Journal of Hazardous Materials 344 (2018) 220–229

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Original Research Article

Fabrication of porous covalent organic frameworks as selective and advanced adsorbents for the on-line preconcentration of trace elements against the complex sample matrix

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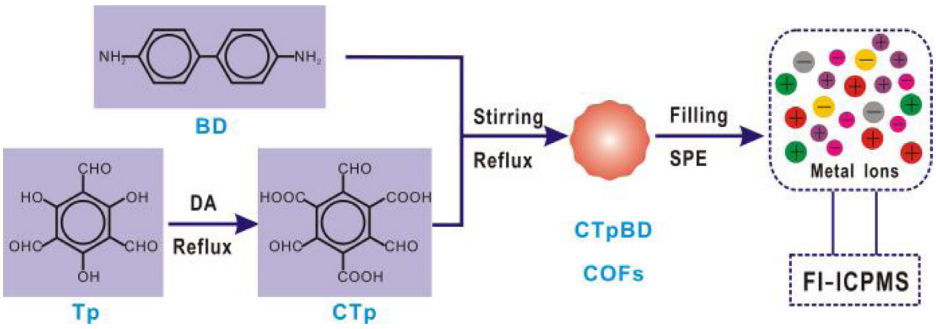
HIGHLIGHTS

- First example of covalent organic frameworks as the efficient adsorbents for metal ions.
- Selective preconcentration and enrichment of 10 ions with CTpBD COFs-involved SPE assay.
- An advisory roadmap for extending the COFs-SPE methods to hazardous substance analysis against complex sample matrix.

GRAPHICAL ABSTRACT

Fabrication of porous CTpBD COFs as robust absorbents for the preconcentration of heavy metals via flow injection followed by ICP-MS detection.



ARTICLE INFO

Article history:
Received 24 June 2017
Received in revised form
22 September 2017
Accepted 6 October 2017
Available online 12 October 2017

Keywords:
Metal ions
ICP-MS
Covalent organic frameworks
Solid phase extraction
Food

ABSTRACT

Herein, for the first time, the typical porous Covalent Organic Frameworks (COFs) CTpBD with superior chemical stability and large surface area were applied as sorbents for solid phase extraction of trace ions *via* flow injection followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. The well-prepared and fully-characterized CTpBD COFs were filled in solid phase extraction cartridge as novel and robust adsorbents for element analysis. Separation and enrichment of Cr (III), Mn (II), Co (II), Ni (II), Cd (II), V (V), Cu (II), As (III), Se (IV), and Mo (VI) was then carried out, and the contents were measured by ICP-MS. Owing to the large surface area and instinctive porous structure of CTpBD, preconcentration of the target trace elements *via* COF-filled on-line SPE column has achieved low detection limits of 2.1-21.6 ng L^{-1} along with a wide linearity range at 0.05–25 μg L^{-1} for all target ions. The relative standard deviations (RSD) of 1.2%-4.3% obtained *via* 11 parallel determinations at the sample concentration of 100 ng L^{-1} revealed excellent repeatability of the developed methods Our proposed methods have been successfully utilized for trace element analysis in environmental and food samples.

1. Introduction

Recently, heavy metal pollution is one of the most important problems in the global contamination monitoring program, due

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https://doi.org/10.1016/j.jhazmat.2017.10.013
0304-3894/

to their characteristic of invisibility and long-term accumulation [1–3]. Although the content of heavy metals in nature is relatively low, they could gradually accumulate through the water matrix and food chain into the human body, and long-term exposure can lead to severe diseases [4]. The representative toxic ions, such as Cr (III), Mn (II), Co (II), Ni (II), Cd (II), Cu (II), and As (III), can cause severe damage on human body by long-term accumulation to almost whole body organs [5,6]. Besides, the necessary trace elements, such as vanadium (V), copper (Cu), selenium (Se), and molybdenum (Mo), do good benefits for human body under the appropriate amount, but long-term exposure can also cause a variety of diseases [7]. Excessive intake of vanadium (over 20 $\mu g\,d^{-1}$) has been recognized as potentially dangerous, and can cause poisoning and hindering to the teeth and bone [8]. Cu has great influence on arterial strength, liver and kidney damage as well as stomach and intestinal irritation [9]. Excessive intake of Se (over 800 $\mu g\,d^{-1}$) or Mo (over 350 $\mu g\,d^{-1}$) would lead to the opposite role to their beneficial functions, and long-term exposure will cause damage to the human eye and skin, or lead to breathing difficulties [10]. Therefore, accurate analysis, specific recognition, precise measurement, and strict limits on monitoring the content of harmful elements in environment and food samples are of great practical significance. In this situation, an essential goal of modern analytical chemistry is to develop accurate and reliable methodologies for identification and quantification of various toxic metal elements, especially with high sensitivity and multi-detection ability against complex sample matrix.

