



## Dummy molecularly imprinted polymers on silica particles for selective solid-phase extraction of tetrabromobisphenol A from water samples

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### ABSTRACT

Surface molecular imprinted polymers (MIPs) on silica gel particles for highly selective recognition of tetrabromobisphenol A (TBBPA) were prepared by a sol-gel process. Diphenolic Acid (DPA) and bisphenol A (BPA), whose structures were similar to that of TBBPA were selected as dummy template molecules, and 3-aminopropyltriethoxysilane (APTES) and tetramethoxysilane (TEOS) were chosen as functional monomer and cross-linker, respectively. The obtained materials were characterized by FT-IR with diffuse reflectance accessory and the results indicated polymers were successfully grafted on the surface of silica gel supporters. The maximum static adsorption capacities for TBBPA of the DPA-MIPs, BPA-MIPs and non-imprinted polymers (NIPs) were 45, 38 and 22 mg g<sup>-1</sup> respectively, and the results of dynamic adsorption showed that the adsorption equilibrium can be achieved within 15 min for DPA- and BPA-MIPs. Both the DPA- and BPA-MIPs have higher selectivity for TBBPA than that of NIP when they are used as the sorbents for the solid phase extraction (SPE), while the adsorption property of DPA-MIPs was superior to that of BPA-MIPs at low concentration levels of TBBPA. The results indicated DPA-MIPs had more high affinity binding sites for TBBPA, which demonstrated that the strong interactions between the template and the functional monomer were favorable to form high affinity binding sites and improve the selectivity of the polymers. A corresponding analytical method for determination of the TBBPA residues in environmental samples was developed. The recoveries of TBBPA in tap water, river water and lake water were in the range from 85% to 97% with relative standard deviations below 7%, and its limit of detection can reach 2 ng mL<sup>-1</sup>.

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### 1. Introduction

The design of synthetic tailor-made receptors capable of recognizing target molecule with high affinity and selectivity is a persistent long-term goal for researchers in the chemical, biological, and pharmaceutical fields [1]. Compared to biomacromolecular receptors, molecularly imprinted polymers (MIPs) promise simplified preparation processes, less costs and more stable receptor architectures [2]. Consequently, MIPs are widely considered the mimics of natural molecular receptors suitable for a diversity of applications ranging from biomimetic sensors to separations and biocatalysis [3–5].

Molecular imprinting techniques have emerged since 1972 [6], while their practical applications are limited due to some unsurmountable defects [7,8]. Some aspects of the MIP principles are still unclear and not literally expounded from molecular level even though more attentions have been paid to the optimization of the reaction conditions for preparation of the polymers, and so the

design of the MIPs cannot be well guided by the existing theory [9]. Furthermore, the conventional preparation processes of the MIPs are bulk polymerization or precipitation polymerization, so the residual template molecules and the recognition sites are embedded deeply in the matrix; therefore, the traditional MIPs sometime exhibited leakage of the template molecule and poor site accessibility.

Recently, surface molecularly imprinted polymers (SMIPs) have attracted much attention for their some advantages over the traditional MIPs, including adequate selectivity, more accessible binding sites, fast mass transfer rate and binding kinetics [10–13]. To eliminate the undesired leakage for the traditional MIPs, structural analogues of the target molecules have been utilized as the template molecules, namely dummy molecularly imprinted polymer (DMIP) [14–16]. To achieve both proper affinity and sufficient recovery, the selective of the dummy template is of great significance because the interaction of template molecules with that of functional monomer, and the conformation effects between target molecules and rebinding sites may be two key factors that influence on the properties of SMIPs [17,18].

Tetrabromobisphenol A (TBBPA) is a widely used brominated flame retardant, chiefly in epoxy resins applied to circuit board laminates [19] and it can microbiologically transform in anaerobic

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environments to bisphenol A (BPA) and in aerobic environments to TBBPA dimethyl ether (TBBPA DME) [20]. The release of TBBPA into the environment from these products has drawn great attention all over the world because of its estrogenic and thyroid hormonal activities [21]. The latest research showed that the relative toxicity of TBBPA exhibited higher potency than BPA and TBBPA DME [22], as a consequence, it is very essential to monitor the trace TBBPA rapidly and sensitively in the environmental samples. Chromatographic methods, such as gas chromatography (GC) and high-performance liquid chromatography coupled with mass spectroscopy (HPLC–MS) were usually used to the identification and quantification of TBBPA [23–26], while the key step was how to efficiently enrich and extract the TBBPA residues from complicated samples. Solid-phase extraction (SPE) provides an effective way for the clean-up of complex matrixes and preconcentration of target analyte via non-specific adsorption [27], however, the application of the traditional sorbents is to some extent limited due to their inefficient selectivity, which can be improved by the use of MIPs. In recent years, MIPs have been widely used in SPE as affinity chromatography supports [28–30], but unfortunately, there are few reports as respect to the exploitation of MIPs for the detection of TBBPA.

