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Sensitive monitoring of trace nitrophenols in water samples using multiple monolithic fiber solid phase microextraction and liquid chromatographic analysis

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ABSTRACT

In this work, a simple, efficient and environmentally friendly method—multiple monolithic fiber solid-phase microextraction (MMF-SPME) combining with high-performance liquid chromatography (HPLC) was first established for the determination of six trace nitrophenols in water samples. In order to prepare MMF-SPME, 1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl] imide was co-polymerized with ethylene dimethacrylate to get single thin fiber (0.5 mm in diameter). Subsequently, four thin fibers were bound together to obtain the MMF-SPME. The effect of preparation conditions of MMF-SPME on the extraction performance was investigated in detail. In order to obtain the optimal extraction conditions of MMF-SPME for nitrophenols, several extractive parameters, including desorption solvent, extraction and desorption time, pH values and ionic strength in sample matrix were optimized. Under the optimum conditions, the linear ranges of 4-nitrophenol, 2,4-dinitrophenol, 5-methyl-2-nitrophenol, 5-methoxyl-2-nitrophenol were 0.5–200 μg/L and 1.0–200 μg/L for 2-nitrophenol and 4-tertbutyl-2-nitrophenol. The limits of detection ($S/N=3$) for the target analytes were 0.075–0.27 μg/L. At the same time, excellent method reproducibility was achieved in terms of intra- and inter-day precisions, indicated by the RSDs of both $<10.0\%$, respectively. Finally, the proposed method was successfully used to detect nitrophenols in different environmental water samples. Satisfactory recoveries ranged from 82.6% to 116% and the RSDs for reproducibility were less than 10% for target analytes in all real samples.

1. Introduction

Nitrophenols (NPs) are generated by a number of polluting processes, including those in industries such as dyestuffs, petroleum, pesticide, paper pharmaceutical [1,2]. NPs have become one of the most important contaminants present in the environment. Because of the toxicity and carcinogenicity, some of NPs are included in the list of priority pollutants in many countries. For instance, *p*-nitrophenol (*p*-NP) is one of the 129 organic pollutants listed by EPA [3]. At the same time, the maximum limits for *p*-NP in drinking water have been set by the European Commission, the Brazilian Environmental Council and EPA. The corresponding values are 0.1 μg/L, 100 μg/L and 60 μg/L, respectively [3,4]. Thereby, it is important to develop an efficient approach for the sensitive detection of NPs in environmental water samples.

So far, there are several analytical methods, including spectrophotometry [5], electrochemical method [6], HPLC [7], capillary electrophoresis [8] and gas chromatography [9], have been used to detect NPs compounds. Among them, chromatographic methods are used more frequently due to the high separation efficiency [7–9]. However, when GC is used to separate NPs, a derivatization step is required in order to improve the chromatographic performance and sensitivity. The derivatization of NPs is inconvenient and toxic derivatization reagents should be used. Compared with GC, HPLC is simple and convenient to separate NPs. Before HPLC analysis, enrichment step is necessary because the contents of NPs compounds in real samples are generally quite low. Because the contents of NPs compounds in real samples are generally quite low, prior to their determination an enrichment step is necessary. Up to now, various pretreatment techniques have been developed to extract NPs from aqueous samples, such as liquid-liquid extraction (LLE) [10], liquid-liquid microextraction (LLME) [11], solid-phase extraction (SPE) [12], solid-phase microextraction (SPME) [13,14], single-drop microextraction (SDME) [15] and stir bar sorptive extraction (SBSE) [16]. However, LLE is labor-intensive. Furthermore, it consumes much

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organic solvents. The extraction capacity of LLME is limited because low extraction solvent is used. SPE requires large volumes of toxic solvent, and the process is complicated and time consuming. The shortcomings of SDME include instability and volatility of the extraction solvent. For SBSE, long extraction times are needed.

Among above-mentioned extraction approaches for NPs, SPME has attracted much interest from researchers because there are several distinct advantages such as simplicity, rapidity, low sample consuming and environmental friendliness. The extraction medium plays an important role in SPME. It determines the extraction targets and performance. At the same time, the sensitivity and precision of the analysis are also affected strongly by the extraction medium of SPME. Up to now, there are a number of commercial and lab-made polymer-coated fibers for SPME such as polydimethylsiloxane (PDMS) [17], polyacrylate (PA) [18], polyaniline [19,20], nanomaterials [21,22], molecularly imprinted polymers (MIP) [23] and polymeric ionic liquids [24]. However, polymer-coated fibers suffer from insufficient chemical/thermal coating stability and limited extraction capacity. To overcome these advantages, coating-free fibers for SPME have been developed, such as graphene [25], pencil lead [26], carbon monolith [27], etcetera. Coating-free fibers eliminate the problems of coating stability and low extraction capacity associated with coated fibers. However, because of the thick sorbent in substrateless fibers, longer time should be spent in order to reach extraction equilibrium. Therefore, developing new extraction fibers with high extraction performance is highly desired.

