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Molecularly imprinted sol-gel nanofibers based solid phase microextraction coupled on-line with high performance liquid chromatography for selective determination of acesulfame

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ABSTRACT

Sol-gel based molecularly imprinted polymer (MIP) nanofiber was successfully fabricated by electrospinning technique on the surface of a stainless steel bar. The manufactured tool was applied for on-line selective solid phase microextraction (SPME) and determination of acesulfame (ACF) as an artificial sweetener with high performance liquid chromatography (HPLC). The selective ability of method for the extraction of ACF was investigated in the presence of some selected sweeteners such as saccharine (SCH), aspartame (ASP) and caffeine (CAF). Electrospinning of MIP sol-gel solution on the stainless steel bar provided an unbreakable sorbent with high thermal, mechanical, and chemical stability. Moreover, application of the MIP-SPME tool revealed a unique approach for the selective microextraction of the analyte in beverage samples. In this work, 3-(triethoxysilyl)-propylamine (TMSPA) was chosen as a precursor due to its ability to imprint the analyte by hydrogen bonding, Van der Walls, and dipole-dipole interactions. Nylon 6 was also added as a backbone and support for the precursor in which sol could greatly growth during the sol-gel process and makes the solution electrospinable. Various effective parameters in the extraction efficiency of the MIP-SPME tool such as loading time, flow rate, desorption time, selectivity, and the sample volume were evaluated. The linearity for the ACF in beverage sample was in the range of 0.78–100.5 ng mL^{-1}. Limit of detection (LOD) and quantification (LOQ) were 0.23 and 0.78 ng mL^{-1} respectively. The RSD values ($n=5$) were all below 3.5% at the 20 ng mL^{-1} level.

1. Introduction

Solid phase microextraction (SPME) has been the center of focus by many researchers ever since it emerged in early of 1990 s [1]. SPME is a green, fast, simple, adsorbtion-desorbtion based, and single step sample preparation process. It has been well accepted as a powerful sample preparation technique and widely used in different area of analytical, bioanalytical, and environmental chemistry [2–5]. Although, there have been many improvements in this regard such as preparation of biocompatible sorbent for in-vivo extraction, unbreakable fibers, and nano composite sorbent [6–10], it is still needed to be improved in some aspects. Preparations of selective sorbents, unbreakable substrates, and sol-gel based fibers have been challenging issues in recent years and they have been studied with some research groups [8,11]. In addition, common conventional SPME fibers are breakable and sensitive when exposed to organic solvents. Some studies have been developed for the preparation of unbreakable sorbents with molecularly imprinted polymers and sol-gel [12–17]. Demand for the preparation of the sorbents with high chemical and thermal stability, long lifetime, and good repeatability has directed research groups toward sol-gel technology. Sol-gel technology has been successfully applied for the preparation of sorbents, but it still has a few problems. Lack of selectivity is the main problem of sol-gel technology. Recently molecularly imprinted sol-gel sorbents have been prepared [12,18], but it still needed more attentions and investigations. A further issue of sol-gel technology for preparation of sorbents, particularly molecularly imprinted sol-gel, could be attributed to inappropriate homogeneity and aggregation during gelation.

New methodology named electrospinning was recently developed for preparation of nanofibers while the acceptable homogeneity could be obtained. It has been used for preparation of fibers and mats for SPME [19–22]. Electrospinning of polymeric

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fibers provides the capability to create micro/nanofibers through an inexpensive and simple method. Electrospun micro/nanofibers have been applied to many different applications ranging from tissue scaffolds, and electronics [23–27]. The electrospinning process is based on similar phenomena in electrospray ionization mass spectrometry (ESI/MS) [28]. Unlike the ESI, here, producing the fiber jet is preferred over the formation of the charged droplets in ESI/MS. Therefore, in the electrospinning process, a solution of high molecular weight polymer with high viscosity is used. This method consists of placing a high electric field between a polymer solution and a conductive collector. When the electric field is strong enough to overcome the surface tension of the droplet, a Taylor cone is formed. Following the creation of the Taylor cone, polymeric nanofibers are ejected toward the conductive collector [29,30].

This method can be used to fabricate SPME fibers with various polymers. This technique should provide an approach to generate high surface area fibers and the versatility to alter the SPME nanofiber composition by changing the polymer solution for electrospinning.

Molecularly imprinted polymers (MIPs) have been largely applied to the extraction of target analytes from a variety of complex matrices. Most of these applications were based on off-line procedures. Until now, a very few applications were carried out in on-line mode [31–33] while trends in analytical chemistry are for high throughput approaches that involve to minimize the time spent performing analysis. Therefore, MIP coupled on-line with HPLC can create a straightforward and fast pretreatment due to their specific recognition properties. We applied MIPs as artificial receptors for off-line solid-phase extraction of bromhexine [34], metoclopramide [35], verapamil [36], and tramadol [37] in biological fluids. Recently, in our research group the applicability of on-line solid phase extraction method using molecularly imprinted polymers in monolithic column [38] or cartridges [33,39] for the extraction and determination of tramadol, dextromethorphan, and insulin in biological fluids and pharmaceutical samples were studied.

