



Magnetic dispersive micro solid-phase extraction for trace mercury pre-concentration and determination in water, hemodialysis solution and fish samples



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ABSTRACT

A new preconcentration method, magnetic dispersive micro solid phase extraction (MDMSPE) developed for separation and determination of mercury. In this technique, an appropriate mixture of extraction solvent, disperser solvent and nanomagnetite (Fe_3O_4)/chelating agent 1-(2-ethoxyphenyl)-3-(4-ethoxyphenyl) triazene functionalized multi-walled carbon nanotubes with silica shell, as an adsorbent injected rapidly into an aqueous solution containing mercury. After the proper contact time, the nano-adsorbent separated from the aqueous phase by applying magnetic field outside of the vial and transferred to another vial with the elution solvent. The residual solution determined by cold vapour atomic absorption spectroscopy. The main factors affected the preconcentration of mercury investigated and optimized, such as extraction and disperser solvent type, adsorbed amount, sample pH value, effluent concentration, extraction time, the volume of chelating agents and temperature. The adsorption equilibrium data obeyed the Langmuir isotherm models and the kinetic data were well suited to the pseudo-second-order model. Thermodynamic studies revealed the endothermic nature of the procedure. Under the optimum experimental conditions, the detection limit for Hg(II) found to be $1.5 \pm 0.27 \text{ ng mL}^{-1}$ and its limit of quantification (LOQ) was $5.0 \pm 0.32 \text{ ng mL}^{-1}$ ($n = 5$). The linear range of the calibration curve was 9 ± 0.51 – $1000 \pm 0.03 \text{ ng mL}^{-1}$ with a correlation coefficient of 0.9994.

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1. Introduction

Industrial growth and urbanization cause major environmental pollution by various agents such as heavy metals [1]. Mercury is one of the most pollutant heavy metals, which is imputable to its toxicity, persistent character in the environment and biology as well as bioaccumulation along the food chain [2]. Mercury has been widely used in several different kinds of products such as, plastic, paper, paint and pharmaceutical products [3–5]. It has the negative effects on human health such as kidney and liver toxicity [6,7], neurological damage [8], chromosome breakage and birth defects [9]. Some other important contributors of mercury to the environment are anthropogenic activities like increased mining and high rate of fossil-fuel burning [10].

The most usual methods for determination of mercury are X-ray fluorescence (XRF) [11], atomic absorption spectrometry [12], voltammetry [13] and inductively coupled plasma (ICP) [14]. Among these techniques, in the present study, cold vapour atomic absorption spectroscopy (CVAAS) selected for magnetic dispersive micro solid phase extraction of mercury.

Flame atomic absorption spectroscopy is not sufficiently sensitive for the determination of mercury. Thus, atomic absorption employing the cold trap generation technique has been developed to improve the sensitivity for mercury.

In the CVAAS, an acidified solution containing mercury reacted with Tin(II) chloride in a vessel external to the atomic absorption instrument. The produced mercury atoms transported to an absorption cell installed in the instrument by the air flow. So, traditional flame atomic absorption spectrometer sensitivity increased about up to five times.

Dispersive solid phase extraction (dSPE) [15] is a promising sample pre-handling technique. In dSPE, an SPE adsorbent dispersed in a sample solution containing the target analytes. After extraction, the adsorbent settled by centrifugation. This approach enables the analytes to interact equally with all the adsorbent particles, achieving greater capacity per amount of adsorbent and avoiding common problems of conventional SPE method such as channelling or blocking of cartridges or discs.

Multi-walled carbon nanotubes (MWCNTs) have drawn much interest due to their strong adsorption power, exceptional mechanical properties, high chemical stability and a large specific surface area [16], besides the advantages, they suffer some disadvantages which limit the application of MWCNTs such as poor dispersion and tedious isolation in aquatic phase. At present, Fe_3O_4 magnetic nanoparticles have

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become more and more important as adsorbents for solid phase micro extraction [17], because they easily isolated using a magnetic field placed outside of the extraction container. Therefore, combine magnetic properties into MWCNTs system have the advantages of high adsorption capacity of MWCNTs and the separation convenience of magnetic materials.