Multiple monolithic fiber SPME (MMF-SPME) with monolithic material as extractive medium is a new extraction format which developed in our group [28]. The MMF-SPME is consisted of four independent thin monolithic fibers. In MMF-SPME, the aqueous samples can form convection during extraction because there are gaps between fibers. The formation of convection accelerates the extraction procedure. Therefore, the extraction speed of MMF-SPME is faster than that of coating-free fibers. At the same time, the total amount of sorbent in MMF-SPME is larger than that of coating-based fiber. Hereby, the MMF-SPME possesses higher extraction capacity. Furthermore, MMF-SPME is very flexible. According to the character of target analytes, the extraction medium-monolithic fiber can be easily designed and prepared to realize effective extraction of analytes. In present study, six nitrophenols were selected as target analytes. According to the structural characters of these NPs, there are hydrophobic aromatic rings and strongly polar hydroxyl and nitro groups (Table S1). A novel extractive medium based on poly (1-allyl-3-methylimidazolium bis [(trifluoro methyl) sulfonyl] imide-*co*-ethylene dimethacrylate) (AMED) monolith was designed and prepared. In the monolith, the aromatic ring can interact with the analytes through π-π conjugation. The imidazole groups in the polymer can produce hydrogen-bond and dipole-dipole interactions with hydroxyl and nitro groups NPs. Therefore, the MMF/AMED-SPME is expected to extract NPs effectively. After the optimization of extraction conditions, a simple and sensitive methodology combining the MMF/AMED-SPME and liquid desorption (LD), followed by high performance liquid chromatography with diode array detection (MMF/AMED-SPME-LD-HPLC/DAD) for the direct analysis of trace NPs in water samples was developed.

2. Experimental

2.1. Chemicals

1-Allyl-3-methylimidazolium bis [(trifluoro methyl)sulfonyl]imide (AM) (98%) was purchased from Cheng Jie Chemical Co. LTD (Shanghai, China); Ethylene dimethacrylate (ED) (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China); Azobisisobutyronitrile (AIBN) (97%, recrystallized before use) and N,N-dimethylformamide (DMF) (98%) 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).

2-Nitrophenol (2-NP) (98%), 4-nitrophenol (4-NP) (97%), 2,4-dinitrophenol (2,4-DNP) (98%), 5-methyl-2-nitrophenol (5-M-2-NP) (97%), 5-methoxy-2-nitrophenol (5-MO-2-NP) (97%) and 4-tertbutyl-2-nitrophenol (4-TB-2-NP) (98%) were supplied by Alfa Aesar Ltd. (Tianjin, China). The chemical properties of the above analytes are shown in 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 NPs were prepared at a concentration of 10.0 mg/L by dissolving methanol and renewed monthly. The standard mixtures of NPs 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. Instruments

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 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 NPs was performed on a Phenomenex 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: 0–10.0 min = 50% B, 10.0–12.0 min = 50%B-20% B and kept to 15 min, 15.0–19.0 min = 20%B-90% B and kept to 25.0 min, 25.0–27.0 min = 90%B-50% B and kept to 30 min. The detector wavelength was set at 270 nm for 2-NP and 4-TB-2-NP, 300 nm for 4-NP and 5-MO-2-NP, 342 nm for other NPs. The flow rate was 1.0 mL/min, and injection volume was 20 μL.

2.4. Preparation of MMF/AMED-SPME

The preparation procedure of MMF/AMED-SPME is quite convenient. It includes two steps. The first step is the synthesis of single thin poly (AM-*co*-ED) monolithic fiber (AEMF). AIBN was used as polymerization initiator (1% (w/w) of the total monomer amount) and DMF was used as porogen in the all polymerization reaction. Different concentrations of monomer and porogen were used for different AEMF (Table 1). The monomer mixtures, porogen and AIBN were mixed ultrasonically into a homogenous solution, and then the reactant solution was purged with nitrogen for 5 min. Subsequently, the reactant mixture was introduced into a glass capillary (0.5 mm in diameter and 10 cm in length) with the aid of a syringe. After that, both ends of capillary were sealed with two small pieces of rubber. The filled glass capillary was placed in an oven and heated at 75 °C for 12 h. After the polymerization, 2 cm length of glass capillary was cut off carefully with grindstone. Firm, integrated and elastic AEMF (2 cm in length and 0.5 mm in diameter) (Fig. 1a) was obtained. For