



Development of a novel magnetic molecularly imprinted polymer coating using porous zeolite imidazolate framework-8 coated magnetic iron oxide as carrier for automated solid phase microextraction of estrogens in fish and pork samples



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ARTICLE INFO

Article history:

Received 16 May 2014

Received in revised form 16 July 2014

Accepted 31 August 2014

Available online 6 September 2014

Keywords:

Zeolite imidazolate framework-8 coated magnetic iron oxide
Molecularly imprinted polymer coating
Automated solid-phase microextraction
Estrogens
High performance liquid chromatography

ABSTRACT

A high-performance magnetic molecularly imprinted polymer (MIP) coating using zeolite imidazolate framework-8 coated magnetic iron oxide ($\text{Fe}_3\text{O}_4@\text{ZIF-8}$) as a carrier was developed for simultaneous automated solid phase microextraction of four estrogens in 24 food samples. The coating material, abbreviated as MZMIP, was synthesized through time-efficient layer-by-layer assembling of ZIF-8 and MIP film on Fe_3O_4 particles. It was characterized and automatically coated on the surface of SPME fibers by electromagnetic bonding. The extraction performance, reusability, repeatability, and validity of the MZMIP–SPME system was evaluated for high-throughput analysis of estrone (E1), estradiol (E2), estriol (E3), and ethinylestradiol (EE2). Various factors affecting the quality of MZMIP coating were optimized. Compared with traditional magnetic MIP coating based on $\text{Fe}_3\text{O}_4@\text{SiO}_2$ carrier, the MZMIP coating exhibited high extraction capacity and quick adsorption and desorption kinetics to E1, E2, E3, and EE2 owing to the larger amount of imprinting sites in MZMIP. Under optimum conditions, the proposed system requires only 25 min for pretreatment of all 24 samples (62.5 s per sample). The limits of detection and quantitation of the proposed automated system for analysis were found to range from 0.4 to 1.7 and 1.1 to 6.2 ng g^{-1} , respectively. During analysis of spiked fish and pork, the new coating showed better recovery and selectivity compared with $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MIP}$ (MMIP) and commercially available SPME. The results indicated that the MZMIP coating could be effectively employed for pretreatment of ultra-trace level of estrogens in food.

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1. Introduction

Estrogens are a group of potent endocrine-disrupting chemicals, which include naturally occurring estrone (E1), estradiol (E2), estriol (E3), and synthetic ethinylestradiol (EE2). Especially EE2, as a kind of xenoestrogens, has been identified as the most potent estrogenic chemical in all endocrine-disrupting chemicals until date [1]. Estrogens could enter human body through the food chain, disturb the normal endocrine system, and alter the normal reproduction and development of human beings [2,3]. Further, those compounds

have attracted large societal and political attention because of their widespread presence in certain food matrices, such as fish and pork [4–6]. Thus, it is of great significance for food safety supervision to develop sensitive, selective, and simple methodologies to determine estrogens in food.

Solid-phase micro-extraction (SPME), pioneered by Arthur and Pawliszyn in 1990s [7], has been widely applied for monitoring estrogens either in food samples, in environment matrices or in biologic samples [8–12]. SPME has many advantages because of its integration of analytes extraction, pre-concentration, and sample clean up in a single step [13–15]. To improve the sample preparation strategies for quick analysis of complex samples and high-throughput analysis, there has been a growing need for an automated SPME method. Recently, Pawliszyn's research groups have developed many automated SPME devices in multi-well

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format using a robotic autosampler to prepare several samples in parallel [16–22]. In our previous work [23], we developed a novel automated SPME device that could simultaneously treat up to 24 samples. In addition, a highly selective and sensitive magnetic molecularly imprinted polymers MMIP-SPME analytical method was established using $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{MIP}$ (MMIP) as a coating of SPME and coupled with high performance liquid chromatography (HPLC) for detection. $\text{Fe}_3\text{O}_4@\text{SiO}_2$ was applied as the matrix of MMIP due to the modifiable silicon hydroxyl on the surface of SiO_2 nanoparticle. However, the grafting and molecularly imprinted polymerization procedures on SiO_2 were time-consuming. In Ding's work [24], to modify MIP film using MAA as functional monomer on the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$, the γ -methacryloxypropyl trimethoxysilane (KH570) was employed to introduce grafting C=C group to the surface of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ by reacting in toluene for 24 h at 120 °C. The molecularly imprinted polymerization procedure even reached up to 38 h. In the process, a large volume of organic solvent was needed. To simplify the immobilizing procedure of MIP film on superparamagnetic iron oxide nanoparticles as coating for automated MMIP-SPME, choosing a new carrier instead of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ and polymer monomer instead of MAA was a big challenge.

Metal–organic frameworks (MOFs) have recently received considerable attention due to their unusual properties such as large surface area, good thermal stability, and the availability of in-pore functionality and outer-surface modification [25]. Owing to the above merits, Kun's group reported MIP preparation by using MOF-5 as matrix, and the synthesized MOF@MIP showed a homogeneous polymer film, thermal stability, and exhibited a higher specific surface area and a faster transfer-mass speed compared with that of the bulk MIP [26]. Zeolite imidazolate frameworks (ZIFs), a new class of microporous MOFs are synthesized by the crystallization of a transition metal species bound to the nitrogen atom of an imidazolate compound [25]. ZIF-8, which has the formula $\text{Zn}(\text{MIM})_2$ (MIM: 2-methylimidazole), has hydrophobic pores [27]. ZIF-8 has been reported to possess good extraction capacity to steroidal hormones due to the presence of a benzene ring by forming a coordinate bond and intermolecular π – π interactions [28]. Considering the superior properties of ZIF-8 and their potential absorbing capacity for the benzene series and related organic groups, the design and synthesis of magnetic ZIF-8 as a carrier of coating are especially desirable for automated SPME.

