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Molecularly imprinted hollow spheres for the solid phase extraction of estrogens

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ABSTRACT

Solid phase extraction (SPE) is widely used in many different areas, such as environmental, biological, and food analysis, where cleaning and pre-concentration of samples are key steps in the analytical protocol. New materials have significant impact on the development of solid phase extraction. In this paper, monodispersed molecularly imprinted hollow spheres (MIHSs) of β-estradiol (E2) were synthesized using silica nanospheres particles as the sacrificial matrix. Compared to the corresponding non-imprinted hollow spheres (NIHSs), the MIHSs with uniform size of 290 nm have outstanding affinity in aqueous solution. Static saturation adsorption required only 15 min to achieve equilibrium, with a binding capacity (Q_{max}) of 44.5 μmol g^{-1}. The extraction of E2, ethinyl estradiol (EE), diethylstilbestrol (DES), ethisterone (ES) and estrone (E1) from water samples by MIHSs was also investigated. In the spiked samples of tap water, Qinghe river water and Zhanjiang river water, more than 90.42% of E2, but less than 79% of EE, DES, ES and E1 were recovered. The limits of detection (LOD) ranged from 0.1 to 0.26 μmol L^{-1} after solid phase extraction by MIHSs and HPLC–UV analysis. The adsorption capacity of the MIHSs showed no significant deterioration after six rounds of regeneration.

1. Introduction

β-Estradiol (E2) interferes with hormonal functions and can increase the incidence of cancer even at extremely low concentrations [1–7]. However, this harmful endocrine disruptor compound (EDC) has been found in domestic waste effluent and surface water [8–11]. Numerous analytical methods, including mass spectrometry [12], GC–MS [13,14], UPLC [15,16], HPLC–MS [17,18] and chemiluminescence [19–22] have been applied to monitor E2 and other EDCs. Owing to the low abundance of EDCs in environmental matrixes, clean-up and pre-concentration procedures are commonly performed prior to the analysis.

Solid phase extraction (SPE) is the most widely used pre-concentration method due to its convenience, good recovery and low cost. Among the numerous sorbents for SPE, molecularly imprinted polymers (MIPs) are distinctive for their higher sample load capacity, physical robustness, as well as low cost and ease of preparation. These selective absorbents are widely used in a large variety of applications to remove target compounds from mixtures of structural analogs [23–26]. There have been a number of estrogen extractions using MIPs-SPE. Meng et al. [27] described a simple approach to prepare synthetic receptors for estrogenic compounds using a noncovalent molecular imprinting technique. The MIPs exhibited high binding affinity towards related estrogenic compounds and could be used for the removal of estrogenic pollutants from wastewater (in 2005). Lucci et al. [1] proposed a method for the clean-up and pre-concentration of estrogens from aqueous samples using an EGDMA based MIP; the molecularly imprinted SPE showed higher recoveries than the commercially available C18 SPE (in 2011). Schillinger et al. [28] prepared a polymeric sorbent by terpolymer imprinting using E2 as template. Binding tests revealed that imprinted polymers exhibited higher affinity to E2 compared to the nonimprinted polymer (NIPs) (in 2012). However, traditional MIPs bulk polymers have disadvantages including long response times and low capacity [29–32]. The concept of surface imprinting was proposed to generate accessible binding sites on the imprinted matrix. Jiang et al. [33] prepared a molecularly imprinted amino-functionalized silica gel sorbent as a SPE sorbent, which showed high selectivity and absorption capacity to DES (in 2008). Wang et al. [34] reported that magnetic nanoparticles with MIPs had good adsorption properties (in 2011). Compared to traditional MIPs, these surface

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imprinted polymers improved separation efficiency, but their long equilibration time have prevented their wide spread applications.

Herein we report a simple method to synthesize molecularly imprinted hollow spheres (MIHSs) using silica nanospheres as the sacrificial matrix. The template is readily removed to produce monodispersed MIHSs that have fast mass transfer rates. Moreover, the MIHSs were successfully applied to solid phase extraction of E2 from different water samples.

2. Experimental section

2.1. Materials

Ethinyl estradiol (EE), β-estradiol (E2), diethylstilbestrolum (DES), ethisterone (ES), estrone (E1) and ethylene glycol dimethylacrylate (EDGMA) were purchased from TCI (Tokyo, Japan). 3-(Trimethoxysilyl)propylmethacrylate (KH-570, 98%), 2,2′-azobis-(2,4-dimethylvaleronitrile) (ADVN) and tetraethoxysilane (TEOS, 99%) were purchased from Aladdin (Shanghai, China). Methacrylic acid was obtained from Bodi Chemical Co. (Tianjin, China). Toluene, acetonitrile, triethylamine, hydrofluoric acid, ammonium hydroxide (25–28%) and anhydrous ethanol were obtained from Beijing Chemical Plant. Deionized water was produced from a MilliQ-R04 purification system (Millipore, Germany).

