Talanta 162 (2017) 57–64

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Dummy molecularly imprinted magnetic nanoparticles for dispersive solid-phase extraction and determination of bisphenol A in water samples and orange juice

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ARTICLE INFO

Keywords:
Dummy molecular imprinting
Magnetic nanoparticle
Dispersive solid-phase extraction
Bisphenol A
HPLC-UV

ABSTRACT

A novel dummy molecularly imprinted magnetic nanoparticle (MI-MNP) was prepared by a hybrid imprinting technique for dispersive solid-phase extraction (d-SPE) and determination of bisphenol A (BPA). 2,2′-Bis(4-hydroxyphenyl)-hexafluoropropane was used as the template molecule and Fe_3O_4 nanoparticle as the magnetic core. The MI-MNPs were characterized by FT-IR spectroscopy, thermo- gravimetric analysis, X-ray diffraction, transmission electron microscopy, and vibrating sample magnetometer. The adsorption tests showed that the MI-MNPs had a high binding ability for BPA and presented a fast binding kinetics. When used as a d-SPE sorbent, the MI-MNP showed high extraction efficiency, high enrichment factor and good reusability for BPA, and it can be easily recycled by a magnet. Furthermore, the dummy imprinting strategy can completely avoid the interference of the residual template in sorbent to determination of BPA. Using the MI-MNPs as sorbent, a d-SPE-HPLC-UV method was developed and successfully applied to the analysis of BPA spiked in water samples and orange juice and that in a certified sample with recoveries of 95.0–106.2% (RSD=2.5–4.5%), 93.3–100.0% (RSD=1.2–5.0%) and 100.3% (RSD=3.5%), respectively. The limit of detection (S/N=3) for all samples was 0.3 ng mL^{-1}. The new MI-MNPs can be utilized as a good d-SPE sorbent for BPA in environmental water samples and beverages.

1. Introduction

Bisphenol A (BPA) is an important industrial chemical mainly used for synthesizing polycarbonate plastics, epoxy resins and polyester resins [1,2]. These polymers are widely applied in the production of food and drink containers, tableware, water pipes, thermal paper, electronic equipment and medical facilities [3,4]. Recently, it was estimated that about 100 t/year of BPA may enter environment due to landfill and plastic degradation [2]. As a result, BPA has been found in a variety of matrices, such as packed food, beverages, personal care products, paper, dust, environmental samples, and biological samples [4]. On the other hand, BPA is also well-known as an endocrine disrupting compound. Environmental and human exposure to BPA may not only cause adverse effects on the reproduction of vertebrates, antioxidant systems in plant and proteome of animal [2,3,5], but also influence human health such as reproductive effects, metabolic disorders, type 2 diabetes, obesity, cardiovascular diseases and hormone-dependent cancers [6]. Therefore, it is essential to quantitatively detect BPA in different samples for its toxic assessment.

BPA is generally present at trace concentrations in complex matrices, so the highly sensitive and selective analytical methods are required for its detection [4,7,8]. Sample pretreatment is indispensable to extraction and enrichment of BPA and removal of interferences prior to its analysis. At present, different pretreatment approaches have been used for analysis of BPA, such as solid-phase extraction (SPE), liquid-liquid extraction, dispersive liquid-liquid microextraction, coacervative microextraction, solid-phase microextraction, supramolecular solvent microextraction, stir bar sorptive extraction, pressurized liquid extraction, microwave-assisted extraction, and matrix solid phase dispersion [4,9]. Amongst these pretreatment methods, SPE is the mostly used one for BPA [4,9]. However, the conventional cartridge-based SPE usually needs a high amount (150–5000 mg) of sorbent for column packing and a high consumption of organic solvent for conditioning and elution [10].