In this work, the surface molecular imprinted polymers for extraction and enrichment of TBBPA residues in water samples were prepared. DPA and BPA, whose structures are similar to that of TBBPA, were selected as dummy templates. The properties of the obtained DMIPs were evaluated and compared, and their retention mechanisms for TBBPA were discussed. The established methods had high selectivity and sufficient capacity for enrichment and rapid analysis of TBBPA residues in environmental water samples.

## 2. Experimental

### 2.1. Materials and chemicals

BPA, DPA, TBBPA, diethylstilboestrol (DES), nonylphenol (NP) and trichlorophenol (TCP) were purchased from Acros Organics (NJ, USA), and their chemical structures are presented in Fig. 1. Silica gel particles, 75–150  $\mu\text{m}$  (100–200 mesh) were provided by Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China). 3-Aminopropyltriethoxysilane (APTES) and tetramethoxysilane (TEOS) were obtained from J&K Chemical Ltd. (Beijing, China). Ultrapure water was from a Milli-Q purification system (Millipore, USA). Methanol and acetonitrile were of HPLC-reagent grade supplied by Merck (Darmstadt, Germany), and all the other reagents were of analytical grade and used as supplied without further purification.

### 2.2. Instrumentation

Infrared spectra of the polymers were collected using a Nicolet Nexus 670 FT-IR spectrometer (ThermoFisher, Madison, WI, USA) with a diffuse reflectance accessory. All the spectra were collected in the range of 4000–650  $\text{cm}^{-1}$  with 256 scans at the resolution of 4  $\text{cm}^{-1}$ .

Chromatographic separation of TBBPA was performed with an Agilent 1200 rapid resolution liquid chromatography (RRLC) system with SL autosampler (Agilent Technologies, Palo Alto, CA, USA). The wavelength of diode array detector was set to 212 nm. The injection volume of sample was 10  $\mu\text{L}$ . The column for separation was Agilent ZORBAX Eclipse XDB-C18 (4 mm  $\times$  50 mm, 1.8  $\mu\text{m}$ ) held at room temperature, and the binary mobile phases were acetonitrile and ultra pure water (90:10, v:v) for TBBPA, and those (70:30, v:v) for the mixtures of TBBPA and its analogues with a constant flow rate of 0.3  $\text{mL min}^{-1}$ .

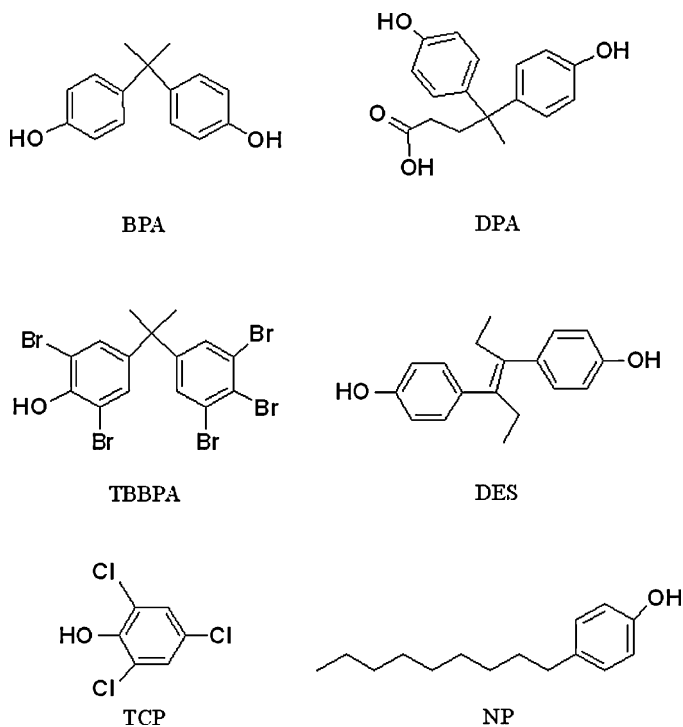


Fig. 1. The molecular structures of bisphenol A (BPA), Diphenolic Acid (DPA), tetra-bromobisphenol A (TBBPA), diethylstilboestrol (DES), trichlorophenol (TCP) and nonylphenol (NP).

### 2.3. Preparation of DMIP sorbents

16.0 g silica gel particles were mixed with 120 mL 6  $\text{mol L}^{-1}$  HCl solutions, and the mixture was refluxed under stirring for 10 h, and then centrifuged at speed 5000 rpm for 10 min. The solid part was washed with 50 mL water for several times until its pH was neutral, and then dried under vacuum at 70  $^{\circ}\text{C}$  for 8 h.

DPA-imprinted polymers and BPA-imprinted polymers were prepared with a sol-gel process [31] at the surface of the silica particles. DPA (1.830 g) and BPA (1.585 g) were dissolved in 10.0 mL methanol, respectively, and then mixed with 5.0 mL of APTES. After magnetically stirring for 30 min, 10.0 mL of TEOS was added and the mixtures were stirring for another 5 min. 4.0 g activated silica gel, which was dispersed in 10.0 mL of methanol by ultrasonic bath, and 2.0 mL 1.0  $\text{mol L}^{-1}$  HAc (catalyst) were subsequently added to above mixtures. After the mixture was incubated for 15 h at the room temperature under stirring, the polymers were isolated by centrifugation at 5000 rpm for 10 min and dried at 70  $^{\circ}\text{C}$  for 12 h.

