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Development of high internal phase emulsion polymeric monoliths for highly efficient enrichment of trace polycyclic aromatic hydrocarbons from large-volume water samples

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ABSTRACT

In this work, polymerized high internal phase emulsion (polyHIPE) monoliths were prepared and applied as monolithic adsorbent materials for preconcentration of trace polycyclic aromatic hydrocarbons (PAHs) from large-volume water samples. The monolithic polyHIPE columns were prepared by in situ polymerization of the continuous phase of a high internal phase emulsion (HIPE) containing styrene (STY), divinylbenzene (DVB) and glycidyl methacrylate (GMA) in pipette tips, and the resulting STY/DVB/GMA polyHIPE monoliths exhibited highly interconnected porosity and large surface areas, making them excellent candidates as adsorbents for enrichment of trace aromatic compounds. The prepared STY/DVB/GMA polyHIPE monoliths were applied to the determination of trace PAHs in environmental water samples by combing with high performance liquid chromatography–fluorescence detection (HPLC–FLD). Under the optimized experimental conditions, the polyHIPE monoliths could effectively enrich trace 13 PAHs from 500 mL of water samples, the mean recoveries at four spiked levels were ranged from 80.7% to 115.0% with the relative standard deviations (RSDs) lower than 14%, and the detection limits (LODs) were ranged from 4.0 to 228 pg/L. In addition, the prepared polyHIPE monolith was stable enough for more than 200 replicate extraction cycles without measurable loss of performance on the enrichment of PAHs, and good column-to-column repeatability was obtained with RSD less than 13%. The proposed method was applied to simultaneous analysis of 13 PAHs in water samples with satisfactory recoveries.

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1. Introduction

Solid phase extraction (SPE) is one of the most commonly used sample preparation techniques for the enrichment of analytes and for the removal of interfering substances, and it was preferred by many researchers on account of high recoveries, good enrichment factors, rapid phase separation, low consumption of organic solvents, less time, and the possibility of combining with chromatography and spectroscopic techniques [1]. Among other aspects of SPE, significant efforts have been devoted to development and characterization of new, advanced adsorbent materials to endeavour to improve selectivity or specificity towards target

analytes, higher sorptive capacity and enhanced chemical or physical mechanical stability [1–3]. Although it is not possible to develop all-powerful and versatile materials to achieving all these goals, and, among them, it is possible to develop some novel sorbents with desired extraction performance to improve SPE efficiency and specificity. At present, a variety of novel sorbents such as metal–organic frameworks, nanostructured materials, molecularly imprinted materials and aptamer-based sorbents is available for SPE [2–4], and ideal SPE sorbents for extraction and enrichment of trace target analytes from complex samples are expected all the time.

Porous polymer monoliths are a new category of materials developed during the last two decades, and are widely used as extraction sorbent materials for SPE and impressive achievements have been obtained in the extraction and enrichment of analytes from complex matrices [5–8], attributing to their simple preparation, versatile surface chemistries, high reproducibility,

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and combining high surface area with excellent permeability and mass transport properties. They as novel SPE materials are ideally suited for a variety of applications including column extraction, separation, purification and enrichment of trace analytes in environmental, food and biological samples, and therefore a variety of monolithic materials and the corresponding preparation methods have been emerged and meanwhile have been successfully applied in sample preparation [2,6,8–10].

PolyHIPEs are porous emulsion-templated polymers synthesized within high internal phase emulsions (HIPEs), they as a kind of porous polymers have attracted much more attentions in recent years for their unique properties including highly interconnected pore network, well-defined porosities, and high specific surface areas [11–14]. HIPEs are highly viscous, paste-like emulsions in which the major, “internal” phase, usually defined as constituting more than 74% of the volume, even high up to 99%, is dispersed as discrete droplets within the continuous, minor, “external” phase [15]. The external phase is converted into a solid polymer and the emulsion droplets are removed yielding (in most cases) a highly interconnected network of micron sized pores of quite well defined diameter [12]. The resultant polyHIPEs possessed two distinct types of pore: the droplet-templated pores as ‘voids’ and the interconnecting holes as “windows”, which make them as ideal adsorbent materials for protein purification [15,16], water purification [17,18], gas capture [19], and other sorption applications [20]. In addition, besides the inherent porous characteristics and highly interconnected networks, monolithic polyHIPE columns exhibited better mechanical properties and much more convenient for miniaturized and automated sample preparation compared with conventional particulate materials, and have been used to successfully capture alkylbenzenes [21], heavy metals [22], and proteins [23,24] with high binding capacity.

