The association constant K_d and specific site capacity $Q_{\max}$ can be determined from the slope and y intercept of the lines obtained by least-squares regression of linear regions of the corresponding Scatchard plots if the Langmuir models can be applied.

As evident from Fig. 7a, the Scatchard plots of MIPs were non-linear. Two straight lines could be drawn, which indicated that the

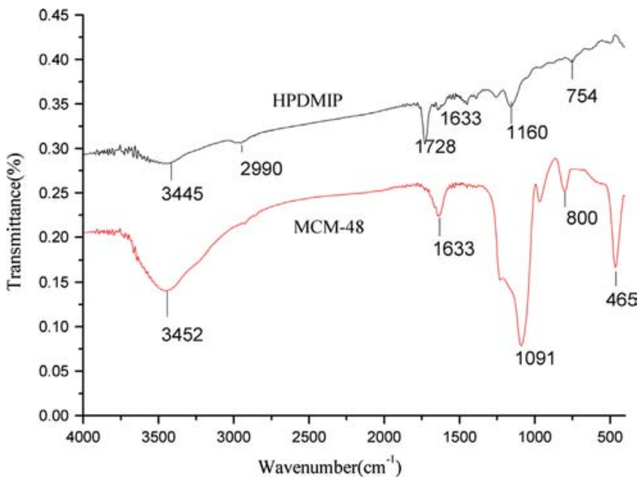

Fig. 3. FT-IR spectra of MCM-48 and HPDMIP spheres.

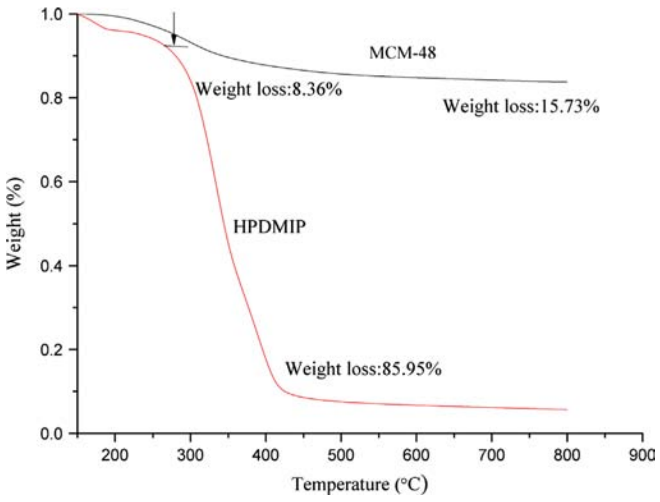

Fig. 5. Thermogravimetric (TG) curve of MCM-48 and HPDMIP recorded in air.

