Talanta 150 (2016) 310–318

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Polyaniline/cyclodextrin composite coated stir bar sorptive extraction combined with high performance liquid chromatography-ultraviolet detection for the analysis of trace polychlorinated biphenyls in environmental waters

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ARTICLE INFO

Article history:
Received 22 October 2015
Received in revised form
30 November 2015
Accepted 10 December 2015
Available online 19 December 2015

Keywords:
Polychlorinated biphenyls
Polyaniline/cyclodextrin composite coating
Stir bar sorptive extraction
High performance liquid chromatography
Environmental waters

ABSTRACT

A novel polyaniline/α-cyclodextrin (PANI/α-CD) composite coated stir bar was prepared by sol–gel process for the analysis of polychlorinated biphenyls (PCBs) in this work. The preparation reproducibility of the PANI/α-CD-coated stir bar was good, with relative standard deviations (RSDs) ranging from 2.3% to 3.7% ($n=7$) and 2.0% to 3.8% ($n=7$) for bar to bar and batch to batch, respectively. Based on it, a novel method of PANI/α-CD-coated stir bar sorptive extraction (SBSE) followed by high performance liquid chromatography-ultraviolet (HPLC-UV) detection was developed for the determination of trace PCBs in environmental waters. To obtain the best extraction performance for target PCBs, several parameters affecting SBSE, such as extraction time, stirring rate, and ionic strength were investigated. Under optimal experimental conditions, the limits of detection (LODs) of the proposed method for seven PCBs were in the range of 0.048–0.22 μg/L, and the RSDs were 5.3–9.8% ($n=7$, $c=1$ μg/L). Enrichment factors (EFs) ranging from 39.8 to 68.4-fold (theoretical EF, 83.3-fold) for target analytes were achieved. The proposed method was successfully applied for the determination of seven target PCBs in Yangtze River water and East Lake water, and the recoveries were in the range of 73.0–120% for the spiked East Lake water samples and 82.7–121% for the spiked Yangtze River water samples, respectively.

1. Introduction

Polychlorinated biphenyls (PCBs), are a class of organic compounds in which hydrogen atoms attached to a biphenyl are replaced by chlorine atoms, and have 209 species of isomers. Due to their excellent thermal, chemical stability and noninflammability, PCBs have been widely applied in industry, such as insulating fluids in electric equipment and additives in paint, carbonless copy paper, sealants, and plastics [1]. As a well-known kind of persistent organic pollutants, PCBs are resistance to degradation, resulting in an accumulation in the environment, such as soils [2] and water [3]. Human can be exposed to different trace PCBs through the food chain. It has been reported that PCBs can cause adverse health effects including carcinogenicity, neurotoxicity, reproductive toxicity and can interfere with human endocrine system [4,5]. Consequently, the use of PCBs had been banned since 1970s, and the content of PCBs in different matrices such as environmental water is limited under legislation in many countries and organizations. Therefore, monitoring trace levels of PCBs in the environment is mandatory, and developing efficient and sensitive analytical methods for the determination of PCBs in environmental samples is of great importance to protect humans from the threat of PCBs.

Conventional methods for the determination of PCBs are based on chromatographic techniques, such as gas chromatography (GC), high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE). GC, which is rapid and sensitive, has been coupled with mass spectrometry (MS) for PCBs determination [6]. CE is a very competitive technique for enantiomeric separation of PCBs due to its high separation efficiency and flexibility [7]. At present, HPLC combined with ultraviolet (UV) detection has also been used for PCBs determination [8]. However, the determination of PCBs in real matrices is generally considered as a challenging task due to the low detection levels required by regulatory bodies and the complex nature of the matrices in which the target compounds are present. Sample preparation is then a crucial step prior to the determination of PCBs.

Traditional sample pretreatment methods such as liquid–liquid

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http://dx.doi.org/10.1016/j.talanta.2015.12.025
0039-9140/

extraction (LLE) [9] solid phase extraction (SPE) [10] and membrane extraction [11,12] which suffer from the drawbacks of consuming large organic solvents, have been used for the analysis of PCBs in environmental and food samples, thus several new environmental friendly sample pretreatment techniques, such as liquid phase microextraction (LPME) [13], magnetic solid phase extraction (MSPE) [14], solid phase microextraction (SPME) [15–17] and stir bar sorptive extraction (SBSE) [18] have been developed for the enrichment of trace PCBs in recent years. Among them, SBSE has many advantages, such as high sensitivity, good reproducibility, and being organic solvent free or less, and has been successfully applied for the analysis of various analytes in food [19–21], environmental [22,23] and biological samples [24]. SBSE is an equilibrium technique which was introduced by Baltussen in 1999, but the coating amount on the stir bar is 50–250 times higher than that on the SPME fiber, resulting in a significant increase in recovery and extraction capacity [25]. However, there are only three kinds of commercial coating in SBSE available at present: polydimethylsiloxane (PDMS), ethyleneglycol (EG)-silicone and polyacrylate (PA). PDMS is suitable for the extraction of semi-polar and apolar compounds, while EG-silicone and PA coatings were developed for the extraction of polar organics. The commercial PDMS-coated stir bar has been used for the extraction of PCBs from different samples [18,26,27]. Poppa and co-workers [26] used commercial PDMS-coated stir bar coupled with thermal desorption–GC–MS to analyze 25 kinds of PCBs in environmental water. Zuloaga and co-workers [27] also employed commercial PDMS-coated SBSE for the simultaneous preconcentration of PCBs and other variety of organic pollutants from water samples, and comparing with membrane-assisted solvent extraction, the SBSE method provided better limit of detection (LOD) but longer extraction time. Vrana and co-workers [18] developed a method of ultrasonic solvent extraction followed by commercial PDMS-coated SBSE for the determination of PCBs in freshwater sediment, and the method was simpler and faster than traditional Soxhlet extraction method. However, in all of the above methods for the analysis of PCBs with commercial PDMS coated stir bar (so-called Twisters), the extraction kinetics was very slow, and long extraction time (about 5 h [28] or more than 10 h [29]) was needed in the extraction procedure. To overcome this problem, the home-made stir bar coatings have been prepared for the extraction of PCBs. However, to the best of our knowledge, only two works were reported on the analysis of PCBs by home-made coating SBSE. In our previous research work [30], a PANI/hydroxyl multi-walled carbon nanotubes composite-coated stir bar was prepared for the extraction of PCBs from environmental samples, and the extraction time was decreased to 50 min. Gan et al. [31] employed magnetic metal-organic framework (MOF-5 (Fe)) as SBSE coating coupled with GC–MS to detect six PCBs in fish samples, and the extraction equilibrium was obtained after 30 min.