Inductively coupled plasma mass spectrometry (ICP-MS) has been recognized as the most effective tool for trace element analysis due to its extinctive features, including high sensitivity and accuracy, multi-element analysis ability, and relative wide linear ranges [11]. However, in practical applications, the target metals are usually present at extremely low levels in complex sample matrix, such as environmental and food samples, which hardly allow the direct determination *via* ICP-MS [12,13]. Various sample preparation methods have been proposed to couple with elemental detection, such as cloud point extraction (CPE) and liquid–liquid extraction (LLE) coupled with ICP-MS or Atomic Emission Spectrometry (AES) to achieve better analytical performance [12,13]. Therein, combination solid phase extraction (SPE) with ICP-MS detection has been proved to be effective to further improve the detection sensitivity and overcome the sample matrix effects [14,15]. Moreover, integration of adsorbent-packed SPE columns with flow injection (FI) technique would produce the on-line SPE assay, which possessed the advantages of higher sample throughput, reduced loss of analyte, and lower contamination risk [16–19]. The adsorbent packed in the SPE columns plays the key role in the on-line SPE-FI system, usually required excellent chemical stability against water or acid, high surface area and certain affinity, and low backpressure in the column.

Covalent organic frameworks (COFs), an exciting new type of crystalline porous organic materials, are ingeniously constructed with organic building units *via* strong covalent bonds [20–23]. COFs presents variety by different structural motifs and connection types, and the various functional sites in the structural motifs facilitated many unique advantages in applications of gas storage[24,25], photoelectric[26,27], catalysis[28] and other fields. Compared with metal organic frameworks (MOFs), COFs have been proved to be more stable in water and acidic media, and are metal-free in their structure, in virtue of which COFs have great potential as excellent sorbent for enrichment of trace metal elements *via* solid phase extraction.

Herein, for the first time, the typical porous COFs CTpBD with superior chemical stability and large surface area were applied as sorbents for solid phase extraction of trace ions followed by inductively coupled plasma mass spectrometry (ICP-MS) detection. The well-prepared and fully-characterized CTpBD COFs were packed in solid phase extraction cartridge as novel and robust adsorbents for elemental analysis, namely, the separation and enrichment of trace elements such as Cr (III), Mn (II), Co (II), Ni (II), Cd (II), V (V), Cu (II), As (III), Se (IV), Mo (VI) in water samples, and the contents were measured by ICP-MS. The affecting factors in solid phase extraction efficiency, such as the amount of the fillers, sampling pH and flow rate, and eluent acid concentration and volume were studied and optimized. Owing to the large surface area and instinctive porous structure of porous CTpBD, preconcentration of the target trace elements *via* COF-packed SPE column has achieved low detection limits of 2.1-21.6 $ng\,L^{-1}$ for target elements. The relative standard deviations (RSD) of 1.2%-4.3% obtained *via* 11 parallel determinations at the sample concentration of 100 $ng\,L^{-1}$ indicated excellent repeatability of the developed methods.

2. Experimental

2.1. Chemicals and materials

All reagents were of the highest available purity and at least of analytical grade. Ultrapure water (Wahaha, Hangzhou, China) was used throughout all experiments. 1, 3, 5-Triformylphloroglucinol (Tp) diglycolic anhydride (DA), and benzidine (BD) were purchased from Aladdin (Shanghai, China). Ethanol, tetrahydrofuran (THF), 1,4-dioxane, mesitylene, and N,N-dimethylformamide (DMF) were obtained from Concord Chemical Research Institute (Tianjin, China). HNO_3 were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Metal environment calibration standard solutions were purchased from Agilent Technologies Trading (Shanghai) Co., Ltd. (Shanghai, China). All the glassware was cleaned with aqua regia ($HCl:HNO_3$ = 3:1, v/v) and thoroughly rinsed with ultrapure water before use.

2.2. Instrumentation

X-ray diffraction (XRD) patterns were acquired on D8 Advance (Bruker-AXS, Germany) equipped with Cu Kα radiation (λ = 1.5418 Å) with a scan speed of 8° min^{-1} and a step size of 0.02° in 2θ. The scanning electron microscopy (SEM) images were recorded on a LEO 1530VP (LEO, Germany) microscope at 10.0 kV. Fourier transform-infrared spectra (FT-IR) (4000–800 cm^{-1}) were measured on a TENSOR 27 spectrometer (Bruker, Germany) with pure KBr as background. The morphology and microstructure of the prepared nanostructures were characterized by high resolution transmission electron microscopy (HRTEM) on a JEM-2100F field emission transmission electron microscope (JEOL, Japan) operating at a 200 kV accelerating voltage. The samples for HRTEM were obtained by drying sample droplets on a 230-mesh Cu grid coated with a lacey carbon film. The elemental analysis was performed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500CX). The standard gradient solution were prepared by Agilent technologies' environment calibration standard solution (10 $mg\,L^{-1}$ of trace elements) to several concentrations of 1 $\mu g\,L^{-1}$↘2 $\mu g\,L^{-1}$, 5 $\mu g\,L^{-1}$↘10 $\mu g\,L^{-1}$, 20 $\mu g\,L^{-1}$. The standard solutions were detected on the set instrument condition. The abscissa of the standard curve is the element concentration, and the ordinate is the ratio of the response value of the measured element and the internal standard element. Adjust the points on the standard curve so that the linear correlation coefficient for each element is greater than 0.99.

2.3. Synthesis of TpBD

TpBD COFs were prepared according to the reported method with some modifications [29]. In a typical synthesis, 1,3,5-