



Mesoporous structured estrone imprinted $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$ for highly sensitive and selective detection of estrogens from water samples by HPLC

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ABSTRACT

In the present work, mesoporous structured estrone (E1) imprinted $\text{Fe}_3\text{O}_4@\text{SiO}_2@m\text{SiO}_2$ (MM-MIPs) was prepared and applied as extraction sorbent for selective pre-concentration and specific recognition of E1, 17 β -estradiol (E2) and estriol (E3) from water samples. MM-MIPs present higher binding capacity, faster mass transfer and higher extraction efficiency for three estrogens than the non-porous structured $\text{Fe}_3\text{O}_4@\text{SiO}_2$. Application of MM-MIPs to dispersive solid phase extraction of three estrogens from spiked tap, river and lake water samples at 0.5, 1.0, 10 $\mu\text{g L}^{-1}$ resulted in good recoveries ranging from 85% to 95% with relative standard deviation values lower than 6.0% in all cases. Limits of detection were in the range of 0.086–0.43 $\mu\text{g L}^{-1}$. The extraction method based on MM-MIPs proved to be a highly-effective enrichment method with enrichment factor about 1700, which is much higher than the value nearly 620 obtained by non-mesoporous $\text{Fe}_3\text{O}_4@\text{SiO}_2$, during the process of simultaneous separation and sensitive determination of estrogens in complicated water samples. Furthermore, the mesoporous silica could be expanded to imprint other compounds.

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1. Introduction

Endocrine disrupting chemicals (EDCs) in water bodies have gained global attention because they may cause adverse effects in aquatic and humans even at low concentrations. Estrogens, as one kind of EDCs, are a group of steroidal hormones, which can adversely affect humans and animals at low concentrations due to their high estrogenic activities. Among those estrogens the prominent compounds are estrone (E1), 17 β -estradiol (E2) and estriol (E3). Currently, liquid chromatography coupled with tandem mass spectrometry is the most employed analytical tool to determine estrogens in many different sources [1]. Considering the low concentration of estrogenic compounds in environmental matrices, improving detection sensitivity is a major analytical challenge. Several sample pretreatment methods, such as solid-phase extraction [2], solid-phase micro-extraction [3], dispersive solid-phase extraction [4] and liquid-phase micro-extraction [5], etc. have been established for clean-up and pre-concentration of these compounds. Low selectivity is the main drawback of conventional extraction sorbents, which resulted in co-extraction of interfering matrix components. Selective extraction can be achieved using

molecularly imprinted polymers (MIPs) as extraction sorbents.

Molecular imprinting technique provides an effective method to construct tailor-made binding sites for a given target or group of target molecules. Due to the higher selectivity, mechanical and chemical stability, easy preparation and low cost, MIPs have been proposed for extraction [6,7], chemical sensors [8,9] and selective photo-degradation [10,11]. MIPs were also used to remove of EDCs from diverse samples [12–16]. Although MIPs prepared by bulk or precipitation polymerization exhibit high selectivity, they still suffer some intrinsic limitations, such as heterogeneous distribution of the binding sites and poor site accessibility. Many strategies like surface imprinting [14–16] and porous MIPs preparation [17,18] have been proposed to solve those problems.

Mesoporous materials, with controllable pore size and particle size, large pore volume and surface area, show versatile applications in separation [19], controlled drug delivery [20], and nanocarriers [21]. Mesoporous materials also are good imprinting matrix candidates. An imprinting cavity in nano-thick matrix wall would offer more accessible binding sites for the target molecule. In addition, the rigid structure of mesoporous materials is highly suitable for formation of recognition site. Considering the advantages of mesoporous materials, diethylstilbestrol [22] and copper ion [23] imprinted mesoporous silica particles have been prepared. The results indicated that highly ordered imprinted mesoporous silica particles exhibited specific recognition and fast

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adsorption kinetics for target molecules.

In this paper, E1 imprinted mesoporous structured $\text{Fe}_3\text{O}_4@ \text{SiO}_2@m\text{SiO}_2$ particles with homogeneous binding sites and fast adsorption kinetics were prepared for detection of estrogens from water samples. Magnetic particles were introduced because magnetic property enable simple, rapid and efficient separation. The structure of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@m\text{SiO}_2$ particles were characterized by transmission electron microscopy (TEM) and nitrogen adsorption–desorption isotherms. Both molecular binding capacity and specific recognition ability of $\text{Fe}_3\text{O}_4@m\text{SiO}_2$ were investigated in detail. The imprinted $\text{Fe}_3\text{O}_4@ \text{SiO}_2@m\text{SiO}_2$, integrating the separation ability of Fe_3O_4 particles, molecule recognition ability of MIPs and faster mass transfer ability of mesoporous silica into one system, can achieve highly sensitive and selective pre-concentration of trace target pollutants from water samples.

2. Experimental

2.1. Materials and chemicals

Dibutyltin dilaurate (DBDU), 3-isocyanatopropyltriethoxysilane (IPTS), 3-aminopropyl triethoxy silane (APTES), tetraethoxysilane (TEOS) and cetyltrimethylammonium bromide (CTAB) were supplied by Shanghai Chemical Reagent Company (Shanghai, China). Estrone (E1), 17 β -estradiol (E2), estriol (E3), diethylstilbestrol (DES), bisphenol A (BPA) and phenol were provided by Tianjin Chemical Reagent Co. Ltd (Tianjing, China). Tetrahydrofuran (THF, 99%, Tianjin Jiangtian Chemicals, China) was refluxed over sodium and then distilled. High performance liquid chromatography (HPLC) grade acetonitrile (ACN) was purchased from Merck (Darmstadt, Germany). HPLC water (18.2 M Ω cm specific resistance) was produced by Pall Cascada laboratory water system (New York, USA). All the other chemicals, such as HCl, ammonia, acetic acid were of analytical reagent grade and used as received without further purification except specified.