Polyaniline (PANI), as one kind of conducting organic polymers, which has the merits of easy-to-synthesis, relative low cost, high surface area, good stability and conductivity, is widely used in sensors, batteries and capacitors. And due to its backbone of benzenoid ring, PANI and its derivatives have good affinity to many organics such as pyrethroids [32], chlorophenols [33], phenolic compounds [34] and organochlorine pesticides [35] through the π–π interaction, hydrophobic effect and hydrogen bonding interaction, resulting in a good application as adsorbents in SPE [36], MSPE [37], SPME [38], SBSE [39, 40]. PANI as the adsorbent material has also been successfully used for the analysis of PCBs [41,42] in real-world samples.

Cyclodextrin(CD), as a class of chiral cyclic oligosaccharide, always contains six or more glucose units, and α-, β-, γ-CD are the most common natural CDs. CDs have hydrophobic interior cavity and hydrophilic periphery so that can form inclusion complexes with a variety of organic molecules via hydrogen bonding, hydrophobic interaction, and electrostatic affinity and so on. They have been widely applied in pharmaceutical fields [43], cosmetics and food industry [44,45] as additives to improve solubility, stability or control flavor. Besides, in analytical chemistry, CDs and their derivatives are effective adsorbents for efficient and selective removal of organic pollutants [46,47] in environment and they had also been used to adsorb or remove PCBs [48]. Akashi and co-workers [49] employed terephthaloyl-cross linked γ-CD (TP-γ-CD) polymer as highly effective adsorbents to remove PCBs in insulating oil, and the methylated TP-γ-CD polymer enabled the complete recovery of the PCBs but could only be recycled for 10 times. Wang and co-workers [50] synthesized a composite of MWCNTs grafted with β-CD to remove 4,4′-dichlorobiphenyl and 2,3,3′-trichlorobiphenyl from water, and the composite showed higher adsorption capacity than MWCNTs, but the sorbents could not be reused.

CDs have good affinity to PCBs and can be efficient adsorbents for the analysis of PCBs. However, due to the excellent solubility in aqueous solutions, the direct use of CDs would easily lead to loss of materials. Considering the parts of composite materials can complement with each other and produce synergistic effect to make its performance better than each raw material, and the preparation of PANI/CD composite is simple and low-cost, we suppose that PANI/CD would be a good SBSE composite coating for the analysis of PCBs. Therefore, the purpose of this work is to prepare a novel PANI/α-CD composite coated stir bar via sol–gel process, and to develop a method by combining PANI/α-CD coating SBSE with HPLC-UV for the analysis of PCBs in environmental water. The effect of different experimental parameters on the SBSE of target analytes, such as extraction time, stirring rate, ionic strength and organic modifier was investigated. The performance of the proposed PANI/α-CD-SBSE-HPLC-UV method was validated under the optimal experimental conditions. And the method was successfully applied to the analysis of target PCBs in East Lake and Yangtze River waters.

2. Experimental

2.1. Standard solutions and reagents

2,4,4′-Trichlorobiphenyl (PCB-28), 2,2′,5,5′-Tetrachlorobiphenyl (PCB-52), 2,2′,4,5,5′-Pentachlorobiphenyl (PCB-101), 2,3′,4,4′,5-Pentachlorobiphenyl (PCB-118), 2,2′,3,4,4′,5′-Hexachlorobiphenyl (PCB-138), 2,2′,4,4′,5,5′-Hexachlorobiphenyl (PCB-153) and 2,2′,3,4,4′,5,5′-Heptachlorobiphenyl (PCB-180) were purchased from AccuStandard (New Haven, CT, USA). The structure and properties of target analytes are listed in Table S1. The individual standard stock solutions of each analyte (100 mg/L) were prepared by dissolving a specific amount of corresponding PCBs in methanol, and then stored at 4 °C in a refrigerator. The working solutions were prepared by diluting the standard stock solution to required concentration daily using high-purity water.

Hydroxyl-terminated polydimethylsiloxane (OH-PDMS) was purchased from Aldrich (Milwaukee, WI, USA). Methyltrimethoxysilane (MTMS), poly(methylhydrosiloxane) (PMHS) were obtained from WD Silicone Co. Ltd. (Wuhan, China). Methanol (CH_3OH), ethanol (C_2H_5OH), acetonitrile (CH_3CN), sodium chloride (NaCl), hydrochloric acid (HCl), ammonium persulfate (APS), aniline, N,N-dimethyl formamide (DMF), β-cyclodextrin (β-CD), trifluoroacetic acid (TFA, 95%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). α-cyclodextrin (α-CD) was purchased from Aladdin (Shanghai, China). γ-cyclodextrin (γ-CD) was purchased from Shenshi Chemical Co. Ltd.(Wuhan, China). Capillary glass bars were obtained from West China