Dispersive solid-phase extraction (d-SPE) is a new sample pretreatment technique introduced by Anastassiades et al. [11]. Compared with traditional SPE, d-SPE is time-saving, low-cost, easy to operation and low consumed for toxic organic solvent [10]. Several sorbents have

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http://dx.doi.org/10.1016/j.talanta.2016.10.007
Received 5 July 2016; Received in revised form 17 September 2016; Accepted 2 October 2016

been successfully used for d-SPE of BPA such as graphitised carbon [10], charcoal activated powder [10], primary-secondary amine [10] and C-18 bonded silica [10,12], and chitin [13]. Unfortunately, it was inconvenient to isolate these sorbent particles from the sample solution in d-SPE procedure. The use of magnetic sorbents can address this issue because they can be separated easily by an external magnetic field. At present, a variety of magnetic sorbents have been applied to the d-SPE of BPA including magnetic nylon 6 composite [14], tetraethylene- pentamine-functionalized magnetic polymer [15], ionic liquid-coated magnetic nanoparticles (MNPs) [16], aniline-polymerized magnetic microspheres [17], graphene-modified mangetic composites [18–20], hemimicelles-chemisorbed MNPs [21], and chitosan-coated magnetic microspheres [22]. However, these sorbents all suffered from their low selectivity for BPA.

Molecularly imprinted polymers (MIPs) have been widely used as highly selective sorbents for SPE due to their specific recognition ability to the template molecules [23–29]. The magnetic MIPs (MMIPs) not only can be easily isolated from sample solution, but also can greatly improve their adsorption selectivity [30,31]. Some magnetic MIPs (MMIPs) have also been used as sorbents for d-SPE of BPA. These sorbents included multiwalled-carbon-nanotubes-based MMIPs [32], dual-responsive MMIPs [33], multi-functional MMIP beads [34], MMIP microphere [35], MMIP nanoparticles [36,37], fly-ash-cenosphere-based MMIPs [38], MMIP particles [39], and restricted-access-media MMIP microspheres [40]. The main drawback of these BPA-imprinted MMIP sorbents is that the possible leakage of the residual template molecules interfere the determination of trace BPA. The dummy imprinting strategy, utilizing a structural analogue of the analyte as the imprint template to prepare MIP for recognizing the analyte molecules, can effectively avoid this interference [41,42].

In this work, a new type of dummy molecularly imprinted magnetic nanoparticles (MI-MNPs) was prepared by a hybrid imprinting method for the d-SPE of BPA. The MI-MNPs were characterized by several techniques, and then their adsorption and d-SPE abilities for BPA were studied. Finally, using the new MI-MNPs as sorbents, a d-SPE-HPLC-UV method was developed and successfully applied to determination of trace BPA in real water samples and orange juice.

2. Experimental

2.1. Chemicals and materials

$FeCl_2 \cdot 4H_2O$ (98%) and $FeCl_3$ (97%) were all of analytical grade supplied by Tianjin Institute of Fine Chemicals (Tianjin, China). 2,2′-Bis(4-hydroxyphenyl)- hexafluoropropane (BPAF, 95%), bisphenol A (BPA, 96%), dibutyltindilaurate (98%) and tetrahydrofuran (superdry, 99.5%) were obtained from J & K Scientific LTD (Beijing, China). 3-(Triethyloxysily)propyl isocyanate (ICPTES, 95%) was purchased from TCI (Tokyo, Japan). Tetraethoxysilane (TEOS, 99%) was bought from Alfa Aesar (Tianjin, China). BPA standard sample (Catalog No. M-1626-01S, with certified concentration of 990 μg mL^{-1} in methanol) was bought from Accu Standard (New Haven, CT, USA). 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.

2.2. Preparation of MI-MNPs

The $Fe_3O_4@SiO_2$ magnetic nanoparticles (MNPs) were prepared as previously reported [43]. The template-monomer covalent complex (BPAF-Si) was synthesized for the hybrid imprinting *via* reaction of BPAF and ICPTES according to our recent works [41,42].

