Arsenic sorption and speciation with branch-polyethyleneimine modified carbon nanotubes with detection by atomic fluorescence spectrometry

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ABSTRACT

Multi-wall carbon nanotubes (MWNTs) are modified with branched cationic polyethyleneimine (BPEI). The MWNTs–BPEI nanocomposites serve as a novel adsorbent and exhibit favorable selectivity toward adsorption of As(V). Appropriate amount of MWNTs–BPEI suspension containing ca. 5 mg of the composites is used to pack a mini-column for on-line solid phase extraction preconcentration of inorganic arsenic in a sequential injection system, following detection by hydride generation atomic fluorescence spectrometry. At pH 5.8, an sorption efficiency of 80% is achieved for As(V) at 10 $\mu g\,L^{-1}$, resulting in a sorption capacity of 26.18 mg g^{-1}. Meanwhile, the sorption efficiency for As(III) is $<$ 5%. The retained As(V) is readily recovered by 100 μL NH$_4$HCO$_3$ (0.6%, m/v). With a sample volume of 2.0 mL, an enrichment factor of 16.3 for As(V) is obtained along with a detection limit of 14 ng L^{-1} within a linear range of 0.05–1.50 $\mu g\,L^{-1}$. A RSD of 3.6% is derived at 0.5 $\mu g\,L^{-1}$. Total amount of arsenic is obtained by converting As(III) to As(V) and following the same procedure. The speciation of inorganic arsenic is realized by difference. This procedure is validated by analyzing a certified reference material of human hair (GBW09101), achieving satisfactory agreements between the certified and the obtained values. Speciation of As(V) and As(III) is also performed in snow water and rain water samples.

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1. Introduction

Arsenic is a ubiquitous element existing widely in air, soils, rocks, natural waters and organisms [1]. Arsenic is a toxic element to human health and its toxicity is associated closely to the existing forms, inorganic arsenic species are more toxic than organic counterparts [2,3]. Nowadays, the quantification of total arsenic in various sample matrixes is no longer sufficient to reflect the risks of arsenic to the environment and human health [4]. In this respect, it is highly important to perform arsenic speciation in complex sample matrixes.

For the speciation of inorganic As (III) and As (V), the methodologies for separation and preconcentration reported in the literatures are usually based on liquid chromatography [5], capillary electrophoresis [6] or in combination with hydride generation (HG) [7]. Generally, the concentrations of arsenic species in environmental samples are found at trace levels, thus high sensitive detection techniques are necessary for this purpose, including inductively coupled plasma-mass spectrometry (ICP-MS), electrothermal atomic absorption spectroscopy (ETAAS), atomic emission spectroscopy (AES) and atomic fluorescence spectroscopy (AFS) [8–11]. ICP-MS is most widely employed for the detection of

arsenic species because of its very high sensitivity. AFS has comparable sensitivity with respect to ICP-MS for the detection of hydride and/or vapor generation elements. In addition, the running cost of AFS is much lower than that by ICP-MS. Therefore, AFS has been an alternative to ICP-MS [12–14]. Some recent advances on hydride/vapor generation have been reviewed [15,16]. It demonstrated that in the field of arsenic speciation, hydride generation atomic fluorescence spectrometry is one of the most powerful strategies. However, when handling ultra-trace amount of arsenic in complex sample matrix, the direct determination of arsenic species is difficult and therefore preliminary sample pretreatment with separation and preconcentration is highly desired. Solid phase extraction (SPE) is widely applied for the adsorption and preconcentration of ultra-trace arsenic from complex sample matrixes [17]. SPE can readily provide favorable enrichment factor with low sample and reagent consumption, at the same time it tends to avoid the risk of sample contamination and analyte loss. This feature is particularly useful when pursuing on-line automatic operation by coupling with a sequential injection system [18–20]. Among various sorbent materials, e.g., biological cells, PTFE particles or turnings, nanometer-sized TiO$_2$, activated carbon, yeast and activated alumina, carbon nanomaterials have been employed for the sorption of targets of interest [21–27]. Recently, carbon nanotubes (CNTs) have been exploited as sorbent due to high surface area, the ability of establishing π–π interactions as well as mechanical, chemical, and thermal stability [28]. The analytical capabilities

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of CNTs can be further improved or manipulated by surface modification to meet the demand for retaining different type of analytes attributed to its orientation and specificity [29,30]. We have previously reported the functionalization of multi-wall carbon nanotubes with positively charged hydrophilic branched architecture polymer. The introduction of basic functional groups on the carbon nanotubes well facilitated the isolation of acidic protein [31].

In the present work, multi-wall carbon nanotubes were functionalized with branched cationic polyethyleneimine (BPEI), and the BPEI–MWNTs composites were for the first time employed as adsorbent for the selective retention of As (V) in the presence of As(III) which are usually existing as anionic species in natural waters. The adsorption was realized in a flow system and the retained As (V) was stripped off by using dilute NH_4HCO_3 solution as eluent. The quantification of arsenic was performed by hydride generation-atomic fluorescence spectrometry, and arsenic speciation was done by difference.

2. Experimental

2.1. Instrumentation

A AFS-9130 atomic fluorescence spectrometer (Titan Instruments Co., Beijing, China) is employed, with arsenic hollow cathode lamp (Beijing General Research Institute for Nonferrous Metals, China) as radiation source. The operating parameters of the AFS instrument, including the atomizer height, negative high voltage of the photomultiplier, lamp current, carrier and shield argon flow rate, are investigated in terms of sensitivity and reproducibility. The optimized experimental parameters are summarized in Table 1.

