Preconcentration and separation of ultra-trace amounts of lead using ultrasound-assisted cloud point-micro solid phase extraction based on amine functionalized silica aerogel nanoadsorbent

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ABSTRACT

A new method based on ultrasound-assisted cloud point-micro solid phase extraction (USA-CP-MSPE) with amine functionalized silica aerogel (AFSA) was used for separation and preconcentration of Pb(II) ions in water samples. At optimized pH, the mixture of AFSA and Triton X-100 as a nanoadsorbent and nonionic surfactant, respectively, was added to the aliquot of lead standard solution. Then, the sample was transferred to an ultrasound bath and placed in a thermostat water bath, and cooled in an ice-bath. In this step, the nanoadsorbent easily settled down in the surfactant phase and the enriched surfactant phase was separated from the aerogel nanoadsorbent by centrifugation. The analyte was back-extracted from nanoadsorbent with nitric acid solution (1.0 M) and its concentration was determined by electrothermal atomic absorption spectrometry (ETAAS). Under the optimized conditions, the linear range was 0.04–1.45 µg L^{-1} for Pb(II) and the limit of detection was evaluated as 0.01 µg L^{-1} (peak area). An enrichment factor of 102 was achieved. Afterwards, the optimized method was applied to the determination of lead in real water samples that includes sea, river, tap and rain water.

1. Introduction

In recent years, research in the field of the environmental pollution has expanded beyond classical contaminants—pesticides, biocides, PHA, PCBs and pharmaceuticals [1]. Contamination of water, soil and plants by heavy metal ions is of great concern due to their associated ecological and health toxic effects even at very low concentrations. Among them, lead is one of the most toxic metals owing to its accumulative toxicity for the human body [2]. Lead accumulates in the vital organs of humans and animals. Consumption of food with high concentrations of this element can produce problems for human health, such as damage to the kidneys and central nervous system; therefore, different legislations have established maximum levels of these elements in food to avoid these problems [3]. Because of its high toxicity, enhanced by the indicated mobility, it is very important and necessary to determine and control the lead content at trace and ultra trace levels in waters [4]. In order to determine trace levels of Pb, a separation and enrichment step prior to the determinations may be beneficial. Several methods have been proposed for separation and preconcentration of trace Pb including liquid–liquid extraction (LLE) [5], solid-phase extraction (SPE) [6], dispersive liquid–liquid microextraction (DLLME) [7], cloud point extraction (CPE) [8], and liquid-phase microextraction (LPME) [9]. SPE is one of the pre-treatment methods for the preconcentration of trace analytes from a sample. The major advantages of solid phase extraction are the high selectivity and high enrichment factor that could be achieved with this technique. This method gives a higher concentration ratio of analytes than other separation methods. Therefore, extraction is possible even outside the context of polluted solvents leading to reduced detection limits and enhanced reliability [10]. In contrast, SPE is more effective for sample cleanup because the sample matrix can be removed from the system except for improving concentration sensitivity; therefore, SPE has been proposed for use in sample cleanup and preconcentration at trace levels [11].

Nowadays, nanomaterials have been shown to be one of the most promising adsorbents for preconcentration of the metal ions [12,13]. One of the specific properties of nanomaterials is their high surface areas, which could strongly chemisorb many substances and present very high adsorption capacities towards metal ions. Nevertheless, limitations of using nano-sized materials as adsorbents in the SPE method is changing the shape and size of nanomaterials which results in the accumulation and decrease of the surface area and also slows the flow rate which leads to long process times. To overcome the

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aforementioned problems, NPs could be used in the CPE method for preconcentration of the analytes. CPE using micelles is a well-known methodology for designing new analytical procedures for different analytes such as organic compounds [14], metal ions [15], pharmaceuticals [16] and dyes [17]. CPE is a safe and green methodology, which uses small amounts of surfactant that limit environmental pollution. Liu et al. have successfully evaluated the CPE of several NPs with various sizes and different capping agents using nonionic surfactant Triton X-114 [18]. Their suggested method has illustrated that CPE can be used for concentration and recycling of NPs in aqueous media.

Most adsorbents are easily available and low-cost but they have some disadvantages such as poor mechanical and heat resistance and relatively limited adsorption capacity [19]. Thus, researchers are interested on focusing on the modification of adsorbents. Among a great variety of adsorbents, silica is of particular interest because of its stability, possible reuse, relative rapidity in reaching equilibrium, high mechanical resistance and high surface area [20]. Silica is a modifiable material and the modified silica has new surface functional groups, which are capable of interacting with various analytes [21]. A wide variety of techniques such as precipitation [22], coagulation/co-precipitation [23], electrodialysis [24] and nanofiltration [25] are available for extraction of heavy metals from liquid effluents. In these techniques, the adsorption method has received a great deal of attention due to the low cost of the materials, relatively simple process and reusability [26]. Despite these advantages, the sequestration efficiency of the heavy metal ion in water is restricted from the amount of the adsorption active sites. Therefore, most researches have concentrated on enlarging the surface area of the adsorbent for the immobilization of large amounts of adsorption sites [27].

