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Sensitive determination of estrogens in environmental waters treated with polymeric ionic liquid-based stir cake sorptive extraction and liquid chromatographic analysis

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ABSTRACT

A simple, sensitive and environmentally friendly method using polymeric ionic liquid-based stir cake sorptive extraction followed by high performance liquid chromatography with diode array detection (HPLC/DAD) has been developed for efficient quantification of six selected estrogens in environmental waters. To extract trace estrogens effectively, a poly (1-ally-3-vinylimidazolium chloride-co-ethylene dimethacrylate) monolithic cake was prepared and used as the sorbent of stir cake sorptive extraction (SCSE). The effects of preparation conditions of sorbent and extraction parameters of SCSE for estrogens were investigated and optimized. Under optimal conditions, the developed method showed satisfactory analytical performance for targeted analytes. Low limits of detection ($S/N=3$) and quantification limits ($S/N=10$) were achieved within the range of 0.024–0.057 μg/L and 0.08–0.19 μg/L, respectively. Good linearity of method was obtained for analytes with the correlation coefficients (R^2) above 0.99. At the same time, satisfactory method repeatability and reproducibility was achieved in terms of intra- and inter-day precisions, respectively. Finally, the established SCSE-HPLC/DAD method was successfully applied for the determination of estrogens in different environmental water samples. Recoveries obtained for the determination of estrogens in spiked samples ranged from 71.2% to 108%, with RSDs below 10% in all cases.

1. Introduction

Estrogens such as bisphenol A (BPA), 17α-ethinylestradiol (EE2), estrone (ES), diethylstilbestrol (DES), dienestrol (DS) and octylphenol (OP) have been known to interfere with endocrine systems by mimicking, blocking and triggering actions of hormones and thereby influence the health and reproductive system of humans and wildlife [1,2]. Therefore, estrogens have gained increasing environmental and social concerns in recent years. The estrogens enter into the environmental waters through all kinds of ways including the sewage discharge, animal waste disposal, pharmaceutical and aquaculture wastewater. Several studies have reported that trace level concentration of estrogens have been found in environmental waters all over the world [3–5]. Thus, developing a simple, convenient, accurate and reliable analytical method for the determination of trace amounts of estrogens in the environmental waters is important.

In recent years, several chromatographic methods including gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) have been reported for the determination of estrogens. However, the use of GC and CE techniques encounters several drawbacks. For the use of GC, a tedious derivatization process is needed to increase the volatility of estrogens as most of them are high boiling compounds [6,7]. CE possesses high separation performance, but it lacks stability and sensitivity for real samples with complicated matrices [8]. In comparison to GC and CE, HPLC is simple and convenient. HPLC can analyze estrogens directly without derivatization and exhibit good reproducibility [9,10]. However, considering the complexity of the matrices and the very low concentration, effective sample pretreatment steps are necessary prior to injection into the analytical system.

Up to now, several sample pretreatment methods have been used to extract estrogens from various samples. These methods mainly include solid phase extraction (SPE) [11,12], solid phase microextraction (SPME) [13], stir bar sorptive extraction (SBSE) [14], liquid–liquid extraction (LLE) [15,16], liquid phase microextraction (LPME) [17,18], hollow fiber liquid–liquid microextraction (HFLLME) [10] and thin-film microextraction (TFME) [9], etc.. Above methods have achieved expected extraction performance

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for estrogens, however, there are some shortcomings of these methods. Multi-step processes, including extraction, elution, evaporation and sample reconstitution steps, are involved in SPE method. Commercial SPME fiber is expensive and limited choice, and too small volume of the coating limits the recovery of analytes. Major limitations of SBSE include the possibility of physical damage to the extraction phase when stirring at high speed, limited number of available extraction sorbents. The LLE method demands time-consuming extraction and cleanup procedures, as well as large volumes of sample and toxic organic solvent. For LPME, HFLLME and TFME, the extraction capacity is limited because low extractant is employed. Therefore, there is still an urgent need to develop convenient, high extraction capacity, cost-effective and environmentally friendly sample pretreatment method for the analysis of estrogens.

