Preparation and evaluation of magnetic core-shell mesoporous molecularly imprinted polymers for selective adsorption of tetrabromobisphenol S

Xuemei Wang[a,b,*], Pengfei Huang[a], Xiaomin Ma[a], Huan Wang[a], Xiaoquan Lu[a,b], Xinzhen Du[a,b]

[a] College of Chemistry and Chemical Engineering, Northwest Normal University, PR China
[b] Key Laboratory of Bioelectrochemistry & Environmental Analysis of Gansu Province, Lanzhou 730070, PR China

ARTICLE INFO

ABSTRACT

Novel magnetic mesoporous molecularly imprinted polymers (MMIPs) with core-shell structure were prepared by simple surface molecular imprinting polymerization using tetrabromobisphenol-S (TBBPS) as the template. The MMIPs-TBBPS were characterized by fourier-transform infrared spectrometry (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 adsorption-desorption transmission, and vibrating sample magnetometry. The resultant MMIPs-TBBPS were successfully applied magnetic solid-phase extraction (MSPE) coupled with HPLC determination of TBBPS in spiked real water samples with recoveries of 77.8–88.9%. The adsorption experiments showed that the binding capacity of MMIPs-TBBPS to TBBPS and six structural analogs were significantly higher than that of the magnetic nonimprinted polymers (MNIPs). Meanwhile, the MMIPs-TBBPS possessed rapid binding affinity, excellent magnetic response, specific selectivity and high adsorption capacity toward TBBPS with a maximum adsorption capacity of 1626.8 µg g^{-1}. The analytical results indicate that the MMIPs-TBBPS are promising materials for selective separation and fast enrichment of TBBPS from complicated enviromental samples.

1. Introduction

Brominated flame retardants (BFRs) are a broad class of additive and reactive substances and technical mixtures used in print circuit boards, plastics, etc [1]. Tetrabromobisphenol-S (TBBPS) as a new type of BFRs has been widely used for preparation of various heat-resistant products [2,3]. TBBPS and commercially analogs, such as tetrabromo-bisphenol-A (TBBPA), TBBPA bis(allyl ether) (TBBPA-ae), TBBPA bis(2,3-dibromopropyl ether) (TBBPA-dbpe), and TBBPS bis(tetrabromobisphenol-SA 2,3-dibromopropyl ether) (TBBPS-dbpe), have been found in soil, dust, sewage sludge, and eggs, with the highest observed concentration being 9.96 µg g^{-1} dry weight [4–8]. Studies showed trace TBBPS can result in carcinogenic effect, hepatotoxicity, and disruption of endocrine system [9]. Therefore, it is very important to determine of the concentration of TBBPS and its derivatives in environment and minimize of the exposure and health risk of them. At present, gas chromatography coupled with mass spectrometry (GC-MS), atmospheric pressure photoionization mass spectrometry (APPI-MS/MS), and reactive extractive electrospray ionization tandem mass spectrometry (EESI-MS/MS) methods for detection of TBBPS and its derivatives in complex samples have already been reported [10,11]. However, due to relatively low concentration and complex matrices, sample

pretreatment has become an inevitable procedure prior to instrumental analysis. Thus, the investigation of convenient pretreatment, separation and enrichment methods with high efficiency and selectivity is particularly important for the analysis and removal of trace TBBPS.

Molecular imprinting technology is an attractive method for molecular recognition with high sensibility and selectivity. The technology has been extensively applied in biomimetic sensors [12], solid-phase extraction [13], chromatography [14], and separation or enrichment [15,16]. Three-dimensional cavities formed during the synthesis process of molecularly imprinted polymers (MIPs) are complementary to the template in terms of shape recognition, size, hydrogen bonding, and functional groups enabling the re-identification of target molecules. Thus, MIPs become promising and facile adsorption materials for separation procedures and chemical analyses during sample pretreatment [17–19]. However, the separation of MIPs from sample matrix requires a series of post-treatments, including crushing, sieving, and high speed centrifugation. Given the heterogeneous internal distribution of binding sites, the mass transfer of target molecules from solution to cavities is obstructed by the adsorption of the template on the surface of MIPs, which causes low binding affinity, time and labor consuming [20,21]. To overcome these problems, magnetic molecularly imprinted polymers (MMIPs) has been applied for sample