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings with natural as well as anthropogenic sources, and also are ubiquitously present environmental contaminants that have detrimental biological effects, toxicity, mutagenicity and carcinogenicity [25,26]. Therefore, PAHs have been listed as priority pollutants by the United States Environmental Protection Agency (US-EPA) and European Union (EU), and many studies have already been conducted to determine the amount of PAHs in water, food, soil and other samples, and many excellent review papers related to PAHs analysis have been published over the years [27–29]. Since PAHs exist in the environment, especially water media in the trace levels (their maximum contaminant levels should not exceed 200 ng/L according to the US-EPA regulations) [30], a sensitive method is desired to preconcentrate these analytes more efficiently prior to detection, and at present several preconcentration methods, including solid phase extraction (SPE), stir bar sorptive extraction (SBSE), solid phase microextraction (SPME) and liquid–liquid microextraction (LLME), have been developed and applied to enrichment of PAHs, especially these listed sixteen PAHs, from water samples [31–41]. Of those sample preparation methods, SPE was preferred by many researchers in the extraction and enrichment of trace PAHs. So far, many different SPE sorbents, such as metal–organic frameworks [31,32,36], molecularly imprinted polymers [33], multiwalled carbon nanotubes (MWCNTs) [40] and carbon coated Fe₃O₄ nanoparticles [41], have been used to enrich PAHs from complex aqueous samples, and exhibited good enrichment performance. However, to the best of our knowledge, monolithic polyHIPEs columns for extraction and enrichment of trace PAHs from complex samples have not yet been reported.

The aim of this study was to develop a monolithic polyHIPE column for extraction and enrichment of trace analytes from complex samples. PolyHIPE monolith was prepared in polypropylene pipette tips by in situ polymerization of the continuous phase of a

HIPE, consisting of monomers styrene (STY), divinylbenzene (DVB) and glycidyl methacrylate (GMA). The obtained polyHIPE monoliths were applied to extraction and enrichment of thirteen PAHs from environmental water samples.

2. Experimental

2.1. Materials and methods

Styrene (STY), divinylbenzene (DVB), glycidyl methacrylate (GMA), potassium persulfate (K₂S₂O₈, ≥99.0%), and surfactant sorbitan monooleate (Span 80) were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). STY and DVB were purified by 10% NaOH, deionized water and anhydrous sodium chloride for removing the inhibitors prior to use. GMA was passed through a basic alumina column prior to use in order to remove the inhibitors. HPLC grade acetonitrile, methanol and formic acid were obtained from Dikma (Dikma Corporation, Beijing, China).

Fifteen PAHs, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA) and benzo[g,h,i]perylene (BghiP), were purchased from Sigma–Aldrich (Shanghai, China). Toluene, phenol, benzaldehyde and aniline were obtained from Aladdin Chemistry Co. Ltd (Shanghai, China). The related chemical structure information of the investigated aromatic compounds can be found in Table S1. All other chemicals and solvents were of analytical-reagent grade or better and were used without further purification.

Stock solutions were prepared by dissolving each standard PAH in acetonitrile, and working solutions were prepared daily by appropriate dilution of the stock solutions with 10% (v/v) acetonitrile for HPLC analysis and with water for extraction experiments before use. All stock solutions were stored and refrigerated at 4 °C. Deionized water from Arium® 611UV ultrapure water system (Sartorius Stedim Biotch GmbH, Germany) was used throughout the work.

2.2. Preparation and characteristics of polyHIPE monoliths

The STY/DVB/GMA polyHIPE monolith was prepared by in situ polymerizing the continuous phase of a HIPE consisting of organic (continuous) and water (discontinuous) phase with different ratio in a 5-mL pipette tip that pre-filled with a glass fibre layer (0.1320 g) as blocking matrix in the tip (Tables S2 and S3). Organic phase consisted of monomers STY, DVB, GMA and surfactant Span 80. Aqueous phase contained degassed water and K₂S₂O₈. The detailed method was described in Supplementary Material. The obtained STY/DVB/GMA polyHIPE monoliths were washed with 5.0 mL of water, 6.0 mL of ethanol, 6.0 mL of 10% acetonitrile, and 6.0 mL of water in turn. The washing procedure was performed at a flow rate of 1.0 mL/min by peristaltic pump system.

The characteristics of the polyHIPE monoliths were studied by Nicolet Nexus 470 FT-IR spectrometer (Thermo Electron Corporation, USA), field emission scanning electron microscope (SEM, Hitachi, S4800) and Micromeritics ASAP (accelerated surface area and porosimetry) -2020 (Micromeritics, USA), respectively.

2.3. Procedure of monolithic polyHIPE column for enrichment of PAHs

Before extraction, the prepared monolithic polyHIPE column was firstly washed with 1.0 mL of desorption solvent and then with 2.0 mL of 20% (v/v) acetonitrile to remove leftover components for avoiding matrix effects and interferences. 20.0 mL sample solution

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