After that, BPAF-Si (0.553 g, 0.77 mmol) and TEOS (1.93 mL, 8.6 mmol) were first dissolved in 7 mL of methanol, and then 0.5 g of $Fe_4O_3@SiO_2$ MNPs were added, followed by ultrasonic treatment for 5 min. Subsequently, 0.5 mL of 1 mol L^{-1} acetic acid (HAc) was added, and the mixture were mechanically stirred at room temperature for 24 h. After the resultant particles were isolated by a magnet, washed three times with methanol and dried at 120 °C for 24 h, the template-incorporated MNPs were obtained, which were called as $Fe_4O_3@SiO_2@$MIP-T.

To remove the template, the obtained $Fe_4O_3@SiO_2@$MIP-T MNPs were suspended in the mixture of DMSO and water (5:1, v/v). After the mixtures were heated at 160 °C for 5 h, the resultant particles were rinsed four times with ethanol and ultrapure water alternately and then dried at 120 °C for 24 h. The final MI-MNPs, called as $Fe_4O_3@SiO_2@$MIP, were obtained.

For comparison, the non-imprinted MNPs (NI-MIPs), called as $Fe_4O_3@SiO_2@$NIP, were also prepared through the similar procedure except that BPAF-Si was replaced by ICPTES (0.379 g, 1.54 mmol).

2.3. Characterization of MI-MNPs

FT-IR spectra were collected using a Nicolet Avatar 360 FT-IR spectrometer (Thermo Fisher Scientific, USA) within a scan range of 4000–500 cm^{-1}. Transmission electron microscopy (TEM) images were obtained on a JEM-2010 (Japanese Electronic Optical Co., LTD, Japan). Thermo-gravimetric analysis (TGA) data were analyzed on a TGA/DSC 1 Thermal Analyzer (Mettler Toledo, Switzerland). X-ray diffraction (XRD) patterns were recorded on a Philips X′Pert PRO SUPER X-ray diffractometer (X′ Pert PRO, Holland Philips) using monochromated Cu Kα irradiation (λ=1.5418 Å). Magnetic property was measured by a Model 7407 Vibrating Sample Magnetometer (VSM, Lake Shore Cryotronics Inc., USA).

2.4. Adsorption experiments

In static adsorption tests, 20 mg of sorbent (MI-MNPs or NI-MNPs) was added in 1 mL of BPA aqueous solution (containing 25% methanol) with a concentration range of 0.05–4.0 mmol L^{-1}, followed by ultrasonic treatment for dispersion. The mixtures were shaken continually in a thermostatic bath at 25 °C for 4 h. After the sorbent was separated by a magnet, the concentration of BPA in the supernatant was determined by HPLC method.

The adsorption capacity and the dissociation constant (K_d, μmol L^{-1}) were obtained according to the Eqs. (1) and (2) [41,42]:

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

$$\frac{Q}{c_f} = -\frac{1}{K_d}Q + \frac{Q_{max}}{K_d} \tag{2}$$

where c_0 (μmol L^{-1}) and c_f (μmol L^{-1}) are the initial and final concentrations of BPA, v (L) is the total volume of sample, m (g) is the mass of sorbent, Q and Q_{max} (μmol L^{-1}) are the adsorption amount of BPA at equilibrium and saturation stage, respectively.

In the kinetic adsorption test, 20 mg of sorbent was added in 1.0 mL of 4 mmol L^{-1} BPA aqueous solution (containing 25% methanol), and then the mixtures were oscillated at 25 °C for different time (1–10 min). After the sorbent was rapidly isolated by a magnet, the adsorption amount of BPA on sorbent was measured.

2.5. d-SPE experiment

One hundred milligram of MI-MNPs were added into 15 mL of BPA aqueous solution (containing 5% methanol) with different concentration (5, 10, 20, 30, 50 or 100 ng mL^{-1}), followed by ultrasonic treatment for dispersion. After that, the mixtures were shaken at 25 °C for 1 h. After separated from the mixtures by a magnet, the MI-MNPs were eluted by 2 mL of methanol, and then the solvent in the effluent was evaporated to dryness by nitrogen. Finally, the dry