---

pretreatment, in which most of the binding sites on the surface of polymers are exposed to facilitate the recognition and removal of the template [22–25]. In addition, apart from the advantages of high affinity and specificity of MIPs, MMIPs can be rapidly and easily separated using an external magnetic field with high efficiency and low cost.

In this study, we developed a novel magnetic mesoporous MIPs with core-shell structure (MMIPs-TBBPS) by Fe_3O_4 nanoparticles as magnetic cores, mesoporous polymers as shell and TBBPS as the template molecule. The MMIPs-TBBPS were prepared successfully by simple surface molecular imprinting polymerization using tetrathyl orthosilicate (TEOS) as the cross-linker and 3-ammonia propyl triethoxy silane (APTES) as functional monomer. The polymers were applied to the sorbent materials of magnetic solid-phase extraction (MSPE) coupled with HPLC for the selective adsorption and determination of TBBPS in real samples. Adsorption results showed that the MMIPs-TBBPS possessed special selectivity and high adsorption capacity toward TBBPS with maximum adsorption capacity compared with the MNIPs. The characteristics, selectivity and application of the MMIPs-TBBPS were investigated in detail. The process of this work was depicted in Graphical Abstract.

2. Experimental

2.1. Materials and chemicals

BPA, TBBPA, tetrabromobisphenol-A-bis (allyl ether) (TBBPA-ae), tetrabromobisphenol-A-bis (2,3-dibromopropyl ether) (TBBPA-dbpe), TBBP-A bis (2-hydroxyethyl ether) (TBBPA-hee) were obtained from Sigma-Aldrich. Tetrabromobisphenol S (TBBPS), TBBPS bis(2,3-dibromopropyl ether) (TBBPS-dbpe) were from Beijing APIS Biotechnology LTD., the structures of the seven BFRs were given in Table S-1.

Iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ethylene glycol (EG), poly(ethylene glycol)–20000 (PEG-20000), sodium acetate anydrous (NaAc), tetraethylorthosili-cate (TEOS), ammonium hydroxide, acetic acid and ethanol of analytical grade were obtained from Shanghai Chemical Corporation. 3-ammonia propyl triethoxy silane (APTES) was purchased from Aladdin Chemical Corporation (Shanghai, China). Methanol and acetonitrile of chromatography grade were purchased from Thermo Fisher Scientific China Ltd. (Shanghai, China). Deionized water in the experiment were prepared by Aquapro Water Purification System (Chongqing, China).

The stock solutions of 100 mg L^{-1} TBBPS and its derivatives were prepared in methanol and stored in amber bottles in the refrigerator at 4 °C. The standard working solutions were prepared by diluting the stock solution with methanol to the required concentration. Four real samples were collected from the upstream and downstream of East River (Industrial wastewater) and West River (Domestic sewage) (Baiyin, Gansu Province, China), tap water was from our lab. All these samples were filtrated through 0.45 μm glass fiber membrane (Automatic Science, China) and stored in brown glass bottles at 4 °C.

2.2. Instrument and chromatographic conditions

FT-IR spectra were recorded on a Digilab FTS3000 FTIR spectrometer using the KBr wafer technique. SEM images were recorded on a ULTRA Plus (Germany Zeiss), operated under high vacuum conditions, to visualize the morphology and size distribution of the particles. TEM were conducted on Tecnai G2 F20 (FEI, USA) with an accelerating voltage of 80 kV was used. Carbon coated copper grids were used for the TEM sample preparation. Nitrogen adsorption-desorption isotherms were performed at 77 K on a Quantachrome AS1Win™. The specific surface area was calculated from the adsorption-desorption isotherm by using the Brunauer-Emmet-Teller (BET) equation and the pore size was calculated from the adsorption isotherm by applying the

Barret-Joyner-Halenda (BJH) method. Magnetization measurements were carried out using a Vibrating Sample Magnetometer (VSM, Lakeshore, 735 VSM Controller) under applied magnetic field at room temperature. Oscillation in extraction procedure was performed by a SHZ-82A environmental incubator shaker (Changzhou Guohua Electric Co., Ltd, China).