In this work, a simple and novel route for the preparation of unbreakable molecularly imprinted sol-gel nanofibers with electrospinning technique was developed. Nylon 6 as a backbone and support of the precursor in the MIP sol-gel process was used to facilitate the electrospinning procedure. The developed method was used for on-line SPME and determination of acesulfame coupled with HPLC. The selectivity of method for the extraction of acesulfame was evaluated in the presence of some sweets (saccharine, caffeine, and aspartame) in the beverage sample. This robust tool can be used for fifty extractions without special obstacle.

2. Experimental

2.1. Reagents

Acesulfame (ACF), saccharine (SCH), aspartame (ASP), and caffeine (CAF) were obtained from Merck (Darmstadt, Germany). 3-(triethoxysilyl)-propylamine (TMSPA) with purity higher than 98% and nylon 6 were purchased from Aldrich (Darmstadt, Germany). Methanol (MeOH), acetonitrile (ACN), trifluoroacetic acid (TFA), and formic acid (FA) were supplied from Merck (Darmstadt, Germany). The stock solution was prepared in distillated water at concentration of 1000 μg L^{-1} and stored at 4 °C. Working standard solutions of different concentrations were prepared daily by diluting the intermediate standard solution with mobile phase solution and spiked in beverage samples for all sections. Also, beverage sample was purchased from local market.

2.2. Apparatus

A DIONEX HPLC instrument was used for chromatographic analysis of ACF. This chromatographic system was composed of a multi solvent gradient pump, a UVD170U detector and an on-line degasser. A Rheodyne model 7725i injector with a 20 μL loop was used to inject the samples. Chromatographic separation was achieved on an ACE C18, 5 μm, 4.6 mm × 250 mm column. For the mobile phase, a degassed mixture of ACN: Phosphate buffer (0.02 M) (85:15) was prepared and delivered in isocratic mode at flow rate of 0.8 mL min^{-1}. All of the analyses were carried out at 220 nm and HPLC data were acquired and processed using a PC and Chromeleon Ver. 6.60 chromatography manager software.

The electrospinning setup also contains a high voltage power supply (Gamma High Voltage ES 50 P-10 W) and a syringe pump (JZB 1800D Double Channel Syringe pump from China). The SPME tool for this study was a stainless steel bar which electrospuned by MIP sol-gel. For on-line connecting SPME stainless steel bar to HPLC a homemade cupper tube (3 cm length × 0.3 cm i. d.) tool which has input and output streams for solutions utilized. SPME nanofiber bar was fixed in this cupper tube and ends of the tube sealed carefully with plastic screw to prevent from any leakage. Then, input and output streams were connected to HPLC by peristaltic pump for on-line extraction. The prepared nanofibers were used for on-line SPME and determination of acesulfame coupled with HPLC. SPME process was performed by passing the spiked aqueous samples through SPME nanofiber tool.

2.3. Preparation of MIP- and NIP-SPME nanofiber

For preparation of sol solution with electrospun capability in optimized concentration and ratio (MIP1, Table 1), 0.15 mL of standard of ACF solution (0.8 mmol L^{-1}, as the template molecule), 0.3 mL of TMSPA as the precursor was mixed and sonicated for 10 min. Then, 0.3 mL ACN as solvent, 0.2 mL of TFA (100%) as catalyst was slowly added in four steps (each time 0.05 mL). Then, 0.05 mL distillate water was added to start the hydrolysis process and solution was kept in this state for 30 min.

In addition, Nylon 6 solution (12% w/w) in 4 mL FA as backbone solution was prepared and was added to the above solution and sonicated for 20 min. This solution was used for electrospinning process to prepare MIP sol-gel nanofiber.

Electrospinning of MIP sol-gel solution without backbone compounds is a complicated process, to overcome this problem, nylon 6 as a backbone for precursor was used. This backbone is needed to have some functional group to produce hydrogen bonding with silane groups. The schematic process of this binding is shown in Fig. 1.

Electrospinning of imprinted polymer nanofibers were carried out at room temperature at a high voltage of 15 kV (Fig. 2A). The syringe used in the experiments had a capillary tip with a diameter

Table 1
Optimization of compounds ratio of sol solution with electrospun capability.

MIP/ NIP	ACF (mL)	TMSPA (mL)	TFA (mL)	Distillated water (mL)	Extraction (%) (mean ± RSD)[a]
MIP1	0.15	0.2	0.2	0.05	69 (± 1.3)
MIP2	0.15	0.3	0.2	0.05	91 (± 2.3)
MIP3	0.15	0.4	0.2	0.05	77 (± 1.1)
MIP4	0.15	0.5	0.2	0.05	60 (± 3.3)
NIP1	—	0.2	0.2	0.05	29 (± 1.1)
NIP2	—	0.3	0.2	0.05	30 (± 3.1)
NIP3	—	0.4	0.2	0.05	38 (± 4.1)
NIP4	—	0.5	0.2	0.05	40 (± 2.2)

[a] Average of five determinations