To remove the template DPA or BPA, the polymers were washed with a mixture of methanol (50 mL) and 1.0  $\text{mol L}^{-1}$  HCl (50 mL) for four times, and then with NaOH (0.50  $\text{mol L}^{-1}$ ) and water until its pH reached to neutral. The products (DPA-MIPs and BPA-MIPs) were dried under vacuum at 70  $^{\circ}\text{C}$  for 12 h.

For comparison, the non-imprinted polymer (NIP) was also prepared by an identical method without addition of the dummy template molecule during the polymerization process.

### 2.4. Static and kinetic adsorption of DMIPs

20.0 mg of DPA-imprinted or BPA-imprinted polymers on silica gel particles were equilibrated with 2.0 mL various concentrations of TBBPA methanol solutions (0.1–1.2  $\text{mg mL}^{-1}$ ), respectively. The mixtures were shaken in a rocking table at room temperature for 1 h, and then centrifuged. The amount of TBBPA in the

supernatant was detected by RRLC. The same procedure was performed on the NIP.

Kinetic adsorption tests were carried out using 20.0 mg of DMIPs or NIP which were mixed with 2.0 mL methanol solution containing  $1.2 \text{ mg L}^{-1}$  TBBPA. The samples were incubated at room temperature with shaking. The residual concentrations of analyte at certain time intervals (5, 7.5, 10, 15, 20, 25 and 30 min, respectively) were monitored by RRLC.

## 2.5. Evaluation of MIPs used as the stationary phase of SPE

### 2.5.1. Procedure for DMIP-SPE

BPA-MIPs or DPA-MIPs (each 500 mg) were packed in empty polypropylene SPE cartridges, respectively. The sorbents in the columns were activated with 5.0 mL methanol, and then 10 mL certain concentration of TBBPA methanol solution was loaded on the SPE cartridge with a flow rate of  $0.5 \text{ mL min}^{-1}$ . The analyte was eluted with 2 mL solution of methanol:acetic acid:ultra pure water (90:5:5, v/v) (mixtures of eluant), and the eluent was analyzed by RRLC. The recoveries of TBBPA were calculated by the ratio of the peak areas of target analytes to those of control samples.

### 2.5.2. Competition studies

In order to explore the selectivity of the DMIPs toward TBBPA, the selective assays were investigated on DMIPs-SPE and NIP-SPE columns, respectively. The SPE procedures were as described above. Loading solutions were 10 mL methanol, the mixture of methanol and water (v/v = 1:1) and water containing the same concentration of BPA, TBBPA, DES, NP and TCP, respectively. Compounds present in the eluent were detected by RRLC, but their recoveries were calculated.

### 2.5.3. Comparison of extraction performance between DPA-MIP and BPA-MIP

The DPA-MIP (500 mg) and BPA-MIP (500 mg) SPE cartridges were preconditioned with 10 mL methanol, respectively, and then 20 mL methanol solutions spiked with different concentrations of TBBPA ( $0.01$ ,  $0.05$  and  $0.5 \text{ } \mu\text{g mL}^{-1}$ ) were loaded. The cartridges were eluted with 2 mL mixtures of eluant and the compounds present in the eluent were detected by RRLC.

### 2.5.4. Reusage of DPA-MIP SPE cartridges

The DPA-MIP SPE cartridges (500 mg) were preconditioned with 10 mL methanol, and then 10 mL TBBPA methanol solution ( $0.5 \text{ } \mu\text{g mL}^{-1}$ ) were loaded. The analyte was eluted with 2 mL mixtures of eluant. The procedures were repeated to inspect how many times the cartridge can be utilized to enrich the TBBPA.

## 2.6. Application of the DPA-MIP SPE cartridges to water samples

To test the enrichment ability of the DPA-MIP SPE columns for TBBPA, various volumes of methanol solution (10 mL, 20 mL, 50 mL and 100 mL) with concentration of  $2 \text{ ng mL}^{-1}$  TBBPA were loaded to the DPA-MIP SPE cartridges, individually, at a speed of  $1 \text{ mL min}^{-1}$ . Then, the cartridges were accordingly eluted with 2 mL mixtures of eluant at a speed of  $0.2 \text{ mL min}^{-1}$ , and compounds present in the eluent were detected by RRLC.

The calibration curve was established by analyzing the elution of TBBPA standard solutions after DPA-MIP SPE procedures in six different concentrations ( $1$ – $1000 \text{ ng mL}^{-1}$ ). The limit of detection (LOD) was defined as three times of the signal to noise (S/N) ratio.