The Agilent 1260 series HPLC-UV system (Agilent Technologies, USA) with a variable wavelength detector and a reverse phase C_{18} HPLC column (5 μm, 150 mm×4.6 mm) were used for quantitative analysis. The mobile phase at a flow rate of 1 mL min^{-1} was mixture of water (component A) and acetonitrile (component B) with gradient elution of 0–3.0 min 20% A, 80% B; 3.0–10.5 min 0% A, 100% B; 10.5 min stop. The full scan of ultraviolet spectra of TBBPS and its derivatives have been checked, 214 nm was optimum absorb wavelength for most compound. Therefore, the wavelength of UV detector was set at 214 nm and the sample injection volume was 20 μL.

2.3. Preparation of magnetic microspheres

Monodisperse magnetite (Fe_3O_4) were prepared by solvothermal reduction method according to previous report [26]. In brief, 5.4 g $FeCl_3 \cdot 6H_2O$ was dissolved in 160 mL EG to form a clear solution, followed by the addition of 14.4 g NaAc and 4.0 g PEG 10000. The mixture was stirred vigorously for 30 min then sealed in a Teflon lined stainless-steel autoclave. The autoclave was maintained at 200 °C for 48 h, and then cooled to room temperature. The black Fe_3O_4 were washed several times with ethanol and dried at 60 °C for 3 h.

2.4. Preparation of magnetic core-shell mesoporous MIPs (MMIPs-TBBPS)

Briefly, 0.283 g of TBBPS and 2 mL of APTES were dissolved in 10 mL of methanol solution and kept 2 h at room temperature (named as Solution 1). 0.2 g of Fe_3O_4 nanoparticles were dispersed 60 mL of methanol and 10 mL of distilled water and dissolved by sonication, afterwards, 4 mL of TEOS and 1 mL of ammonium hydroxide (28%) were mixed under mechanical stirring at room temperature for 5 min, solution 1 were subsequently added into this mixture under vigorous stirring at room temperature for 1 h. The resulted product was collected by an external magnet and washed with ethanol and deionized water and dried at 60 °C. Subsequently, the dried product was eluted using a Soxhlet apparatus with methanol/acetic acid (9:1, v/v) at 117 °C for 48 h to remove template molecules. The resulting product (MMIPs-TBBPS) was repeatedly washed with high-purity water and then dried at 60 °C under vacuum. The MNIPs were prepared following the same procedure but in the absence of template molecules (TBBPS).

2.5. Binding experiment

The adsorption capability for MMIPs-TBBPS and MNIPs were determined by the following procedure. 8 mg of MMIPs-TBBPS (or MNIPs) was added into the centrifuge tubes containing 15 mL of methanol/water (3/7, v/v) solution (because of its low solubility in water) with TBBPS concentration varying from 0.10 to 6.0 μg mL^{-1} and shaken with 50 r min^{-1} for 30 min at 30 °C. The supernatant and polymer were separated by a permanent magnet. The concentration of TBBPS in the supernatant was measured by HPLC. According to the TBBPS concentration before and after adsorption, the equilibrium amount of substrate bound to the polymer (Q, μg g^{-1}) was calculated by following Eq. (1):

$$Q = \frac{(C_0 - C_e) \times V}{W} \tag{1}$$

where C_0 and C_e represent the initial and equilibrium concentrations (μg mL^{-1}) of TBBPS, respectively, V (mL) is the solution volume, and