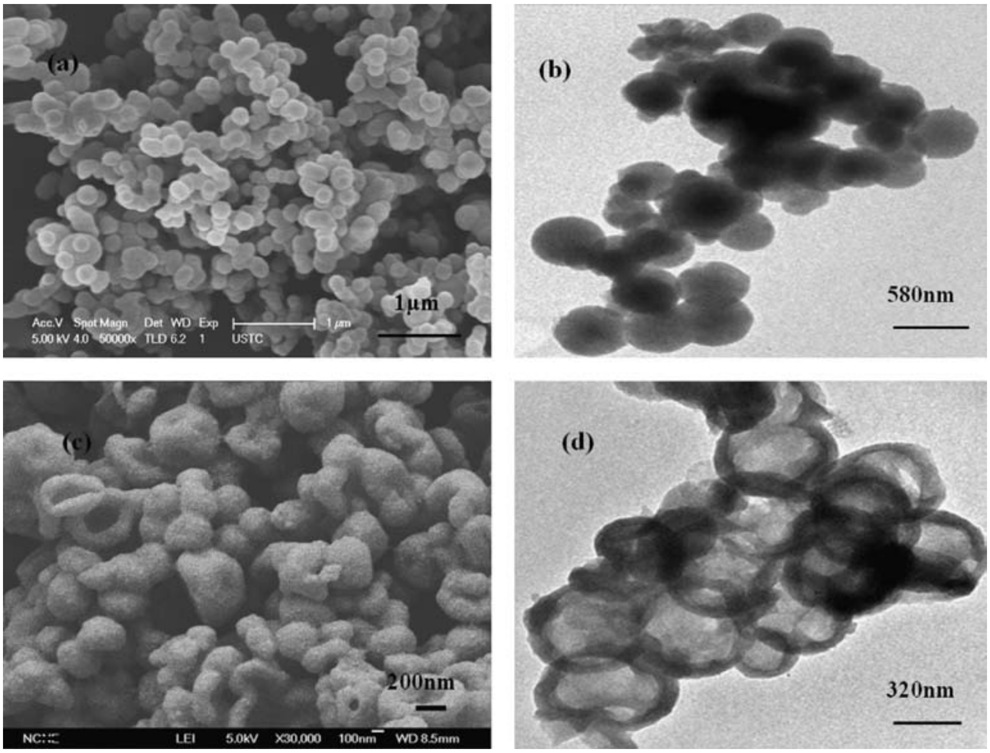

Fig. 4. SEM (a) and TEM (b) images of the MCM-48 spheres, SEM (c) and TEM (d) images of the synthesized HPDMIP spheres.

affinities of the binding sites in HPDMIP were heterogeneous and could be approximated by two dissociation constants corresponding to the high- and low-affinity binding sites that are usual phenomena in the Scatchard analysis [33]. From the plots, K_{d1} for specific binding sites and K_{d2} for non-specific binding sites in HPDMIP were calculated to be 173.38 and 610.24 μmol L^{-1}, respectively. Likewise, an equilibrium dissociation constant for HPNIP was estimated to be 512.18 μmol L^{-1}. It indicated that HPDMIP showed high selectivity for BPA.

Dynamic adsorption of the HPDMIP sorbent towards BPA was also examined. As shown in Fig. 8, the imprinted sorbent had a fast kinetics to uptake target molecules and 73% of the binding capacity was obtained within 10 min. If the concentration of BPA was lower, the time to saturation became shorter, indicating that surface imprinting facilitated the diffusion of the analyte to the binding sites significantly. It was, therefore, clear that the prepared HPDMIP showed a higher adsorption capacity and faster adsorption rate than other kinds of BPA–MIPs [34,35], which might be owing to the close distance between the binding sites and the surface of HPDMP, a large surface area and a good steric structure to match its imprint molecules; all these merits were especially favourable for SPE processes.

3.3. Selectivity of the imprinted sorbent

In order to verify that HPDMIP was selective for BPA, two different analogues (BIP and PTBP) were selected to test the binding characteristics of HPDMIP and HPNIP. Selectivity of the imprinted or non-imprinted sorbents was evaluated using the formulas (2–4) [10]. The distribution coefficient (K_d), selectivity coefficient (k) and relative selectivity coefficient (k') were significant indicators for evaluating the adsorption performance of polymers. The distribution coefficient (K_d), which reflects migration and separation capacity of the solute in two phases, is the ratio of the concentrations or amounts of the compound in each of the two phases.

$$K_d = \frac{C_i - C_f}{C_f} \times \frac{V}{W} \tag{2}$$

where C_i and C_f represent the initial and equilibrium concentration (mmol L^{-1}), respectively. V (mL) and W (g) are the volume and mass of the sorbent, respectively.

$$k = \frac{K_{\mathrm{dBPA}}}{K_{danalogue}} \tag{3}$$

$$k' = \frac{K_{imprinted}}{K_{nonimprinted}} \tag{4}$$

As can be seen in Table 1, K_d of BPA was larger than that of others (PTBP and BIP), which indicated that the separation capacity of HPDMIP for BPA was stronger than that of others. Moreover, the selectivity coefficient of HPDMIP to BPA was estimated to be larger than that of the corresponding HPNIP, which explained the selective re-binding of BPA from real complex samples depending on the imprinting effect of HPDMIP.

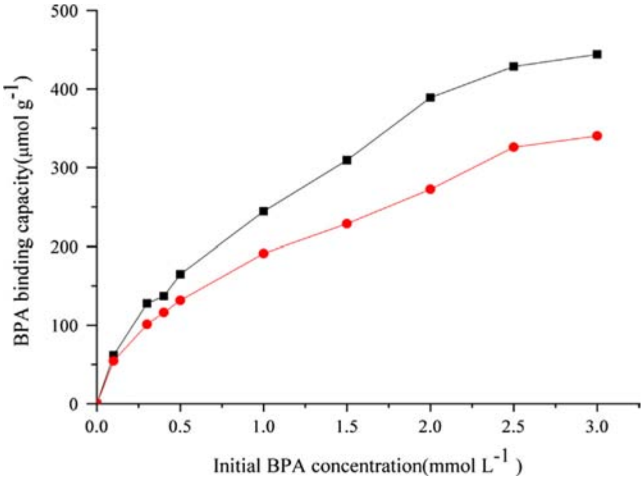

Fig. 6. Binding isotherms of BPA on the HPDMIP(■) and HPNIP(●)nanoparticles at room temperature.

