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# Novel surface dummy molecularly imprinted silica as sorbent for solid-phase extraction of bisphenol A from water samples

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## ABSTRACT

A novel surface molecularly imprinted silica composite was prepared by a dummy-template imprinting strategy for the solid-phase extraction (SPE) of bisphenol A (BPA). 2,2-Bis(4-hydroxyphenyl) hexafluoropropane (BPAF) was chosen as the template molecule, and a hybrid technique was used for imprinting procedure. The imprinted silica was characterized by FT-IR spectroscopy, scanning electron microscope, thermo-gravimetric analysis, and nitrogen adsorption-desorption isotherms. The static binding test verified that the imprinted silica had much higher recognition ability for BPA than the non-imprinted silica, and the kinetic adsorption test presented the fast binding kinetics of the surface imprinted silica for BPA. When used as a SPE sorbent, the imprinted silica showed high extraction efficiencies and high enrichment factor for BPA. Based on the imprinted silica, a SPE-HPLC-UV method was developed and successfully applied to the detection of BPA in BPA-spiked lake water, tap water and drinking water samples with a high recovery of 97.3–106.0%, a RSD of 1.2–3.8% ( $n=3$ ) and a limit of detection ( $S/N=3$ ) of 0.3 ng/mL. The analysis results of a certified BPA sample also demonstrated the reliability of present method. The new surface dummy molecularly imprinted silica completely avoided the interference of the residual template molecules and greatly improved the binding kinetic of the target molecules. Therefore, it can be used as a good sorbent for SPE of BPA in environmental water samples.

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## 1. Introduction

Bisphenol A (BPA) is an industrial chemical used in numerous products such as polycarbonate plastics and epoxy resins, food and beverage packing, dental sealants, and thermal paper [1,2]. Due to its migration from these products, BPA has been widely found in a variety of food, beverages, environmental matrices, and biological samples [3–7]. BPA is also well known as a xenoestrogenic endocrine-disrupting compound, which causes cardiovascular disease, diabetes, neuro-behavioral disorders, carcinogenic hypersensitivity, and reproductive impairment [8–10]. Therefore, it is essential for environmental health and human exposure assessments to quantitatively detect BPA in different samples. Owing to the complexity and the low concentration of real samples, highly selective pretreatment and enrichment steps are necessary prior to analysis. Solid-phase extraction (SPE) is the most favorable pretreatment strategy because of its low cost, high enrichment factor, and simple operation. However, the traditional SPE methods suffer

from the low selectivity of their sorbents for BPA such as hydrophilic lipophilic balanced sorbent [6], C18 solid sorbent [11], divinylbenzene/*N*-vinylpyrrolidone copolymer [12], mixed-mode cationic exchanger [13], modified attapulgite [14], and  $K_2CO_3$ -treated silica [15].

Molecularly imprinted polymers (MIPs) have been widely used as affinity sorbents due to their high selectivity, good stability, ease of preparation, and low cost [16–23]. Some BPA-imprinted materials have also been prepared for its SPE, such as sponge-like molecularly imprinted mesoporous silica [5], MIP microspheres [24], molecularly imprinted mesoporous SBA-15 [25], MIP particles [26], hierarchically molecularly imprinted mesoporous silica [27], molecularly imprinted mesoporous organosilica [28], commercial MIP particles [29], nanofibrous molecularly imprinted membranes [30], dual-templates molecularly imprinted stir bar [31], and magnetic MIP particles [32]. These MIP sorbents have effectively improved the selectivity of SPE for BPA. However, they were all prepared using BPA as template. As a result, the possible leakage of residual template molecules in these sorbents can have a serious impact on the accuracy of analysis [33].

The use of dummy template offers an easy way to circumvent

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this problem as the leached template will be different from the analytes. Several dummy molecularly imprinted polymers (DMIPs) have been prepared using different analogs of BPA as template for SPE of BPA [34–40]. These materials included a DMIP synthesized using bisphenol S as template [34], a surface DMIP prepared using tetrabromobisphenol A (TBBPA) as template [35], DMIPs grafted on the surface of silica particles obtained using 4,4'-dihydroxybiphenyl and TBBPA as templates [36], a hollow porous DMIP synthesized using TBBPA as template [37], a DMIP-coated stir bar obtained using TBBPA as template [38], DMIP-coated magnetic nanoparticles prepared using bisphenol F as template [39], a DMIP-coated stir bar synthesized using 4,4'-dihydroxybiphenyl as template [40], and DMIP particles using bisphenol E as template [41]. However, these DMIPs were all synthesized by non-covalent imprinting strategies that required excess functional monomers, resulting in a large number of non-specific binding sites [17,42]. Recently, a dummy molecularly imprinted mesoporous silica was prepared, using 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (BPAF) as template, by a hybrid imprinting method for SPE of BPA in our group [43]. This dummy imprinted silica not only avoided the interference of the leakage of residual template molecules, but also reduced the number of non-specific binding sites.

Furthermore, conventional MIPs were mostly prepared by bulky or precipitation polymerization. The main drawbacks of these MIPs are the poor accessibility to the target molecules, slow mass transfer, and problems with template removal. The surface imprinting techniques can improve these issues [44,45]. Several surface molecularly imprinted materials have been prepared for SPE of BPA, including a DMIP-coated vinylized silica [36], a DMIP-coated superparamagnetic nanoparticles [39], a surface BPA-imprinted silica [46], and a BPA MIP-coated magnetic nanocrystals [47]. These surface imprinted materials greatly improved the binding kinetics of BPA with saturation time less than 30 min. However, they were synthesized by non-covalent imprinting approaches and consequently could not avoid the occurrence of excess non-specific binding sites.