Three kinds of real water samples (tap water, river water and lake water) were collected from Beijing. The pretreatment procedures of the water samples were as follows: after centrifugated for 5 min, the water samples were mixed with methanol (v/v = 1:1) and this was used later to study the influence of the volume of water

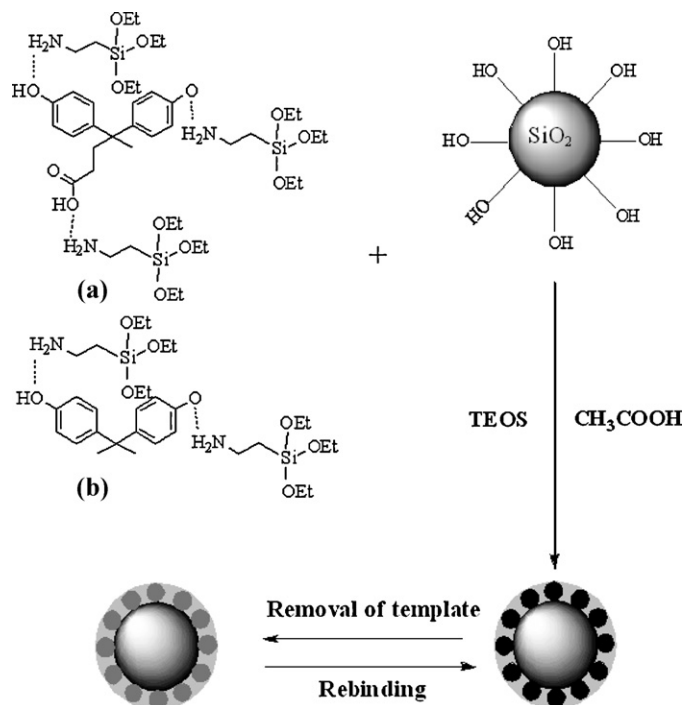


Fig. 2. Schematic procedures for preparing the DPA-imprinted polymers (a) and BPA-imprinted polymers (b) on the surfaces of silica gel particles.

sample. The cartridges were prepared by packing 500 mg MIP and NIP, and washing with 10 mL methanol, respectively. Different volumes of water samples (10 mL, 20 mL and 50 mL) were loaded on the cartridges at a flow rate of  $0.5 \text{ mL min}^{-1}$ . The retained TBBPA was then eluted with 1 mL mixtures of eluant, and each sample was assayed five times ( $n=5$ ). If the samples were verified to be free of TBBPA, the spiking and recovery studies were performed with three different concentration levels ( $0.01 \text{ } \mu\text{g mL}^{-1}$ ,  $0.02 \text{ } \mu\text{g mL}^{-1}$ , and  $0.05 \text{ } \mu\text{g mL}^{-1}$ ) of TBBPA as the same procedures.

## 3. Results and discussion

### 3.1. Preparation and characterization of DPA- and BPA-MIPs

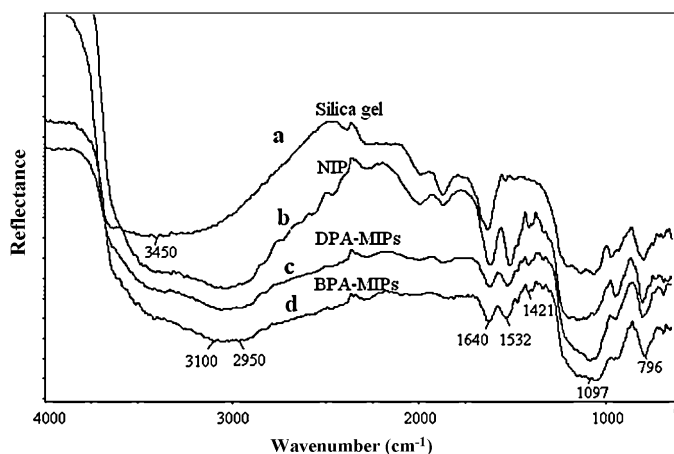
To improve the adsorption properties and eliminate the template leakage, surface molecular imprinted polymers on silica gel particles for specifically recognizing TBBPA were synthesized using DPA and BPA as the dummy template molecules, respectively. The schematic illustration of the routes for preparation of the polymers is shown in Fig. 2.

The structural skeletons of DPA and BPA are similar with that of TBBPA (see Fig. 1), while DPA contains a carboxyl group, which would form strong hydrogen bond with the amino group of the functional monomer, APTES. It can be seen from Fig. 2 that DPA can bind with three molecules of APTES, while BPA only with two in the pre-organization process. It should be noticed that the pre-organization of APTES around TBBPA was infeasible because a white precipitate generated when the APTES was added into the solutions containing TBBPA.