In this work, the magnetic functionalized MWCNTs modified with silica compound and a new triazene ligand (1-(2-ethoxyphenyl)-3-(4-ethoxyphenyl) triazene (EET), (MWCNTs-Fe₃O₄ MNPs-silica-EET) to the selective Hg(II) adsorption from the solution.

Triazene compounds have recently drawn attention due to a miscellany of interesting properties [18,19]. Triazene's characterized by having a diazoamino group (—N=N—) studied for over one hundred years on their interesting structural and anticancer properties [20].

In our experiments, during the sol-gel reaction of 3-(trimethoxysilyl) 1-propane thiol (TMOSPT) with triazene solutions and magnetic multi-walled carbon nanotubes (MWCNTs-Fe₃O₄ MNPs), the silica particles formed interconnecting rigid networks and immobilized on the surface of the MWCNTs-Fe₃O₄ MNPs nanoparticles, while the triazene (EET) and MWCNTs-Fe₃O₄ MNPs were simultaneously fixed on the silica particle surface. MWCNTs-Fe₃O₄ MNPs-silica-EET applied for separation and enrichment of trace amounts of Hg(II) by MDMSPE and then desorbed Hg(II) with HNO₃, determined by using CVAAS.

The developed method used for mercury determination in fresh and spring water, Caspian Sea, hemodialysis solution and canned tuna fish samples.

2. Experimental

2.1. Material and solutions

Ferric chloride hexa-hydrate (FeCl₃·6H₂O), ferrous chloride tetra-hydrate (FeCl₂·4H₂O), ammonium hydroxide (NH₄OH), sodium hydroxide (NaOH), hydrochloric acid (HCl), mercury nitrate di-hydrate (Hg(NO₃)₂·2H₂O), stannous chloride, tetramethoxyorthosilicate (TMOS), tetraethylorthosilicate (TEOS), and 3-(trimethoxysilyl) 1-propane thiol (TMOSPT) were of analytical grade and all obtained from Merck (Darmstadt, Germany). All aqueous solutions prepared with de-ionized water. Tin(II) chloride solution (25% w/v) as the reducing agent prepared by adding 25.00 g of stannous chloride to a 20 mL of conc. hydrochloric acid. The mix heated to dissolve the stannous chloride then allowed to cool before diluting the solution to 100 mL with water and mixing.

A 1000 mg·L⁻¹ Hg(II) stock solution prepared by dissolving accurate amounts of their salts in water. The daily working solutions were ready by appropriate dilutions of the stock solution immediately prior to use in the experiments.

2.2. Canned tuna fish sample preparation and digestion

Persian Gulf canned tuna fish samples purchased from popular supermarkets in Ghazvin, Iran. The contents of cans of tuna homogenized thoroughly in a food blender. The 2 ± 0.001 g of homogenized mixture then digested according to the following procedure: the test sample weighed into a 500 mL glass digestion tube, and 10 mL of conc. HNO₃ and 5.0 mL of H₂SO₄ added drop wise. The tube was then placed on a steam bath to complete dissolution. It was then removed from the steam bath, and after cooling the solution transferred into a 50 mL volumetric flask. This solution is placed under the extraction process, according to the procedure described in Section 2.8. Then, mercury determined in the digested test sample using cold vapour atomic absorption spectrophotometry. The other real samples were analysed after the extraction, without any treatment.

2.3. Instruments

An atomic absorption spectrometer (Spectra AA 220 FS, Varian) equipped with a vapour generation accessory (VGA-77, Varian) and a T-shaped quartz absorption cell used for mercury determination.

A mercury hollow cathode lamp applied as light source. The operating condition of the instrument adjusted according to the manufacturer's instruction as follows: lamp current 4.0 mA, absorbance wavelength at 253.7 nm, spectral bandwidth at 0.5 nm, vapour type cold vapour, flow rate of Tin(II) chloride solution as the reducing agent 1.0 mL/min, and flow rate of samples 7.0 mL/min.