Herein, to avoid the interference of the leached template molecules, reduce the number of non-specific binding sites and improve the binding kinetics, we combine a dummy molecular imprinting with a hybrid strategy to prepare an imprinted silica coating on the surface of silica microparticles for SPE of BPA. BPAF was used as template. The imprinted material was characterized by FT-IR spectroscopy, scanning electron microscope (SEM), thermo-gravimetric analysis (TGA) and nitrogen adsorption-desorption isotherms, and then its adsorption and SPE abilities were investigated. Finally, using the imprinted silica as sorbent, a SPE-HPLC-UV method was developed and applied to the determination of BPA in water samples.

## 2. Experimental

### 2.1. Chemicals and materials

2,2-Bis(4-hydroxyphenyl)hexafluoropropane (BPAF, 95%), bisphenol A (BPA, 96%), dibutyltindilaurate (DBDU, 98%) and tetrahydrofuran (THF, superdry, 99.5%) were purchased from J&K Scientific LTD (Beijing, China). BPA standard sample (Catalog no. M-1626-01S, with certified concentration of 990 µg/mL in methanol) was bought from AccuStandard (New Haven, CT, USA). 3-(Triethoxysilyl) propyl isocyanate (ICPTES, 95%) was obtained from TCI (Tokyo, Japan). Tetraethoxysilane (TEOS, 99%) was bought from Alfa Aesar (Tianjin, China). Methanol of HPLC grade was supplied by Merck (Darmstadt, Germany). The ultrapure water was obtained from the KL-III-40 purification system (AK, Taiwan). All of other reagents were of analytical grade and used as supplied

without further purification. Silica gel with particle size of 200–300 meshes was purchased from Qingdao Haiyang Chemical Co., LTD (Qingdao, China).

### 2.2. Preparation of imprinted silica

The template–monomer complex (BPAF-Si) was synthesized for the hybrid imprinting procedure *via* reaction of BPAF and ICPTES according to our previous report [43].

Sixteen grams of silica and 120 mL of 6 M HCl were charged in a 250 mL flask and then were refluxed for 10 h. After the resultant silica particles were washed with ultrapure water thoroughly and dried under vacuum at 70 °C overnight, the activated silica particles were obtained.

BPAF-Si (0.966 g, 0.96 mmol) and TEOS (3.6000 g, 17.2 mmol) were first dissolved in 10 mL of methanol, and then 3.0 g of activated silica was added, followed by ultrasonic treatment for 10 min. After that, 1.5 mL of 1.0 M HAc was added, and subsequently the mixtures were stirred at room temperature for 24 h. After the resultant particles were washed three times with methanol, cured at 80 °C for 24 h and dried under vacuum for 2 days, the template-incorporated silica particles were obtained, which were called as SiO<sub>2</sub>@MIP-T.

Two grams of SiO<sub>2</sub>@MIP-T was suspended in the mixture of 10 mL DMSO and 2 mL water. After the mixtures were heated at 160 °C for 5 h, the resultant particles were rinsed three times with ultrapure water and ethanol alternately and then dried under vacuum for 2 days. The final imprinted silica, called as SiO<sub>2</sub>@MIP, was obtained.

For comparison, the non-imprinted silica was also prepared through the similar procedure except that BPAF-Si was replaced by ICPTES (0.2365 g, 0.96 mmol), which was called as SiO<sub>2</sub>@NIP.

### 2.3. Adsorption experiments

In static adsorption tests, 40 mg of sorbent (SiO<sub>2</sub>@MIP or SiO<sub>2</sub>@NIP) was added in 1.0 mL of BPA aqueous solution (containing 5% methanol) with a concentration range of 0.003–2.0 mM, followed by ultrasonic treatment for dispersion. After the mixtures were shaken continually at 25 °C for 24 h and subsequently centrifuged, the concentration of BPA in the supernatant was determined by HPLC with a UV detector at 276 nm.

The adsorption capacity and the dissociation constant ( $K_d$ , µmol/L) were obtained according to the Eqs. (1) and (2) [34]:

$$Q = \frac{(c_0 - c_f)v}{m} \quad (1)$$

$$\frac{Q}{c_f} = -\frac{1}{K_d}Q + \frac{Q_{\max}}{K_d} \quad (2)$$

where  $c_0$  and  $c_f$  (µmol/L) are the initial and final concentrations of BPA,  $v$  (L) is the total volume of sample,  $m$  (g) is the mass of sorbent, and  $Q$  and  $Q_{\max}$  (µmol/g) are the adsorption amount of BPA at equilibrium and saturation stage, respectively.

For kinetic adsorption tests, 40 mg of sorbent was added in 1.0 mL of 2.0 mM BPA aqueous solution (containing 5% methanol), and then the mixtures were oscillated at 25 °C for different times (1–30 min). After rapid separation by centrifugation, the adsorption amount of BPA on sorbent was measured.

### 2.4. Solid-phase extraction

The SPE cartridge was prepared by packing 0.6 g of SiO<sub>2</sub>@MIP or SiO<sub>2</sub>@NIP into a 3-mL empty polyethylene syringe between two sieve plates, and then it was rinsed with methanol and water in

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