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Selective and simultaneous extraction and determination of hydroxybenzoic acids in aqueous solution by magnetic molecularly imprinted polymers

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HIGHLIGHTS

- Novel MMIPs were prepared to selectively remove hydroxybenzoic acids from aqueous solution.
- Sorption capacities of two MMIPs based on BA and 4-HBA as templates were compared.
- Molecular analog degree and stereochemistry affect their adsorption capacities.
- Two MMIPs were favorable to remove hydroxybenzoic acids from real sample.

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ABSTRACT

Two novel magnetic molecularly imprinted polymers (MMIPs) based on benzonic acid (BA)/4-hydroxybenzoic acid (4-HBA) as template have been successfully developed to selectively and simultaneously extract and determine five hydroxybenzoic acids [BA, 4-HBA, salicylic acid (SA), protocatechuic acid (PCA), and gallic acid (GA)] in aqueous solution. Various parameters affecting adsorption/desorption behavior are evaluated for achieving optimal recovery. Under optimum conditions, adsorption process between MA/4-HBA and MMIPs follows Langumuir adsorption isotherm and pseudo-second-order reaction kinetics. Thermodynamic parameters reveal that adsorption process is spontaneous, endothermic and entropy driven one. Both MMIPs show high adsorption capacity, good selectivity, rapid kinetic binding (40 min) and magnetic separation (10 s), favorable reproducibility (RSD < 4% for batch-to-batch evaluation), and stability (only 6% decrease after six cycles). The adsorption capacities of 4-HBA, PCA and GA on 4-HBA-MMIPs are higher because of higher molecular analog degree to template, whereas BA and SA with higher capacities on BA-MMIPs are observed. Spiked recoveries of five hydroxybenzoic acids on BA-MMIPs and 4-HBA-MMIPs range from 83.2% to 103.0% with RSD less than 6.9%. Results demonstrate that both resulting MMIPs could be reliably applied to direct extraction and determination of hydroxybenzoic acids from real aqueous solution.

1. Introduction

Efficient extraction and determination of hazardous pollutants (e.g. organic aromatic compounds and inorganic heavy metals) from wastewaters or environmental water is a significant concern to ecosystem and human health due to their high toxicity and very slow biodegradation [1]. Several hydroxybenzoic acids, such as benzoic acid (BA), 4-hydroxybenzoic acid (4-HBA), salicylic acid (SA), protocatechuic acid (PCA), and gallic acid (GA), are widely used pharmaceutical intermediates, chemical preservatives in cosmetics, pharmaceutical and personal care products, and foodstuffs, or always produced from some agroindustrial activities (e.g. manufacturing of olive oil, wine, and spirits) [2–5]. Hydroxybenzoic acids are now extensively studied organic pollutants on the basis of their potential toxicities on plants, animals and human beings [6–7]. Given the presence of a large variety of contamination sources for hydroxybenzoic acids, effective separation methods are required. A large number of physical [5–6], biological [8] and chemical [9–10] methods have been employed to remove hydroxybenzoic acids from aqueous solution. Among them, adsorption-based process based on broad range of sorbents (e.g. normal-phase and reversed-phase [11–12], activated carbon [5,13], synthesized polymeric sorbents [4,11,14], hydrotalcites [6], mesoporous materials [3,15], and MIPs [16–18]) is the most

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attractive and widely used method due to its efficacy, practicality and economic feasibility. Adsorption capacity of hydroxybenzoic acids on synthesized polymeric sorbents and mesoporous materials is over 100 mg/g [4,11,14,15], however, the basic disadvantage of them is lack of selectivity for extraction of hydroxybenzoic acids from complicated matrix, and then the interferences make it difficult to quantify target hydroxybenzoic acids efficiently. Moreover, the nonselective properties of sorbents decrease their adsorption efficiency because of the existence of competition between hydroxybenzoic acids and other high-abundance compounds.

MIPs are relatively novel selective and specific materials, which are achieved by copolymerizing functional and cross-linking monomers in the presence of template. Once the template is removed, complementary microcavities with special size, shape and functionality are obtained that allow rebinding the template and some structurally related compounds by either non-covalent interactions or reversible covalent interactions with high specificity. Therefore, compared to some commercial sorbents (e.g. C_{18}, mesoporous/macroporous resin), MIPs have high selectivity for isolation of predetermined components (especially for low-abundance components) with high recovery and matrix clean-up from complex mixtures (e.g. environmental and biological samples [19–20], food [21], and natural products [22]). Another powerful feature of MIPs is that the reversible adsorption provides consecutive operations without the obvious loss of binding capacity, as showcased by Madrakian and coworkers in the repeated extraction of tramadol from urine samples [23].

Surface imprinted polymers have been suggested for improving homogeneous distribution of binding sites, small diffusion resistance, which result in large extraction capacity [24]. Up to now, surface imprinted polymers have been developed on the different surfaces, such as silica particles [25], carbon nanotubes [26], titanium dioxide particles [27], polymeric supports [28] and magnetic nanoparticles/microspheres [29]. It is noted that magnetic materials (e.g., Fe_3O_4) possess significant advantages including but not limited to high supermagnetism for easy separation. Then, MMIPs can be dispersed in solutions and rapidly separated under external magnetic field, which will avoid the column-packing procedure or centrifugation procedure, and then make the pretreatment step simple [30]. On the other hand, the core–shell magnetic MIPs (e.g. Fe_3O_4 as core and SiO_2 as shell) can be better designed to enhance the biocompatibility and stability of MMIPs [31].