The molar ratio of the template: functional monomer (APTES): cross-linker (TEOS) was a critical factor that influences the adsorption properties of the MIPs [1]. Different molar ratios (1:3:6, 1:4:8, and 1:5:10) of template: APTES: TEOS were chosen to optimize the conditions for preparation of the MIPs, and the results are listed in Table 1. The data showed that the maximum adsorption capacity ( $Q_{\text{max}}$ ) of the MIPs for TBBPA increased with increasing the ratios of functional monomer and

**Table 1**  
Effect of the molar ratio of template:APTES:TEOS in imprinted process.

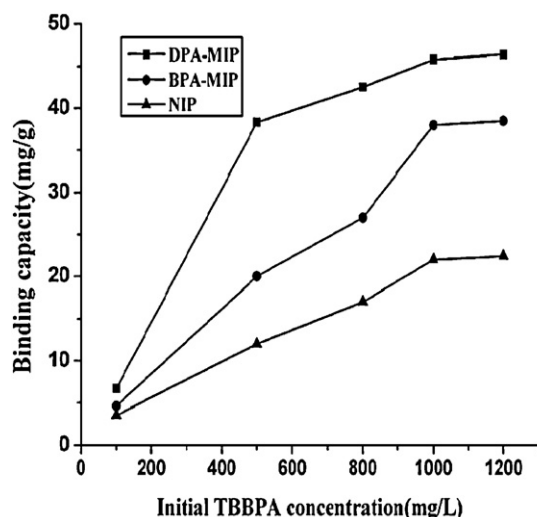
Molar ratio	Value of $Q_{\max}$ ( $\text{mg g}^{-1}$ )		
	DPA-MIPs	BPA-MIPs	NIP
1:3:6	38	30	15
1:4:8	45	38	19
1:5:10	50	40	30



**Fig. 3.** FT-IR spectra of the activated silica gel (a), NIP (b), DPA-MIPs (c) and BPA-MIPs (d).

cross-linker, while that of the non-specific adsorption on NIP was also drastically augmented. Considering the difference of the  $Q_{\max}$  between MIPs and NIP, the molecular ratio of 1:4:8 for the template:APTES:TEOS was selected to prepare the MIPs and NIP sorbents.

The FT-IR diffuse reflectance spectra of activated silica gel particles, non-imprinted polymer, DPA-imprinted and BPA-imprinted polymers are shown in Fig. 3. The IR bands at about 3450, 1640 and 1097  $\text{cm}^{-1}$  were the characteristic vibration absorption of the Si–OH for the silica gel particles. For NIP, DPA-MIPs and BPA-MIP sorbents, the broad IR bands from 2800 to 3600  $\text{cm}^{-1}$  can be ascribed to stretching vibration of N–H and –CH<sub>3</sub>, and the bands at 1532 and 1421  $\text{cm}^{-1}$  were attributed to the bending vibrations of N–H and –CH<sub>3</sub>, which suggested the existence of the aminopropyl



group, and it indicated that APTES and TEOS were grafted on the surface of the activated silica gel particles.

### 3.2. Static and dynamic adsorptions of the polymers

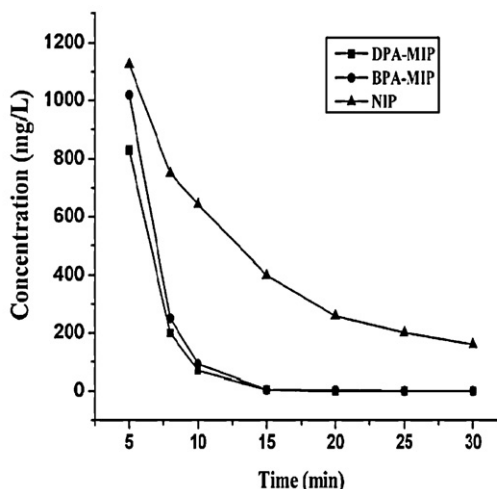
The static adsorption capacities of the DMIPs and NIP sorbents for TBBPA were determined in the concentrations ranged from 100  $\text{mg L}^{-1}$  to 1200  $\text{mg L}^{-1}$  (see Fig. 4a). It can be noted that the adsorption capacities of both the DMIPs and NIP increased with increasing the initial concentrations of TBBPA, and the maximum adsorption capacities ( $Q_{\max}$ ) of the DPA-imprinted, BPA-imprinted and non-imprinted sorbents for TBBPA were calculated to be 45, 38 and 22  $\text{mg g}^{-1}$  respectively, indicating that the imprinted polymers displayed a much higher affinity to TBBPA than non-imprinted polymer. Moreover, it can be also observed that the  $Q_{\max}$  of the DPA-imprinted polymers was about 1.2 times as much as that of the BPA-imprinted polymers, and the results suggested that TBBPA adsorption onto the DPA-imprinted polymer was relatively favorable.

Fig. 4b shows the dynamic adsorption curves of the DMIPs and NIP for TBBPA. It can be seen from the figure that the adsorption processes were very quickly for the DMIP sorbents, and the adsorption equilibrium can be achieved within 15 min, while it cannot reach equilibrium in more than 30 min for the NIP sorbents. The results illustrated that the specific recognition cavities for TBBPA at the surface or in the proximity of the surface of the silica gel particles have been formed [32] and the affinity sites catch the analyte via hydrogen bonds or acid-base pairing interaction [5]. It was important to notice that the mass transfer rate of TBBPA for the DMIP sorbents was faster, which needed less time to attain the adsorption equilibrium, and the feature was much better than those for the materials previously reported [28,33,34], and the merit was especially favorable for SPE processes.