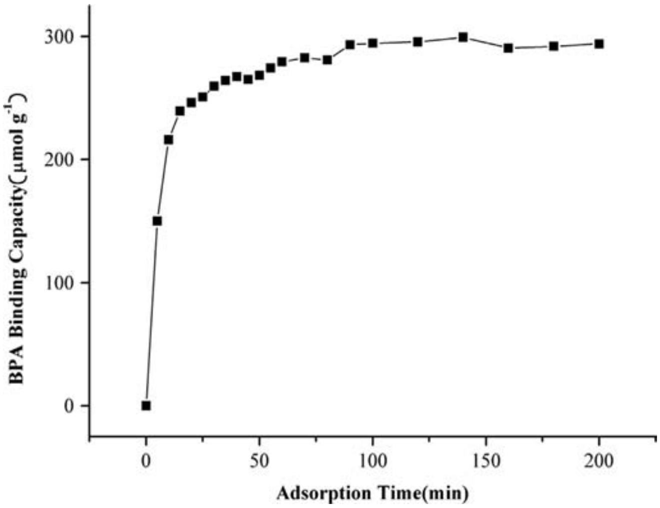

Fig. 8. Adsorption kinetics of the HPDMIP for BPA (0.5 mmol L^{-1}).

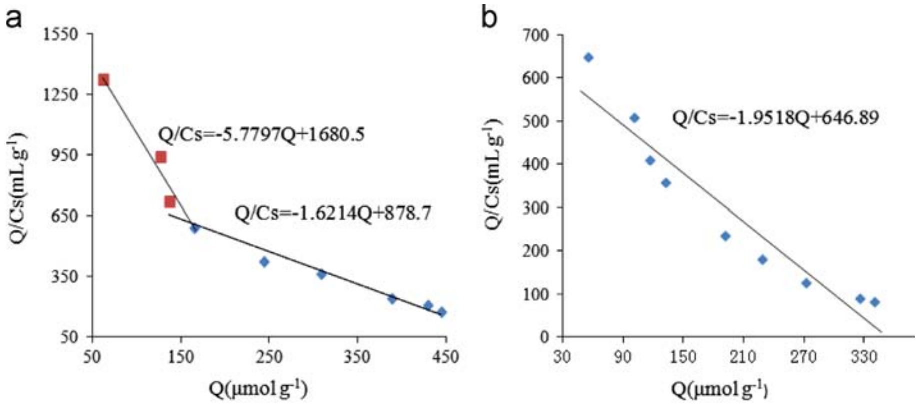

Fig. 7. Scatchard plot BPA in HPDMIP sorbent (a) and HPNIP sorbent(b).

Table 1
Adsorption and selectivity capability of HPDMIP for BPA and its structural analogues.

Compounds		C_o (mg mL^{-1})	K_d		k		k'
			HPDMIP	HPNIP	HPDMIP	HPNIP	
1	BPA	0.25	1002.4	306.5	–	–	–
2	BIP		138.2	101.0	7.25	3.03	2.39
3	PTBP		305.3	285.9	3.28	1.07	3.06

Table 2
Cross-sensitivity between BPA and analogues.

Initial solution (mg L^{-1})			Recovery (%)	R.S.D (%)
BPA	BIP	PTBP	BPA	BPA
1	1	1	99.8	2.75
1	10	10	99.5	3.12
1	50	50	98.8	2.89
1	100	100	96.5	3.46

Table 3
Recovery (%) and relative standard deviation (R.S.D.) of BPA after adsorption with HPDMIP of spiked tap water samples (n=3).