Some novel monomers that can auto-polymerize without cross-linking or an initiator agent, such as dopamine [29], polydopamine [30,31], or 3-aminobenzenboronic acid (APBA) [32–34], can be used to quickly prepare the MIP film for the automated SPME method. APBA is an attractive functional monomer that is water-soluble and provides a mild aqueous environment during polymerization [34]. Moreover, the benzene rings of APBA can be absorbed on ZIF-8, which has imidazole ring, through π – π stacking interaction. Thus the MIP film using APBA polymer can be easily immobilized on $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ without any grafting procedure, which can greatly simplify the preparation step of MIP film on the carrier. Furthermore, the MIP film is prepared by an organic solvent-free synthesis. Moreover, the template (E2) can be uniformly and stably distributed on the surface of porous ZIF-8 through π – π stacking interactions to simply the MIP film immunization procedure.

In this work, to develop a new coating with high extraction capacity and stability for the automated SPME system, we prepared a novel MZMIP coating using $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ as the carrier and APBA as the functional monomer. The MMIP coating, using $\text{Fe}_3\text{O}_4@\text{SiO}_2$ as the carrier, was also synthesized to compare the extraction performance with the new MZMIP coating. The MZMIP-coated automated SPME system coupled with HPLC was evaluated for high-throughput analysis of estrogens (E1, E2, E3, and EE2) in real fish and pork samples.

2. Experimental

2.1. Chemical reagents and materials

In this work, estrone (E1, 97%), estradiol (E2, 99%), estriol (E3, 98%), and ethinyloestradiol (EE2, 98%), β -naphthol (β -nap, 99%) and poly (styrenesulfonate, sodium salt) (PSS, 30 wt%) were obtained from Sigma–Aldrich (Shanghai, China). 3-Amino phenyl boronic acid (APBA) was from J&K Chemical Co. Ltd. Acetonitrile (HPLC grade) was acquired from CNW Technologies (Dusseldorf, Germany). 2-methylimidazole (H-MeIM, 99%) were purchased from Aladdin Chemistry (Shanghai, China). Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 99%), sodium acetate (NaAc, 99%) and ethylene glycol ($(\text{HOCH}_2)_2$, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All other reagents were of analytical grade. Ultrapure water (Hangzhou Wahaha Foods Co. Ltd., Hangzhou, China) was used throughout this work. A mixed stock solution of the four estrogens (E1, E2, E3, and EE2) was prepared in methanol at a concentration of 100 mg L^{-1} and stored at 4 °C in darkness. All solutions used for HPLC mobile phase were filtered through a nylon 0.22 μm filter prior to use.

The commercial SPME fibers with 85 μm polyacrylate (PA), 85 μm carboxen/polydimethylsiloxane (CAR/PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), and 50/30 μm carboxen/divinylbenzene/polydimethylsiloxane (CAR/DVB/PDMS) coatings, which were purchased from Supelco (Bellefonte, PA, USA) were used for the comparison study.

2.2. Synthesis of MZMIP core–shell particles

2.2.1. Preparation of Fe_3O_4 particles

The Fe_3O_4 particles were synthesized as described in our previous work [23].

2.2.2. Preparation of $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ particles

The core–shell $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ particles were prepared according to Zhang et al. [35]. In a typical procedure, 0.05 g Fe_3O_4 was added to 150 mL aqueous solution contains of 0.3% poly (styrenesulfonate, sodium salt) (PSS) under ultrasonication for 30 min. The resultant $\text{Fe}_3\text{O}_4@\text{PSS}$ particles were recovered by an external magnetic field and washed with purified water for three times, then redispersed in a mixture containing 150 mL methanol, 1.125 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3.11 g 2-methylimidazolate under stirring and the reaction was allowed to proceed at 50 °C for 3 h for ZIF-8 shell growth. Finally, the obtained $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ nanoparticles were separated by a magnet and washed with ethanol.

2.2.3. Preparation of MZMIP particles

MZMIP was prepared as follows. E2 (0.1 mmol) as the template was first dissolved in 1.25 mL acetonitrile, then mixed with 5 mL phosphate buffer sodium (PBS, pH = 7.2), which contains 0.5 mmol APBA as the functional and cross-linking monomer, and the mixture was then incubated at room temperature for 1 h. After adding $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ (0.04 g), the solution was incubated for 2 h at room temperature. Prior to use, the $\text{Fe}_3\text{O}_4@\text{ZIF-8}$ particles were subjected to extensive deionized water and absolute ethanol, and washed thoroughly. Subsequently, a 100 mM aqueous solution of ammonium persulfate (6.5 mL) as initiator was slowly added dropwise to the above solution for about 20 min and the polymerization process was executed at room temperature. After 8 h, $\text{Fe}_3\text{O}_4@\text{ZIF-8}@\text{MIP}$ (MZMIP) particles were obtained. Finally, MZMIP was collected magnetically, and the template was removed using 20 mL methanol/acetic acid (4/1, v/v) solution (with shaking) until no E2 adsorption was detected by HPLC. The particles were washed with water three times again and vacuum dried at 60 °C.

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