In this study, we first synthesize two MMIPs using BA/4-HBA as template. The characterization, adsorption capacities, selectivity, reproducibility and stability of two MMIPs are investigated and compared. The amenability of the MMIPs for real river water is explored. This proposed protocol has been proved to enable the reliable, effective and selective extraction and determination of hydroxybenzoic acid from aqueous solution.

2. Materials and methods

2.1. Chemicals and reagents

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), polyethylene glycol 6000 (PEG 6000), 2,2-azobis(isobutyronitrile) (AIBN), tetraethoxysilane (TEOS), and HPLC grade methanol were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Ethylene glycol dimethacrylate (EGDMA), methacrylic acid (MAA), acrylamide (AA), 4-vinylpyridine (4-VP) and 3-(trimethoxysily) propyl methacrylate (MPS) were acquired from Shaen Chemical Technology Co., Ltd. (Shanghai, China). Sodium acetate, anhydrous ethanol, anhydrous methanol, acetic acid, anhydrous acetonitrile, anhydrous tetrahydrofuran, ammonium hydroxide, and ethylene glycol were purchased from KeMiOu Chemicals Co., Ltd. (Tianjin, Chain). BA, 4-HBA, SA, PCA, and GA with purities over 99% were obtained from the National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Ultrapure water (18.2 MΩ), collected from a Milli-Q water purification system (Millipore, Bedford, MA, USA), was used to prepare all aqueous solutions. The other reagents were of analytical grade.

2.2. Apparatus and conditions

Transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan) was used to investigate the morphology of microspheres. The infrared spectrum was recorded on a Fourier transform infrared spectrometer (FT-IR) (Nicolet 6700, Thermo Nicolet Corp., Waltham, MA, USA) in the wavelength range of 4000–400 cm^{-1}. The average values of the particle size and polydispersity of microspheres were determined by a particle size analysis (PSA) (Malvern Instruments Ltd., Malvern, UK). The identification of crystalline phase was performed using powder X-ray diffractometer (Rigaku RINT 2500, Rigaku Corporation, Japan) with Cu/Ka radiation at 30 mA, 40 kV. The encapsulation efficiency of microspheres was measured by thermogravimetric analysis (TGA, SDTQ600, TA, USA). The Brunauer–Emmett–Teller (BET) surface area was detected by a Micromeritics ASAP 2020 device (Micromeritics, Norcross GA, USA). Magnetization was measured at room temperature in a vibration sample magnetometer (VSM7307, Lake Shore, USA).

HPLC analysis was performed on an Agilent 1260 HPLC system (Agilent Technologies, Santa Clara, CA), consisting of a high-pressure quaternary pump, an online vacuum degasser, an autosampler, and a diode array detector. Isocratic chromatography was performed on a Zorbax SB-C_{18} column (150 mm × 4.6 mm i.d., 5 μm, Agilent Technologies, Santa Clara, CA) in tandem with a Phenomenex C_{18} guard cartridge (4.0 mm × 3.0 mm, Phenomenex, Torrance, CA). The mobile phase was a methanol/water (V/V = 50/50) mixture containing 0.4% acetic acid. Flow rate was set at 0.8 ml/min while the temperature was controlled at 298 K. The autosampler injection volume was fixed at 5 μl. Spectra were recorded from 190 to 400 nm (peak width 0.2 min and data rate 1.25 s^{-1}) while the chromatogram was acquired at 260 nm.

2.3. Synthesis procedures of MMIPs

The preparation protocol is shown in Fig. 1. At first, Fe_3O_4 microspheres were synthesized according to our previous literature with minor modifications [32]. Briefly, $FeCl_3 \cdot 6H_2O$ (1.35 g), sodium acetate anhydrous (3.60 g) and PEG 6000 (1.00 g) were dissolved in 40 ml of ethylene glycol. The mixtures were stirred vigorously for 30 min to acquire a transparent solution and then sealed in a Teflon lined stainless steel autoclave to be heated at 200 °C for 8 h. Fe_3O_4 microspheres were then separated magnetically and sequentially washed with ethanol and water and dried overnight. Fe_3O_4 microspheres were covered with SiO_2 by hydrolysis of TEOS based on the previous report [33]. Typically, Fe_3O_4 microspheres (300.0 mg) were dispersed in 200.0 ml of 80% ethanol by sonication for 15 min, and then ammonium hydroxide (5.0 ml) and TEOS (0.7 ml) were continuously added. The mixtures were stirred at 40 °C for 12 h. Then the $Fe_3O_4@SiO_2$ composite particles were collected magnetically, washed with water thoroughly, and dried in vacuum. After that, the $Fe_3O_4@SiO_2$ microspheres were modified by vinyl groups: $Fe_3O_4@SiO_2$ microspheres (250.0 mg) were dissolved in MPS solution (150.0 μl of MPS dispersed in 40.0 ml of water containing 10% acetic acid), and the mixtures reacted at 60 °C for 5 h with continual stirring [33]. Then the vinyl-modified $Fe_3O_4@SiO_2$ microspheres were magnetically gathered, repeatedly washed with water and dried in vacuum for 12 h.