2.2. Instruments

A HITACHI S-4800 scanning electron microscope (HITACHI Co., Japan) and a JEOL JEM-1200EX transmission electron microscope (JEOL, Japan) were used to inspect the morphologies of silica and MIHSs. A Shimazu Prominence LC-20A HPLC (Kyoto, Japan) with an Acclaim 120-C18 column (Dionex, USA, 5 μm, 120 Å, 4.6 × 250 mm^2) and UV detector was used to determine the concentrations of estrogens.

2.3. Preparation of the MIHSs

Monodispersed silica colloidal particles were prepared according to the *Stöber* method [35]. Colloidal silica (1 g) was dispersed into toluene (40 mL), and then KH570 (2 mL) dispersed in toluene (20 mL) was added to the suspension dropwise over 10 min. After refluxing at 90 °C for 24 h, the modified nanospheres were collected via centrifugation and washed with acetone (30 mL) and ethanol (30 mL) three times respectively. For a typical imprinting, E2 (0.2 mmol) and MAA (1.2 mmol) in 40 mL were mixed in acetonitrile (40 mL), followed by the addition of modified silica nanospheres (129.3 mg), EDGMA (6 mmol) and ADVN (0.072 mmol) as cross-linker and initiator respectively. The mixture was thoroughly purged with nitrogen for 15 min and then polymerized at 65 °C for 24 h. The resulting nanospheres were collected via centrifugation, washed with methanol (30 mL) to remove unreacted monomers. The silica matrix and template were removed by hydrofluoric acid/ethanol (2/98, v/v) and methanol/acetic acid (8/2, v/v) respectively [36]. MIHSs with E2 "footprints" were obtained (Fig. 1). The corresponding non-imprinted hollow spheres (NIHSs) were prepared in the same manner in the absence of E2, and the solid MIPs were prepared in the same manner without sacrificing the silica spheres.

2.4. Adsorption of E2 on the MIHSs

MIHSs (10 mg) was suspended in methanol/water (4/6, v/v, 1.0 mL) containing different amount of E2. The mixture was

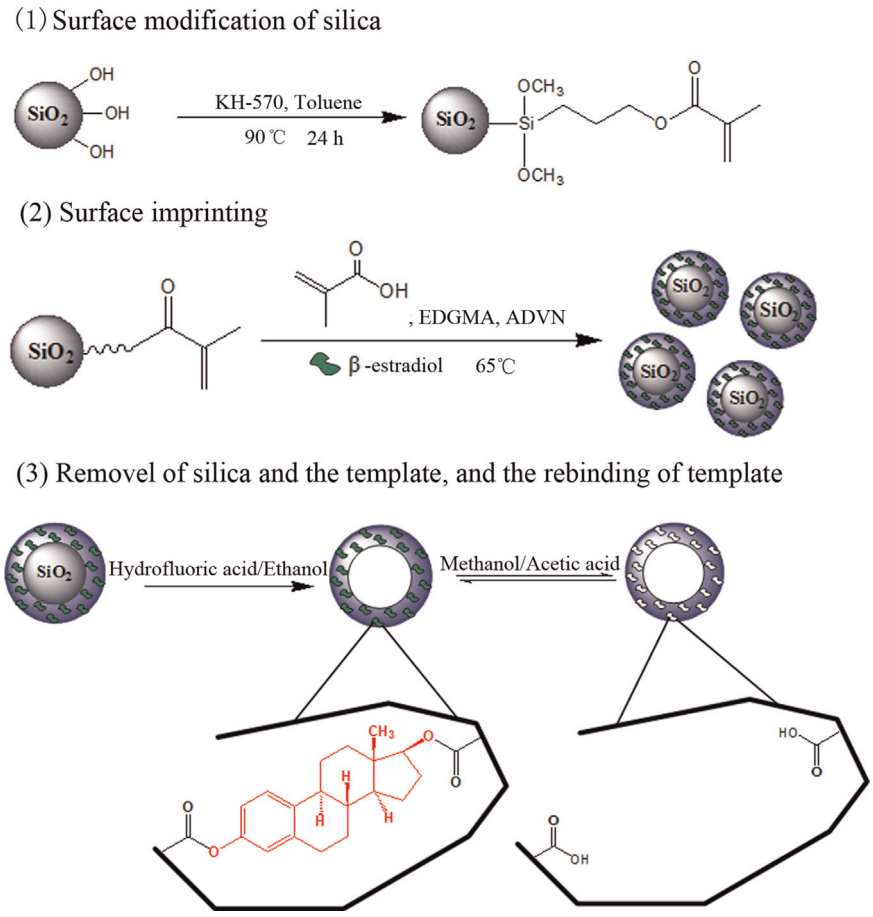

Fig. 1. Schematic of the preparation of MIHSs.