### 3.3. Evaluation of the DMIPs as SPE sorbents

#### 3.3.1. Selectivity

The selectivities of DPA-MIPs and BPA-MIPs as SPE sorbents for TBBPA, BPA, DES, TCP and NP were evaluated, and compared with that of NIP cartridges, and the results are shown in Fig. 5. The recoveries of TBBPA on DPA-MIPs and BPA-MIP cartridges were  $83.1 \pm 3.5\%$  and  $80.6 \pm 4.3\%$  respectively, which were significantly higher than that of NIP cartridge ( $47.1 \pm 3.9\%$ ). Moreover, it was also revealed that both DPA-MIPs and BPA-MIPs exhibited lower



**Fig. 4.** Static (a) and dynamic (b) adsorption curves of the DPA-MIPs, BPA-MIPs and NIP for TBBPA.

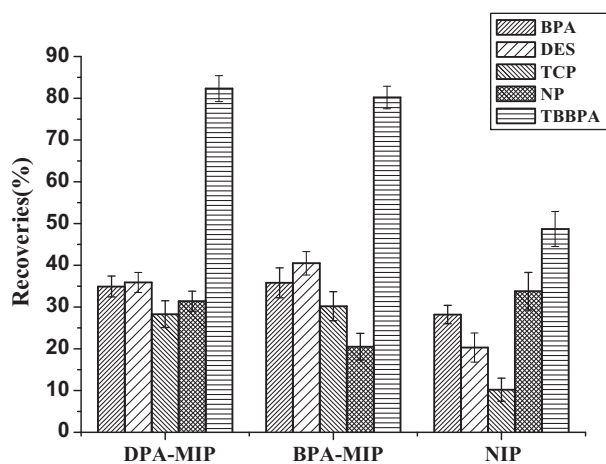


Fig. 5. Recoveries of TBBPA and its analogues BPA, DES, TCP and NP on the DPA-MIPs, BPA-MIPs and NIP, respectively when they were used as SPE sorbents (500 mg).

affinities for BPA, DES, TCP and NP, and the recoveries for these analogues of TBBPA were in the range of 20–40%. The results signified that both the DPA-MIPs and BPA-MIPs have higher selectivities for TBBPA, which could be ascribed to the molecular interaction between the TBBPA and the amino groups of the functional monomers in the specific recognition sites of the imprinted polymers. It has also been found that the recoveries of BPA (lower than 40%) were low, indicating that the DPA-MIPs and BPA-MIPs had weak affinities to BPA. The phenomena may be related to the conditions for preparation of the polymers, the molar ratio of templates:APTES:TEOS or the solvent effect [35], and the reasons should be explored in the future study.

The influences of sample solvents (methanol, mixture of methanol and water, water) on the selectivities of the DMIPs for TBBPA and its analogues were investigated and the results are summarized in Table 2. It can be seen from the data that the recoveries of TBBPA were only slightly decreased when the sample solvent was the mixture of methanol and water, while those were significantly reduced in aqueous medium. It was also noted that the recoveries of BPA were obviously increased from 40.8 and 31.8% to 54.1 and 63.0% when the sample solvents were changed from methanol to water, which illustrated that the behavior of the DMIPs was different in organic than in aqueous media. The recoveries of other analogues on DPA-MIPs were all below 40% and have no obvious differences in different media, while those on BPA-MIPs were significantly higher in water than in methanol, which signified that the selectivity was poor in aqueous media. Otherwise, the DMIPs would be swelling in aqueous media and the sorbents in the cartridge became more tightly, which made the samples difficult to pass through the DMIPs. Therefore, the results indicated that methanol or mixture of methanol and water was suitable sample media.

### 3.3.2. Comparing the retention behaviors of TBBPA between DPA-MIPs and BPA-MIPs

The results obtained from the adsorption test showed that the static adsorption capacity of DPA-MIPs for TBBPA were greater than that of BPA-MIPs. The retention behaviors for different concentrations of TBBPA on the two sorbents were investigated to evaluate their binding properties, and the data are displayed in Fig. 6. It can be seen that the adsorption behaviors of TBBPA on the DPA-MIPs and BPA-MIP SPE cartridges were similar at the concentration level of  $0.5 \mu\text{g mL}^{-1}$ , and their recoveries were 97.3% and 99.1%, respectively. However, at the lower concentration of TBBPA, the recoveries on the BPA-MIP SPE column were only about 60%, which were significantly lower than those (99.2–103.4%) on the

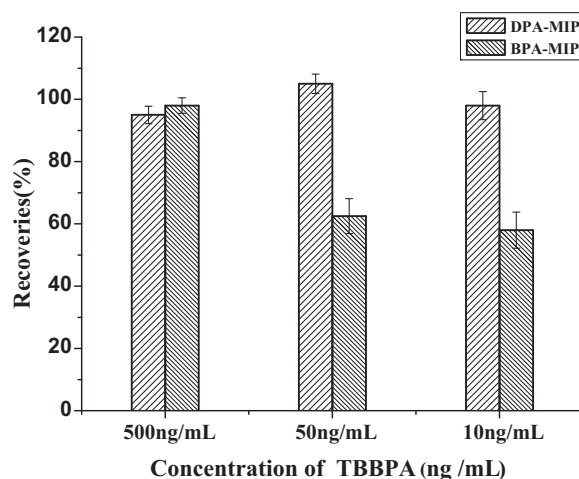


Fig. 6. Recoveries of TBBPA at different concentration levels on the DPA-MIPs and BPA-MIPs when they were used as SPE sorbents (500 mg).