Stock solutions containing 100 mg L⁻¹ of each estrogens were prepared by dissolving the required amounts of the standards in methanol. Working solutions were prepared by diluting the stock solutions with appropriate amounts of water. They were stored in refrigerator at 4 °C until use.

Morphological observation was performed by transmission electron microscopy (TEM; JEOL, JEM-1230, Japan). The specific surface area and the pore size distribution were characterized by the BET method using Micromeritics ASAP 2020 Sorptometer (Micromeritics, ASAP 2020, USA). The concentrations of each pollutant were analyzed by HPLC equipped with a C18 ODS column (250 mm \times 4.6 mm, 5 μ m) and UV detector (Elite Instrument Inc., China). HPLC conditions employed for estrogens were as follows: mobile phase, ACN/water, gradient elution (A: water, B: ACN; 0 min: A=55%, B=45%; 4 min, A=46%, B=54%; 20 min stop); flow rate, 1.0 mL min⁻¹; room temperature; UV detection, 220 nm; injection volume, 20 μ L.

2.2. Preparation and modification of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$

Fe_3O_4 microspheres were synthesized by solvothermal method as reported [24]. Fe_3O_4 modified with SiO_2 shell were prepared according to the previous method [19]. Briefly, 0.10 g of Fe_3O_4 particles were treated with 50 mL 0.1 mol L⁻¹ HCl aqueous solution by ultrasonication for 10 min, then separated and washed with water. After homogeneously redispersed in the mixture of 80 mL of ethanol, 20 mL of water and 1.0 mL of ammonia aqueous solution (28%, w/w), 2 mL of TEOS was added followed by stirring at room temperature for 6 h. Then $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ microspheres were separated and washed with ethanol and water.

2.3. Preparation of E1 imprinted $\text{Fe}_3\text{O}_4@ \text{SiO}_2@m\text{SiO}_2$ (MM-MIPs)

Template-monomer complex (E1-IPTS) was synthesized as reported [25], where template molecule E1 was bonded to functional monomer IPTS by means of thermally reversible urethane bond. Then E1-IPTS was used for imprinting by sol-gel reaction according to Deng et al. [19]. The specific process was as follow, $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ microspheres prepared in the former step redispersed in a mixed solution containing of CTAB (0.30 g, 0.823 mmol), water (80 mL), concentrated ammonia aqueous solution (1.0 mL, 28 wt%) and ethanol (60 mL). The mixed solution was homogenized for 0.5 h to form a uniform dispersion. TEOS (0.42 g, 2.0 mmol) and E1-IPTS (0.21 g, 0.4 mmol) were added to the dispersion under continuous stirring. After reaction for 24 h, the product was collected with a magnet and washed repeatedly with ethanol and water to remove nonmagnetic by-products. Subsequently, template E1 for imprinting was removed by heating at 180 °C in mixture of DMSO and water, and template CTAB for mesoporous silica was removed by calcination at 550 °C for 5 h. The non-mesoporous control polymers $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{SiO}_2$ were synthesized as described above but without CTAB. Non-imprinted polymer (NIPs) were prepared using the above procedure, except APTES was used in place of the template-monomer complex (E1-IPTS).

2.4. Binding property studies of the mM-MIPs

Molecular binding properties of the MM-MIPs including static adsorption, kinetic adsorption and selective binding capacity were estimated by a batch procedure method.

To evaluate the static adsorption, 20 mg of MM-MIPs particles were dispersed into 2.0 mL water with various E1 concentration varying from 0.5 to 100 mg L⁻¹. After shaking at room temperature for 24 h, the supernatant was separated and evaluated by HPLC. The binding amount of E1 was determined by subtracting the residual amount of E1 in solution from the total E1 amount. Meanwhile, the binding kinetics were tested by monitoring the temporal amount of E1 in the solutions. Selectivity experiments were carried out using E2, E3, DES, BPA and phenol as structural analogs.

2.5. Analysis of water samples by dispersive solid phase extraction

The imprinted $\text{Fe}_3\text{O}_4@ \text{SiO}_2@m\text{SiO}_2$ (MM-MIPs) were applied to extract E1, E2 and E3 from tap, river and lake water samples by dispersive solid phase extraction (DSPE) method. Tap water was collected in the laboratory after flowing for about 5 min when needed. Lake waters were randomly collected from an artificial lake located in Linyi University (China). River waters were collected from Yi River near the Luoxin Pharmaceutical Co. Ltd. Water samples were collected and filtered with a 0.45 μ m filter membrane prior to use. The process of DSPE was carried out as follows. 800 mg of MM-MIPs in a beaker were conditioned in sequence with 5.0 mL methanol and 3.0 mL water. After conditioning, 500 mL water sample solution was added. The mixture was ultrasonicated for 15 min. After the extraction step, MM-MIPs were separated and washed with 5.0 mL water. Finally, estrogens were eluted by 5.0 mL of methanol solution containing 0.5% acetic acid. The eluate was evaporated under nitrogen, and the residue was redissolved in 0.2 mL ACN for further HPLC analysis.

3. Results and discussion

3.1. Preparation and characterization of E1 imprinted $\text{Fe}_3\text{O}_4@ \text{SiO}_2@m\text{SiO}_2$ (MM-MIPs)

The synthesis procedure for mesoporous structured E1

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