In this paper, we synthesize silica aerogel as a support material to immobilize the adsorption sites for Pb(II) sequestration. We also report on the effects of the amine group as adsorption sites for Pb(II) ions in samples. In the present study, USA-CP-MSPE based nanostructured silica aerogel (AFSA) as a new nanoadsorbent was used for separation and preconcentration of Pb(II) ions in water samples. For performing CPE method for preconcentration/separation of Pb(II) from aqueous solutions, Triton X-100 as a nonionic surfactant was used. This method has enough sensitively and simplicity for extraction and determination of analytes in environmental samples by ETAAS.

2. Experimental

2.1. Apparatus

Determination of Pb(II) was performed with a spectra GBC electrothermal atomic absorption spectrometer (Model Plus 932, Australia) using a graphite furnace module (GF3000).

The optimum instrumental parameters and temperature program for graphite atomizer are listed in Table 1. A lead hollow cathode lamp (wavelength, 283.3 nm; current, 5 mA) was used. All experiments were performed by using auto-sampler injection. The pH values of the solutions were measured by a digital pH meter (Metrohm, M 744) supplied with a combination glass electrode. All shaking and centrifuging of whole samples were done using Thermo Scientific LP Vortex Mixer (TSLVM) and Thermo Scientific Statspin Express

Table 1
Temperature program of ETAAS for determination of Pb(II).

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Argon flow rate (L min^{-1})	Gas type
Dry step	240	10	20	3.0	Inert
Ash step	400	20	10	3.0	Inert
Gas stop step	400	1	1	0.0	None
Atomize hold step	2000	2	1	0.0	None
Tube clean with maximum gas flow	2100	2	2	3.0	Inert

Centrifuge (Waltham, US). An ultrasound water bath (Model Tecna 6, Taranto, Italy) at a frequency of 60 MHz with 5.8 L water volume contained in the tank, and internal dimensions of 300 mm width,150 mm diameter and 150 mm height was used for cloudy mixture formation. All 10.0 mL polypropylene centrifuge tubes with 110, 17 and 14.5 mm height, external diameter and internal diameter, respectively, were stored in 0.1 M HNO$_3$ to remove any inorganic compounds and washed with deionized water and then with acetone.

2.2. Reagents and materials

All reagents with ultra-trace analytical grade such as nitric acid (HNO$_3$), hydrochloric acid (HCl), sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$), toluene, methanol, ethanol, Triton X-100, Triton X-114, sodium hydroxide (NaOH), 1,1,1,3,3,3-hexamethyl disilazane and lead nitrate salt were purchased from Merck (Darmstadt, Germany). The other reagent such as tetramethoxysilane (TMOS) and ammonium hydroxide were supplied by Sigma-Aldrich (Milwaukee, US). Pb(II) stock solution was prepared from an appropriate amount of the nitrate salt of this analyte as 1000 mg L^{-1} solution in 1% HNO$_3$. Standard solutions were prepared daily by dilution of the stock solution of lead in nitric acid. Ultrapure water was obtained from Millipore Continental Water System (Bedford, US).

2.3. Synthesis of silica aerogel and AFSA

In presented research, the silica aerogel was derived by mixing tetramethoxysilane (TMOS), with ammonium hydroxide (28.0%–30.0%), which was diluted in water and methanol. Firstly, in order to initiate the gelation process, two separate solutions were prepared: TMOS in methanol (solution A) and ammonium hydroxide in methanol (solution B). Then, solution B was slowly poured into solution A and simultaneously stirred. The transparent gels were formed in the next 15 min and afterward the gel samples were extruded to 250 mL glass jars, filled with 100 mL of methanol. In the next stage, the silica gel samples were aged for 3 days. Then, the samples were subjected to supercritical conditions (31.1 °C at 73.7 bar) for a minimum of 2 h and 30 min.

In order to investigate the amine structure relationships for Pb(II) adsorption, 11 mL of 1,1,1,3,3,3-hexzamethyl disilazane and 1 g of silica aerogel were added to 75 mL anhydrous toluene. The coupling reaction was allowed to proceed for 24 h at room temperature with a gentle stirring under a nitrogen atmosphere. After reaction, the AFSA was rinsed with 90 mL ethanol. The modified silica aerogel was dried in an oven at 120 °C for 3 h. After drying, it was rinsed three times with 50 mL toluene, a mixed solution of 100 mL toluene and ethanol (1:1), and 50 mL ethanol, in that order. Finally, amine-functionalized silica aerogel was freeze-dried under vacuum (pressure lower than 5 mtorr) for 48 h after washing with deionized water.

2.4. Characterization

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. It is useful for determining the particle shape, porosity and appropriate size distribution of the nanoadsorbent. From Fig. 1, it is clear that AFSA has a considerable number of pores, there is a good possibility for analytes to be trapped and adsorbed into these pores. The SEM pictures of AFSA samples show very distinguished dark spots which can be taken as a sign for effective adsorption of heavy metal ions in the cavities and pores of this nanoadsorbent.

The FT-IR spectrum of the silica aerogel displays a number of characteristic bands (Fig. 2a). The peak at 3443 cm^{-1} is assigned to stretching vibration of hydrogen bonded silanol group $\upsilon(\equiv$Si-OH) and $\upsilon(^-$OH) of physisorbed water molecule. The peaks at 1086 cm^{-1}, 847 cm^{-1} and