DPA-MIP cartridge. The results indicated that the binding affinity of the DPA-MIPs were superior to that of the BPA-MIP sorbents at lower concentration levels of TBBPA, and this merit was more suitable for enrichment and purification of the trace analytes in complex matrices.

The differences of the adsorption properties for the two sorbents may originate from the molecular structures of their dummy templates. Comparing with BPA, the carboxyl group in DPA can form strong hydrogen bonding with the amino group of the functional monomer, APTES, and the additional interactions were favorable to constitute the high affinity “molecularly designed cavities” [36] for TBBPA. Therefore, DPA-MIPs would have more high affinity binding sites than BPA-MIPs, which would improve its binding affinity and recognizing ability for TBBPA, and so it can adsorb and enrich the TBBPA with high recoveries at low concentration levels.

For dummy template, any change in conformation of the template could lead to incorrectly formed imprinted sites [37], such as non-specific binding sites, macro- and micro-pore binding sites, collapsed or irreversible binding sites [38]. The obtained DPA-MIP sorbent has no such shortcomings, and its high affinity to TBBPA further demonstrated that DPA was an ideal dummy template molecule for preparing the surface imprinted polymers to specifically recognizing TBBPA in complex matrices.

### 3.3.3. Regeneration and breakthrough volume of the DPA-MIP cartridge

The reusability of the DPA-MIP SPE cartridges was tested and the results showed that the recoveries of TBBPA were in the range from 98.5 to 101.6% for reuse of five times, which indicated that the cartridge can be reusable after a regeneration process and the recognizing sites were stable. The characteristics of the sorbents were superior to that of the traditional C18-SPE cartridges, and can save the costs for pretreatment of samples.

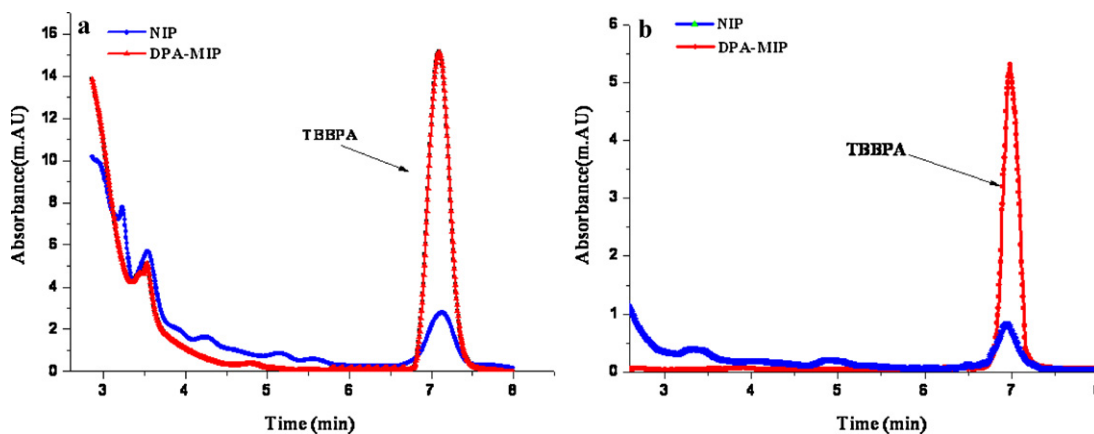
The breakthrough volume is a key factor to show the enrichment ability of the sorbents for target molecule at low concentrations [39]. Various volumes of samples (10, 20, 50 and 100 mL) with the concentration of  $2 \text{ ng mL}^{-1}$  TBBPA were loaded on the DPA-MIP SPE cartridges, and the recoveries of the TBBPA were 101, 99, 93 and 83%, respectively. The results indicated the loss of the analyte was lower than 10% and within 20% when the loading volumes were 50 mL and 100 mL, individually, which demonstrated that the sorbents have high ability to enrich the trace TBBPA residues in environment samples.

In methanol/water (1:1, v/v) and aqueous media, the recoveries of TBBPA on DPA-MIPs were 98.2, 90.2, 83.5 and 80.3, 78.5, 70.2%,

**Table 2**  
The recoveries of TBBPA and its analogues in various media of solvents on DPA-MIPs (D) and BPA-MIPs (B) cartridges.

