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Polymeric ionic liquid-based portable tip microextraction device for on-site sample preparation of water samples

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ABSTRACT

On-site sample preparation is highly desired because it avoids the transportation of large-volume samples and ensures the accuracy of the analytical results. In this work, a portable prototype of tip microextraction device (TMD) was designed and developed for on-site sample pretreatment. The assembly procedure of TMD is quite simple. Firstly, polymeric ionic liquid (PIL)-based adsorbent was in-situ prepared in a pipette tip. After that, the tip was connected with a syringe which was driven by a bidirectional motor. The flow rates in adsorption and desorption steps were controlled accurately by the motor. To evaluate the practicability of the developed device, the TMD was used to on-site sample preparation of waters and combined with high-performance liquid chromatography with diode array detection to measure trace estrogens in water samples. Under the most favorable conditions, the limits of detection (LODs, S/N = 3) for the target analytes were in the range of 4.9–22 ng/L, with good coefficients of determination. Confirmatory study well evidences that the extraction performance of TMD is comparable to that of the traditional laboratory solid-phase extraction process, but the proposed TMD is more simple and convenient. At the same time, the TMD avoids complicated sampling and transferring steps of large-volume water samples.

1. Introduction

Sample preparation is a key step in the whole analytical procedure. So far, various adsorbent-based extraction methods such as solid-phase extraction (SPE) [1–3], magnetic solid-phase extraction (MSPE) [4,5], solid-phase microextraction (SPME) [6–8], pipette-tip solid phase extraction [9], in-syringe SPE [10,11] and tip microextraction (TME) [12,13] have been developed and used to extract all kinds of pollutants in complex samples. In routine ABE, samples are collected and stored, then transported to lab to perform extraction before instrumental analysis. The whole procedure is inconvenient. It needs the storage and transportation of large-volume samples. At the same time, the loss and degradation of the analytes may occur during the transportation process, affecting the accuracy of analytical results. Herein, development of on-site sample preparation approach with portable device is highly desired.

Considering actual application requirements, the device for on-site sample preparation should be miniaturized and portable. The operation should be convenient, reliable and quick. Additionally, the device should be simple and cost-efficient. So far, a few devices have been designed and developed for on-site sample preparation. Ouyang et al used waterproofing fabric stuck to the one side of an aluminum rod which was rotated with a portable electric drill, and then three homemade PDMS fibers were uniformly inserted into the fabric to form a sampler [14]. The sampler was used to on-site enrich polycyclic aromatic hydrocarbons and organochlorine pesticides in seawater. The sampling procedure is quite simple. However, after the adsorption, the fibers should be detached from the sampler and transported back to the laboratory to perform the desorption procedure. A magnetic microsphere-based portable SPE device was developed by Zhou Q and co-workers [15]. The whole extraction procedure can be automated, but the complexity of the apparatus limits the popularization. Recently, Shen's group reported a microsampling device by means of a surface-enhanced Raman scattering-enabled micropipette [16]. The device allows rapid and field analysis of multicomponents of surface organic residues. However, the extraction capacity is not as high as expected because a low quantity of adsorbent is utilized. In addition, there are some other devices such as in-syringe SPE [11], on-site stir bar sorptive extraction [17] and effervescence tablet-assisted switchable solvent-based microextraction [18] have been developed for on-site sample preparation. However, these devices still suffer some disadvantages such as low extraction capacity, long equilibrium time, complex operation and poor repeatability.

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Extraction phase (adsorbent) is the core of adsorbent-based extraction method, it decides the extraction performance. Device for on-site sample preparation is required miniaturization, resulting in the amount of adsorbent used in the device is limited. Developing adsorbent with high extraction performance is particularly important for on-site sample preparation. Polymeric ionic liquids (PILs) are polyelectrolytes which contain polymeric backbone and ionic liquid (IL) species in repeating units. PILs combine the unique characteristics of ILs and polymers [19]. As a result, PILs display high ionic conductivity, large surface area, various chemical properties and functional groups. Monoliths are in-situ synthesized within the confine of a mold by thermal or photo-initiated polymerization of a mixture of monomers. Monoliths possess some merits such as simple preparation, high mass-transfer and good chemical stability [20,21]. PILs-based monoliths integrate the advantages of PILs and porous monolithic materials. Compared with conventional non PILs-based monoliths, there are abundant organic cations and inorganic or organic anions in PILs-based monoliths. These ions can interact with analytes through a variety of mechanisms such as π-π, hydrophobic, hydrophilic, anion exchange and hydrogen bonding interactions. As a consequence of these interesting properties, PILs-based monoliths have become ideal candidates for adsorbents [22–24].

In this work, we try to develop a PIL-based portable tip microextraction device (PIL/TMD) for on-site sample preparation of water samples. Firstly, an IL, 1-methyl-3-allylimidazolium bis(trifluoromethylsulfonyl)imide (MAI) was used as functional monomer to *in-situ* copolymerize with ethylene dimethacrylate (ED)/divinylbenzene (DB) in a pipette tip to form PIL-based adsorbent (PBA). In the second step, the tip was connected to a syringe which was driven by a bidirectional motor. The adsorption and desorption flow rates were controlled accurately by the motor. To demonstrate the applicability of the device, several estrogens including bisphenol A (BPA), diethylstilbestrol (DES), hexestrol (HS), dienestrol (DS) and octylphenol (OP) were selected as target analytes. The effects of some key extraction parameters such as the type and the volume of sample and desorption solvent, adsorption and desorption flow rates, sample pH value and ionic strength on the extraction performance of PIL/TMD were investigated thoroughly. Under the most favorable conditions, the PIL/TMD was applied to on-site sample pretreatment of waters and combined with high-performance liquid chromatography with diode array detection (HPLC/DAD) to measure trace estrogens. Satisfactory results well indicate that the developed TMD is suitable for on-site sample preparation.