BPA in water samples (μg mL^{-1})	Founded (μg mL^{-1})	Recovery (%)	Mean recovery (%)	R.S.D. (%)
0.0	0	–	–	–
0.1	0.103	102.9	99.72	3.21
	0.099	99.7		
	0.096	96.5		
2.0	2.061	102.8	98.10	4.15
	1.914	95.5		
	1.927	96.0		
20.0	20.21	101.2	102.31	3.01
	19.83	99.2		
	21.36	106.5		

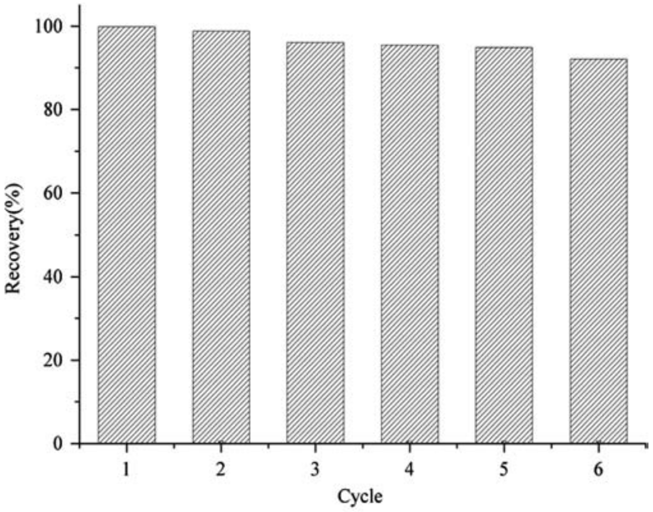

Fig. 9. Reuse results of HPDMIP-SPE for six times.

3.4. Application of the HPDMIP sorbent to the selective off-line SPE-HPLC determination of BPA

3.4.1. Cross-sensitivity between BPA and its Analogues

In order to know how the analogues disturbed the adsorption of BPA onto HPDMIP sorbent, the cross-sensitivity among BPA, BIP and PTBP was studied, as discussed in Section 2.5.2, under selected conditions. As shown in Table 2, when the ratio of concentration of BPA to BIP and PTBP was 1:50:50, the average recovery of BPA was 98.8%, which indicated that the BPA-imprinted silica sorbent had a satisfactory anti-interference ability. However, when the ratio was 100 times of BPA, the average recovery of BPA was reduced to 96.5%, which indicated that some other processes should be adopted when increasing the concentrations of interferents.

3.4.2. Regeneration studies of HPDMIP-SPE

The regeneration of HPDMIP-SPE was often considered to have a great cost benefit on extending their applications. After each use, the HPDMIP-SPE was repeatedly washed by acetic acid/methanol and then by methanol only, to regenerate their imprinted binding cavities. The regenerated SPE was assessed for rebinding the templates (BPA). The results in Fig. 9 showed that the binding capacity of BPA remained a high recovery over 95% during the cycle, which indicated that the recognizing sites were stable and the material could be reusable after a regeneration process. Few researches about the reusage performance of SMIP were reported. So the characteristics of the sorbents were superior to those traditional materials that the SMIP could save the costs for pretreatment of samples.

3.4.3. Validation of the method and determination of BPA in spiked water samples

In order to validate the method for the quantification of BPA in water samples, the linearity of the total analytical method, including the HPDMIP-SPE steps, was estimated by analysing BPA standard solutions at various concentrations ranging from 5 ng mL^{-1} to 100 μg mL^{-1}; the LOD was 3 ng mL^{-1} (S/N=3).

To validate the method developed, recovery of BPA at different spiking levels for the tap water having been pre-treated with the HPDMIP-SPE cartridges was tested. The results showed that the tap water was free of BPA and so they were used as blank samples to examine the spike recoveries of BPA. The recovery of the method was calculated and summarised in Table 3. The data in Table 3 indicate that the recoveries of BPA were in the range from 98% to 102% with RSD below 5% in all cases. As can be seen from the table, the average recovery of the HPDMIP-SPE method was 100.04% at the studied levels, demonstrating that the prepared material had a good recovery. All the results revealed that the developed method was accurate, selective and practical for the determination of trace BPA in environmental water samples.

4. Conclusion

The novel HPDMIPs used for recognising BPA were prepared using mesoporous silica as a sacrificial support and TBBPA as the dummy template. The recognition properties and applications based on the SPE of HPDMIP were evaluated. The resulting HPDMIP showed a large adsorption capacity and fast binding kinetics for recognising BPA, and the HPDMIP-SPE–HPLC method showed good recovery, high selectivity and repeatability in determining the BPA in tap water. These excellent properties make HPDMIP one of the most promising candidates in various applications, especially in the analysis of environmental water samples based on SPE.

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