2.4. (2-Ethoxyphenyl)-3-(4-ethoxyphenyl) triazene (EET) synthesis

A 1000 mL flask charged with 100 g of ice and 100 mL of water and then cooled to 0 °C in an ice-bath. After that, a solution containing 6.9 g (0.05 mol) of 4-ethoxyaniline in 25 mL of methanol and 10 mL (0.12 mol) of hydrochloric acid ($d = 1.18 \text{ g}\cdot\text{mL}^{-1}$) added to the reaction flask. Then, a solution containing 3.45 g (0.05 mol) of NaNO₂ in 25 mL of water added during 15 min under stirring. Afterwards, 6.38 g (0.05 mol) of 2-ethoxyaniline added to the mixture for a period of 30 min under vigorous stirring. Finally, the sodium acetate solution (18% of concentration) added to a pH between 7 and 8 was obtained, and then stirred for 2 h. The yellow colour residue filtered and dissolved in diethyl ether. After evaporation of diethyl ether, the purified orange crystals obtained (yield, 97%) [21].

2.5. Fabrication of MWCNTs-Fe₃O₄ MNPs-silica-EET

MWCNTs oxidized as previously reported, according to the following procedure [22]. Untreated MWCNTs heated in an oven at 550 °C for 45 min to remove amorphous carbon. After thermal treatment, a 500 mg of MWCNTs was dispersed into a flask containing 20 mL of a 70% sodium hypochlorite solution (6 mL of H₂O + 14 mL of NaClO). The result was then rocked in an ultrasonic cleaning bath for 120 min. The solution filtered through a 0.45 μm nylon fibre filter, moving over the activated MWCNTs. Finally, the MWCNTs washed thoroughly with double distilled water several times until the pH of the filtrate was neutral. The filtered solid dried in the oven at 70 °C, obtaining carboxylic acid-functionalized MWCNTs (MWCNT-COOH).

Magnetic carboxylic acid-functionalized multi walled carbon nanotubes (MWCNTs-Fe₃O₄ MNP) prepared as reported by Gong et al. [23]. For this purpose 500 mg of MWCNT-COOH suspended in 250 mL water containing 700 mg (2.5 mM) of iron(II) chloride tetrahydrate and 1350 mg of iron(III) chloride hexahydrate (5 mM). The temperature of the suspension raised to 50 °C under argon atmosphere followed by the slow addition of 5 mL of 8 mol·L⁻¹ ammonium hydroxide solution with stirring. The pH of the suspension controlled in the range of 10–11. After complete addition of ammonium hydroxide solution, the temperature was brought up to 80 °C and reaction allowed to be continued for 30 min. The suspension cooled to room temperature and MWCNTs-Fe₃O₄ MNP isolated from the mixture with the help of a permanent magnet. Separated MWCNTs-Fe₃O₄ MNP washed thrice with deionized water, followed by ethanol. Finally, MWCNTs-Fe₃O₄ MNP dried under vacuum.

The MWCNTs-Fe₃O₄ MNP modified sequentially with TEOS, TMOS, TMOSPT and EET to introduce amine and thiol groups as previously mentioned by Zhang et al. [24]. Typically, 20 mL magneto-suspension (10 mg of MWCNTs-Fe₃O₄ MNP, which dispersed in 10 mL water) diluted with 150 mL ethanol, and the mixture was homogenized by ultrasonication for 15 min prior to the addition of 1 mL NH₃-H₂O. After being stirred vigorously for 30 min at 30 °C, 1.0 mL TMOSPT dropped into the solution. The reaction performed for 45 min and then 0.2–2.0 mL concentrated EET solution introduced and lasted reaction for another 4 h; the suspension cooled to room temperature and MWCNTs-Fe₃O₄ MNPs-silica-EET was isolated from the mixture with

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