The measurement of pH values is performed with an Orion Model 868 pH meter (Thermo Electron). A KQ5200 DB ultrasonic system (Kunshan Ultrasonic Instruments Co., Ltd., China) is used for the dispersion of carbon nanotubes and functionalized composites in aqueous medium.

A FIAlab-3000 sequential injection system (FIA lab Instruments, Bellevue, USA) with a 2.5 mL syringe pump and an 8-port selection valve is employed for fluidic delivery. All the external channels were made of polytetrafluoroethylene (PTFE) tubing (0.8 mm i.d.). The entire system is controlled with a computer running the FIA lab for Windows software.

Surface charge analysis is investigated by measuring the zeta potential of the material with a Zetasizer Nano ZS90 (Malvern, England). Thermogravimetric analysis (TGA) is performed on a HCT-2 thermogravimetric analyzer (Beijing Heng-Jiu Instruments) under nitrogen protection. FTIR spectra are obtained using a Nicolet-6700 FTIR spectrophotometer (Thermo Instruments Inc., USA) within the range of 500 cm^{-1} to 4000 cm^{-1}.

2.2. Reagents and solutions

All the reagents used are at least of analytical reagent grade, and deionized (DI) water of 18 $M\Omega\,cm^{-1}$ is used throughout.

Table 1
Operating parameters of the AFS instrument.

Parameter	Setting
Hollow cathode lamp	Arsenic 197.2 nm
Negative high voltage of PMT	350 V
Lamp current	65 mA
Carried argon flow	350 mL min^{-1}
Shield argon flow	800 mL min^{-1}
Atomizer height	8 mm

Multi-wall carbon nanotubes are obtained from Shenzhen Nanotech Port Co. Ltd., with diameter of 60–100 nm, length of 5–5 mm and specific surface area of 40–30 $m^2\,g^{-1}$ (L.MWNTs-60100).

Branched polyethyleneimine (Mw~25 kDa) is received from Aldrich Milwaukee, MI, USA. It is used without further pretreatment.

Working standard solutions of As(III) and As(V) are prepared by stepwise dilution of stock solutions of 100 mg L^{-1}.

A 1.0% (m/v) $NaBH_4$ solution is prepared by dissolving $NaBH_4$ in 0.5% (m/v) NaOH. This solution is prepared daily.

Other chemicals used are: nitric acid, sodium chloride, ammonium bicarbonate, sulfuric acid and potassium permanganate.

2.3. Preparation of the BPEI–MWNTs composites [31]

Commercial MWNTs are pretreated to remove the residual surface impurities by immersing in 50% ethanol (v/v) and sonicating for 20 min to achieve sufficient dispersion. The MWNTs were collected by centrifugation and washed with DI water repeatedly to ensure the complete removal of the residuals. The MWNTs were then washed with 1% HCl to eliminate any metal residues on the surface and finally rinsed with DI water until neutral washout was obtained. The oxidized MWNTs were prepared by suspending the treated MWNTs in a sulfuric acid/nitric acid mixture (3:1, v/v) and sonicating for 3 h to generate carboxylic acid groups. After washed with DI water, the oxidized MWNTs were collected and mixed with 10 mg mL^{-1} branched polyethyleneimine (BPEI) and 1.0 mol L^{-1} NaCl aqueous solution. The BPEI modification was achieved by electrostatic attraction between the positively charged protonated amines in the polymer and the carboxyl groups on the oxidized MWNTs surface. The BPEI–MWNTs were thoroughly washed with 0.1 mol L^{-1} NaCl and DI water, and then dispersed in water prior to storage for use in the separation and preconcentration of arsenic.

2.4. Column preparation

Appropriate amount of the BPEI–MWNTs composites suspension is injected into a piece of PTFE tubing (1.6 mm i.d.) blocked at both ends with a small amount of glass wool to avoid leakage of the composites during the adsorption process. About 5 mg of the BPEI–MWNTs composites are used to pack a mini-column with an effective length of ca. 10-mm. Before use, the mini-column is flushed alternatively forward and backward with DI water at a flow rate of 15 $\mu L\,s^{-1}$. The mini-column is finally evacuated with air for the ensuing use.

2.5. Sample pretreatment

Snow water and rain water: fresh snow is collected from the campus of Northeastern University and stored in an air-tight flask at 4 °C following melting. Rain water is collected in the same campus. Before starting the preconcentration process, the water samples are filtered through a 0.22 μm mixed cellulose ester membrane (Shanghai Xinya Company, China) and adjusted to pH 5.8 with dilute HCl and/or NaOH solution.

Certified reference material CBW 09101 (human hair): 0.0500 g of the sample is taken into a PTFE digestion vessel along with 5 mL of concentrated HNO_3. After soaking for 2 h at room temperature, the mixture is digested on a microwave oven by using the following program: 140 °C/10 atm for 2 min, 170 °C/18 atm for 2 min, 190 °C/25 atm for 2 min, 220 °C/30 atm for 8 min. Afterwards the mixture is evaporated to ca. 1 mL on a hot plate at 150 °C. An appropriate amount of hydrogen peroxide (30%, v/v) is added into the PTFE digestion vessel, and the mixture is then heated to near dryness. The residue is cooled to room temperature and then dissolved with DI water and transferred to