Stir cake sorptive extraction (SCSE) using monolithic materials as extractive medium is a new extractive format which was developed in our group [19,20]. SCSE combines the processes of extraction, concentration and clean-up as one single step. Furthermore, there are distinct advantages for SCSE, such as simple operation, high extractive capacity, good flexibility, cost-effectiveness, and being environmentally friendly. More important, in comparison to SBSE, the SCSE possesses excellent life-span because the monolithic cake does not contact with the vessel wall during stirring and there is no friction loss of extractive medium. As other extraction formats, the extractive medium is the core of SCSE. Different sorbents possess different extraction performance for analytes. In SCSE, the extraction medium-monolithic cake is flexible. According to the character of target analytes, the monolithic cake can be easily designed and prepared to realize effective extraction of analytes. In present work, BPA, EE2, ES, DES, DS and OP were selected as target analytes. It can be seen from their molecular structures (Supporting information, Table S1), there are abundant polar hydroxyl groups and hydrophobic phenyl groups. According to the structural characteristics of estrogens, a new monolithic cake based on polymeric ionic liquid (PIL) was synthesized. PILs combine the unique properties of ionic liquids with the macromolecular architecture together with intrinsic polymer characteristics such as abundant chemical properties, mechanical stability, improved processability, durability and spatial controllability. Therefore, PIL-based sorbent is an ideal extraction phase for SCSE. In the present work, a PIL-based monolithic cake was obtained by in situ copolymerization of 1-ally-3-vinylimidazolium chloride (AV) and ethylene dimethacrylate (ED). Because there are abundant imidazole, amino and alkyl groups in the new sorbent, it is reasonable to expect that the new AVED/SCSE can extract the above-mentioned compounds effectively because multi-interactions, including π–π, hydrophobic, hydrogen-bonding and dipole–dipole interactions, will involve the extraction procedure. After the optimization of preparation and extraction conditions, a simple and sensitive methodology combining the AVED/SCSE and liquid desorption (LD), followed by high performance liquid chromatography with diode array detection (AVED/SCSE-LD-HPLC/DAD) for the direct analysis of trace estrogens in waters was developed.

2. Experimental

2.1. Chemicals

1-Ally-3-vinylimidazolium chloride (AV) (99%) was purchased from Cheng Jie Chemical Co. Ltd. (Shanghai, China); Ethylene dimethacrylate (ED) (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China); 1-Propanol (97%), 1,4-butanediol (98%) (distilled before use) and azobisisobutyronitrile (AIBN) (97%, recrystallized before use) were purchased from Shanghai Chemical Co. (China); HPLC-grade acetonitrile (ACN) and methanol were purchased from Tedia Company (Fairfield, USA); Water used throughout the study was purified using a Milli-Q water-purification system (Millipore, USA). Bisphenol A (BPA) was purchased from TCI Company (China). 17α-Ethinylestradiol l (EE2), estrone (ES), diethylstilbestrol (DES) and dienestrol (DS) were supplied by Sigma-Aldrich (Germany). Octylphenol (OP) was purchased from Chemservice Company (USA). The chemical properties of the above analytes are shown in Supporting information (Table S1). Water samples were collected from Xiamen city and filtrated through 0.45 μm membranes. All samples were stored at −4 °C before use. Individual stock solutions of estrogens were prepared at a concentration of 10.0 mg/L by dissolving methanol and renewed monthly. The standard mixtures of estrogens were prepared by dissolving 2.00 mg of each compound in methanol in 100 mL volumetric flask. The stock solutions were stored at 4 °C and diluted with ultrapure water to give the required concentration.

2.2. Equipments and materials

HPLC analyses were carried out on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20A). Sample injection was carried out using a RE3725i manual sample injector with a 20 μL loop (Rheodyne, Cotati, CA, USA), all experiments were performed at room temperature.

The morphologies of monolithic materials were examined by a Model XL30 scanning electron microscopy (SEM) instrument (Philips, Eindhoven, The Netherlands). The pore size distribution of the monolith was measured on mercury intrusion porosimeter (MIP) Model PoreMaster-60 (Quantachrome Instruments, Florida, USA). Elemental analysis (EA) was carried out on PerkinElmer (Shelton, CT, USA) Model PE 2400. FT-IR was performed on an Avatar-360 FT-IR instrument (Thermo Nicolet, Madison, WI, USA).

2.3. Chromatographic conditions

The separation of estrogens was performed on a Hypersil BDS C18 column (5 μm particle size, 250 mm × 4.6 mm i.d.). Optimum separation was obtained with a binary mobile phase composed of ultrapure water (solvent A) and ACN (solvent B). The gradient elution program was as follows: 0–7.0 min = 50% B, 7.0–12.0 min = 50% B-100% B and kept to 17.0 min, 17.0–20.0 min = 100% B-50% B and kept to 25.0 min. The detector wavelength was set at 210 nm for ES and EE2, 230 nm for other estrogens. The flow rate was 1.0 mL/min, and injection volume was 20 μL.

2.4. Synthesis of AVED/SCSE

Three steps were involved in the synthesis of AVED/SCSE. Firstly, the polymeric ionic liquid-based monolithic cake was synthesized by in-situ polymerization. In the all polymerization reaction, AIBN (1% (w/w) of the total monomer amount) was used as polymerization initiator. To optimize the preparation parameters, different percentage of monomer and porogen (60% [w/w] 1-propanol and 40% [w/w] 1,4-butanediol) concentration in the polymerization solution was tested (Table 1). The monomer mixture and porogen were mixed ultrasonically into a homogenous solution. Then the reactant solution was purged with nitrogen for 5.0 min to squeeze out the air in the solution. Subsequently, the reactant mixture was poured into a syringe cartridge (1.2 cm i.d.), one side of which was blocked by the plug of syringe. After that, the cartridge was sealed with septa and kept at 65 °C for 18 h. After polymerization, the monolithic cake was pushed out slowly from the syringe manually. The cake was Soxhlet-extracted with methanol for 24 h to remove the residue monomers, porogen,