Polydimethylsiloxane/covalent triazine frameworks coated stir bar sorptive extraction coupled with high performance liquid chromatography-ultraviolet detection for the determination of phenols in environmental water samples

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ABSTRACT

In this work, covalent triazine frameworks (CTFs) were introduced in stir bar sorptive extraction (SBSE) and a novel polydimethylsiloxane(PDMS)/CTFs stir bar coating was prepared by sol–gel technique for the sorptive extraction of eight phenols (including phenol, 2-chlorophenol, 2-nitrophenol, 4-nitrophenol, 2,4-dimethylphenol, *p*-chloro-*m*-cresol and 2,4-dichlorophenol, 2,4,6-trichlorophenol) from environmental water samples followed by high performance liquid chromatography-ultraviolet (HPLC-UV) detection. The prepared PDMS/CTFs coated stir bar showed good preparation reproducibility with the relative standard deviations (RSDs) ranging from 3.5 to 5.7% ($n = 7$) in one batch, and from 3.7 to 9.3% ($n = 7$) among different batches. Several parameters affecting SBSE of eight target phenols including extraction time, stirring rate, sample pH, ionic strength, desorption solvent and desorption time were investigated. Under the optimal experimental conditions, the limits of detection (LODs, S/N = 3) were found to be in the range of 0.08–0.30 μg/L. The linear range was 0.25–500 μg/L for 2-nitrophenol, 0.5–500 μg/L for phenol, 2-chlorophenol, 4-nitrophenol as well as 2,4-dimethylphenol, and 1–500 μg/L for *p*-chloro-*m*-cresol, 2,4-dichlorophenol as well as 2,4,6-trichlorophenol, respectively. The intra-day relative standard deviations (RSDs) were in the range of 4.3–9.4% ($n = 7$, $c = 2$ μg/L) and the enrichment factors ranged from 64.9 to 145.6 fold (theoretical enrichment factor was 200-fold). Compared with commercial PDMS coated stir bar (Gerstel) and PEG coated stir bar (Gerstel), the prepared PDMS/CTFs stir bar showed better extraction efficiency for target phenol compounds. The proposed method was successfully applied to the analysis of phenols in environmental water samples and good relative recoveries were obtained with the spiking level at 2, 10, 50 μg/L, respectively.

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1. Introduction

Phenols are widely used in many industrial domains including dye, plastic and drugs. Due to their carcinogenicity and high toxicity, phenols have been included in the priority pollutants lists of US Environmental Protection Agency (EPA) and European Union (UN) [1] sets a maximum concentration of 0.5 μg/L for total phenols and 0.1 μg/L for their individual concentration in drinking water. Therefore, determination of phenols in environmental water is of great significance for the security of human life.

Many analytical techniques have been applied for the analysis of trace phenols in environmental samples including gas chromatography (GC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). Derivatization of phenols is usually required to increase their volatility in GC analysis, which is time-consuming and may result in loss and contamination of analytes. HPLC analysis of phenols needs no derivatization, which makes HPLC a more suitable technique than GC for phenols analysis. However, direct determination of phenols in environmental samples is usually difficult because of the low concentration of phenols in real samples and complicated sample matrix. Therefore, suitable sample pretreatment techniques are usually required prior to HPLC analysis.

Conventional sample pretreatment techniques, such as liquid–liquid extraction (LLE) [2] and solid-phase extraction

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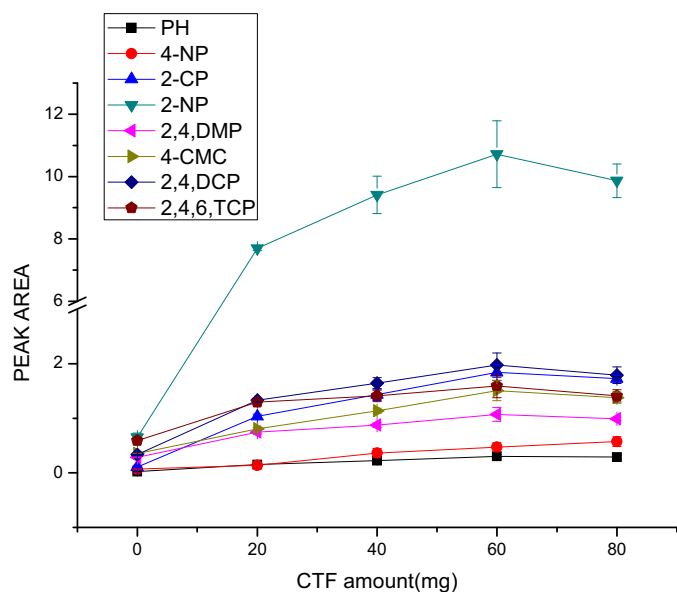C. Zhong et al. / J. Chromatogr. A 1441 (2016) 8–15

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Fig 1. Effect of CTF amount in the PDMS/CTFs coating on the extraction of the target phenols. Conditions: extraction time, 50 min; desorption mode: ultrasound-assisted; desorption time, 30 min; stirring speed, 800 rpm; pH 4; no NaCl addition; desorption solvent, methanol/10 mmol NaOH (1:1, v/v); analyte concentration: each of 200 μg/L.