2. Experimental

2.1. Chemical reagents

MAI (98%) was purchased from ANPLE Laboratory Technologies Inc. (Shanghai, China); ED (98%) and DB (80%) were supplied by Alfa Aesar Ltd. (Tianjin, China); 1-propanol (97%), 1,4-butanediol (98%) and azobisisobutyronitrile (AIBN, 97%, re-crystallized before use) were purchased from Shanghai Chemical Co. (China); HPLC grade acetonitrile (ACN) and methanol were bought from Tedia Company (Fairfield, USA); water used throughout the study was purified using a Milli-Q water-purification system (Millipore, USA). Five estrogens including BPA (99%), DES (99%), HS (99%), DS (98%) and OP (97%) were supplied by Sigma-Aldrich (Shanghai, China).

Real-life water samples including river, reservoir and waste waters were collected from Jiulong river in Zhangzhou city, Tingxi reservoir in Xiamen city and influent of sewage treatment plant in Xiang'an campus of Xiamen University, respectively.

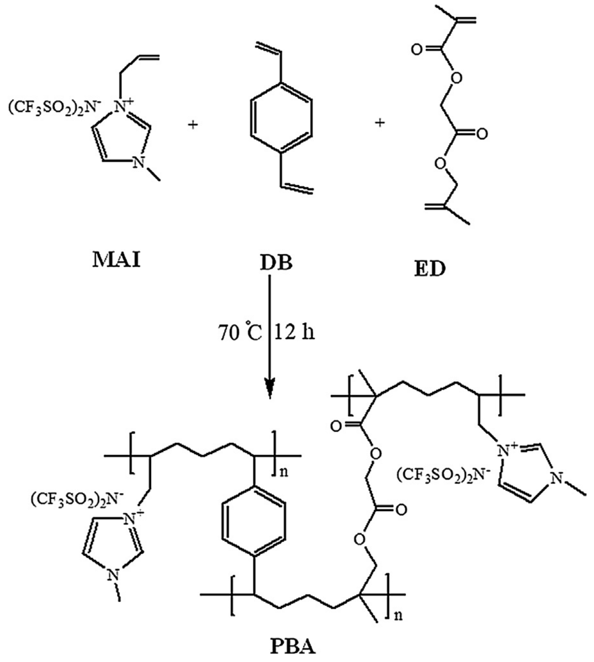

Fig. 1. The preparation sketch of PBA.

2.2. Instruments and chromatographic conditions

HPLC analyses were performed on a LC chromatographic system (Shimadzu, Japan) equipped with a binary pump (LC-20AB) and a diode array detector (SPD-M20 A). A RE3725i automatic sample injector coupled with a 20 μL loop (Rheodyne, Cotati, CA, USA) was utilized to conduct sample injection. The separation of target analytes was carried out on a Kromasil C18 column (250 mm × 4.6 mm i.d., 5 μm particle size). The mobile phase was composed of ultra-pure water (solvent A) and ACN (solvent B) at a flow rate of 1.0 mL/min. The optimal gradient elution program was as follows: 0.0–5.0 min = 55% B, 5.0–10.0 min = 55% B-100% B and kept to 13.0 min, 13.0–15.0 min = 100% B-55% B and kept to 17.0 min. The detection wavelength was set at 210 nm. The instruments used to characterize the PIL are shown in the Supplementary material (Instruments).

2.3. Synthesis of PBA in pipette tip

In-situ polymerization technology of porous monolith is utilized to synthesis of PBA in pipette tip. MAI, the mixture of DB/ED (w/w = 3/2) and AIBN (2% (w/w) of the total amount of polymerization solution) were used as functional monomer, cross-linkers, and initiator, respectively. The mixed solvent of 1-propanol/1,4-butanediol (w/w = 3/2) were employed as porogenic solvent to dissolve MAI, DB/ED and AIBN. To achieve the expected extraction performance for target analytes, the contents of monomer, cross-linkers and porogenic solvent in polymerization solution were investigated (Table S1). Typically, 24 mg MAI, 22 mg DB, 14 mg ED and 4.0 mg AIBN were weighed accurately and put into a 5 mL beaker. After that, 84 mg 1-propanol and 56 mg 1,4-butanediol were added to dissolve the reactants by ultrasonication for 10 min. The oxygen in the solution was removed with high purity nitrogen. Subsequently, 10 μL polymerization solution was injected into a 200 μL pipette tip which one side was blocked. The high of the polymerization solution in the tip was controlled at 3.0 mm. The *in-situ* polymerization was performed at 70 ° for 12 h. After the reaction, the PIL was rinsed with methanol to remove the un-reacted reactants. The polymerization sketch of the PBA is showed in Fig. 1.

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