Compounds	TBBPA		BPA		DES		NP		TCP	
	D	B	D	B	D	B	D	B	D	B
Methanol	84.3	85.8	40.8	31.8	36.2	35.4	31.8	29.0	34.3	33.4
Methanol/water	81.3	79.7	49.8	41.4	36.5	37.1	29.7	20.5	35.8	32.1
Water	70.5	67.8	54.1	63.0	44.2	53.2	27.2	44.8	31.6	49.7

RSD is lower than 5% for all the compounds ( $n=3$ ). The concentrations of TBBPA or its analogues were  $0.5 \mu\text{g mL}^{-1}$ , respectively.



**Fig. 7.** Chromatograms of TBBPA after extracted from 50 mL of lake water (a) and 20 mL of river water (b), spiked with  $0.01 \mu\text{g mL}^{-1}$  of TBBPA, on 500 mg DPA-MIPs and NIP sorbents, respectively.

respectively, when loading volumes were 10 mL, 20 mL and 50 mL. The results showed that the enrichment ability of the sorbent would be significantly decreased in aqueous medium comparing with those in methanol or methanol/water media.

The influence of DPA-MIP amount on the recovery of TBBPA was investigated, and it has been found that the recovery was about 65% when 200 mg DPA-MIPs were used as SPE sorbent and the loading volume of methanol/water (1:1, v/v) was 50 mL. The results may be reasonable. From the dynamic curve of DPA-MIPs for TBBPA (see Fig. 4b), it can be seen that the adsorption equilibrium needed 15 min, while the SPE process was very fast (at a speed of  $1\text{--}2 \text{ mL min}^{-1}$ ), and so large amount of the sorbents would be in favor of increasing the recovery of TBBPA.

### 3.4. Validation of the method

Under optimized RRLC-DAD conditions for separation of TBBPA in water samples, the linearity of the total analytical method, including the DPA-MIP SPE steps, was estimated by analyzing TBBPA standard solution at various concentrations ranging from 1 to  $1000 \text{ ng mL}^{-1}$ . The results showed that the linear ranges of the peak area and the concentration of TBBPA were  $8.4\text{--}800 \text{ ng mL}^{-1}$  with RSD of 3.6% ( $n=6$ ) at  $100 \text{ ng mL}^{-1}$  of TBBPA, and the limit of detection was  $2 \text{ ng mL}^{-1}$  ( $S/N=3$ ).

Fig. 7 shows the chromatograms of TBBPA in spiked river water and lake water samples, which were obtained with DPA-MIP and NIP SPE cartridges, respectively. It indicated that TBBPA had been effectively concentrated after DPA-MIPs pretreatment and the concentration was high enough to be quantitatively analyzed by RRLC, while it was inaccurate using NIP. Moreover, the matrix interference problems was basically solved after DPA-MIP SPE pretreatment, which was clearly demonstrated the advantage of DPA-imprinted polymers as selective sorbents for determining the trace TBBPA in environmental water samples.

To validate the method developed, the recoveries of TBBPA at different spiking levels for the tap water, river water and lake water after pretreatment with the DPA-MIP SPE cartridges were tested,

**Table 3**  
Recoveries of TBBPA in environmental water samples at different spiking levels.

Water samples	Spiked ( $\text{ng mL}^{-1}$ )	Recovery ( $n=5$ )	RSD ( $n=5$ )
Tap water	0	ND	ND
	10	98.70%	3.00%
	20	95.30%	2.80%
	50	96.30%	2.50%
River water	0	ND	ND
	10	92.30%	4.80%
	20	90.20%	3.40%
	50	88.60%	3.20%
Lake water	0	ND	ND
	10	91.30%	6.50%
	20	87.50%	3.80%
	50	85.20%	3.20%

and the results are listed in Table 3. The results showed that the three kinds of environmental water samples were free of TBBPA and so they were used as blank samples to examine the spike recoveries of TBBPA. The data in Table 3 indicate that the recoveries of TBBPA were in the range from 85% to 97% with RSD below 7% in all cases. All the results revealed that the developed method was accurate, selective and practical for the determination of trace TBBPA in environmental water samples.

### 4. Summary and conclusions

The surface molecularly imprinted polymers on silica gel particles for recognizing TBBPA were prepared using DPA and BPA as dummy templates. The adsorption properties of the polymers were evaluated and compared, and the results showed that both DPA-MIPs and BPA-MIPs have high selectivity for TBBPA, while the characteristics of DPA-MIPs were superior to those of BPA-MIPs, especially at low concentration levels of TBBPA. This feature of DPA-MIPs demonstrated that the strong interactions between the carboxyl group of DPA and the amino-group of the functional monomer (APTES) were favorable to form high affinity binding sites

and improve the adsorption property of the sorbents, and it has provided scientific evidences for selecting or designing the template molecules for preparing high affinity dummy MIPs. The analytical method of TBBPA in real water samples by using DPA-MIPs as SPE sorbents was developed, and the results showed that DPA-MIPs can selectively recognize and effectively enrich the analyte from water samples. The developed method was sensitive, rapid, and has high repeatability for determination of the trace TBBPA in environmental water samples.

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