(SPE) [3,4] have been applied to the analysis of phenols in environmental samples. However, they consume large volumes of samples and reagents and are time-consuming. In recent years, the requirements for sample pretreatment techniques are directed toward simple operation, miniaturization and environmental friendly, and some solventless or solvent-free sample pretreatment techniques have appeared, including liquid phase microextraction (LPME) [5,6], solid phase microextraction (SPME) [7,8] and stir bar sorptive extraction (SBSE). SBSE developed by Baltussen et al. [9,10], possesses numerous merits, such as high sensitivity, good reproducibility, high recovery, and low consumption of organic solvent. SBSE has been successfully applied in the trace analysis of environmental [11,12], food [13,14], and biomedical samples [15,16]. However, only polydimethylsiloxane (PDMS), ethylene glycol (EG)-silicone and polyacrylate (PA) are the commercially available coatings for SBSE presently, limiting its application in the real-world samples. Therefore, the development of novel stir bar coatings with high affinity and selectivity toward target analytes is of great interest [17,18]. Montero et al. [19] applied commercial PDMS for the analysis of phenols in lake and ground water samples with the assistant of derivatization procedure which complicated the analytical procedure. To avoid derivatization procedure, ethylene glycol-polydimethylsiloxane (EG-PDMS) [20] and poly(vinylpyridine-ethylene dimethacrylate) and poly(vinylpyrrolididone-divinylbenzene) monolithic stir bar [21] were applied for the enrichment of phenols from lake and sea water. However, the mass transfer rate of phenols in both methods was slow and more than 3 h was needed for the whole extraction process. Hu et al. [22] prepared amino modified carbon nanotubes stir bar, which showed good extraction efficiencies for most of the tested phenols, but the extraction efficiencies were less than 10% for phenols with LogP < 2.

Covalent triazine frameworks (CTFs) [23] is a novel class of porous materials constructed from terephthalonitrile by ionothermal synthesis. It possesses properties such as good thermal/chemical stability, large surface area and has been applied in catalysis [24] and gas separation [25]. The investigation and application of the adsorption property of CTFs is at the initial stage. Liu

et al. [26] compared CTF-1 with XAD-4 resin for the adsorption of aromatic compounds and found that CTF-1 had higher adsorption ability. Zhang et al. [27] synthesized magnetic porous covalent triazine framework composites, which exhibited high adsorption capacity (291 mg/g) for methyl orange. Bhunia et al. [28] studied the adsorption behavior of surfactants on CTF-1, and the adsorption capacity for alkyl polyglycolether surfactants was as high as 4 g/g. However, to the best of our knowledge, the application of CTF-1 in sample pretreatment has not been reported yet.

Considering that phenol compounds contain a hydroxyl group bonded directly to a carbon atom in a benzene ring, while triazine is an aromatic heterocyclic ring that contains N atom, CTFs is expected to be an efficient SBSE adsorbent for phenols based on the possible interaction between triazine and target phenols including π–π interaction, hydrophobic interaction and intermolecular hydrogen bond. Thus, the purpose of this work is to prepare PDMS/CTFs SBSE coating, and to develop a new method of PDMS/CTFs-SBSE-ultrasonic assisted liquid desorption (LD)-HPLC-UV for the determination of phenols in environmental samples. The experimental parameters affecting the extraction efficiencies of target phenols by PDMS/CTFs-SBSE such as extraction time, pH and ionic strength were studied, and the analytical performance of the proposed method was validated. The developed method was finally applied to the analysis of phenols in environmental water samples for validation.

2. Experimental

2.1. Reagents and standards

Hydroxyl-terminated polydimethylsiloxane (OH-PDMS) was purchased from Sigma–Aldrich (Milwaukee, WI, USA). Methyltrimethoxysilane (MTMS) and poly(methylhydrosiloxane) (PMHS) were purchased from the Chemical Plant of Wuhan University (Wuhan, China). Methanol, ethanol, acetone, acetonitrile, phosphoric acid (H_3PO_4), trifluoroacetic acid (TFA), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), N-dimethylformamide (DMF), and sodium chloride (NaCl) were purchased from China Medicine (group) Shanghai Chemical Reagent Corporation (Shanghai, China). Terephthalonitrile and zinc chloride ($ZnCl_2$) were purchased from TCI Development Co., Ltd. (Shanghai, China). The capillary glass bars were obtained from Apparatus Factory of West China University of Medical Sciences (Chengdu, China). Solid reagents and all solvents used in this work were of analytical grade. High purity water obtained by a Milli-Q water purification system (18.25 MΩ cm, Millipore, Molsheim, France) was used throughout the whole experiments. Commercial PDMS stir bars (20 mm long, 0.5 mm thickness, TwisterTM) and PEG stir bars (10 mm long, 0.5 mm thickness, TwisterTM) were purchased from Gerstel GmbH (Mülheim an der Ruhr, Germany).

Phenol (PH), 2-chlorophenol (2-CP), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), p-chloro-m-cresol (4-CMC), 2,4-dimethylphenol (2,4-DMP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were purchased from Alfa Aesar (Tianjin, China). The chemical structures, logKo/w and pK_a values of the target phenols are shown in Fig. S1. Each standard stock solution (1 mg/mL) of phenols was prepared in methanol, and a mixed standard solution containing 0.1 mg/mL of each phenol was also prepared in methanol. All standard stock solutions were stored at 4 °C in the refrigerator.

2.2. Instrumentation

A Dionex ultimate 3000 HPLC (Dionex, Germering, Germany) with a diode array detection detector and an autosampler was