PRECONCENTRATION OF MERCURY IN HUMAN HAIR BY MODIFIED SILICA AEROGEL NANOPARTICLES

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ABSTRACT

Pollution from heavy metals has increased in recent decades and has become an important concern for environmental agencies. Mercury is among the trace elements that have the greatest impact and carry the highest risk to human health. In the present work, a new adsorbent, silica aerogel modified with 4-amino-5-methyl-1, 2, 4-triazole-3(4H)-thion (AMTT) was applied to preconcentration of mercury in scalp hair samples prior to its determination. The adsorbent was characterized by Fourier Transform Infrared Spectra (FTIR), and Thermal Gravimetry (TG) and Scanning Electron Microscope (SEM). The optimum pH for the adsorption of mercury ion ranged from 5 to 6 and the minimum shaking contact time necessary for reaching the equilibrium was about 6h. The enrichment factor is 150 was obtained. The method successfully applied to the determination of trace Hg (II) in spiked hair samples, with recoveries ranging from 90% to 94%.

Keywords: Hair Analysis; Mercury; Silica Aerogel; Preconcentration; Nanoparticles

INTRODUCTION

Scalp hair has been widely used as a biomarker of human mercury exposure (1). Mercury in the hair correlates with mercury in the brain, and MeHg accounts for approximately 70–80% of total mercury (T-Hg) in hair (2). Most common techniques that have been reported for the determination of total mercury in natural samples are inductively coupled plasma mass spectrometry (ICP-MS) (3), inductively coupled plasma atomic emission spectrometry (ICP-AES) (4), gas chromatography (GC) coupled to atomic absorption spectrometry (AAS) (5), cold vapor atomic absorption spectrometry (CV-AAS) (6), atomic fluorescence spectrometry (AFS) (7), anodic stripping voltammetry (ASV) (8), neutron activation analysis (NAA) (9) and so on. Among these techniques, ICP-AES and ICP-MS are useful in determining the ultra-trace of total mercury without any preconcentration step. However, these instruments are very expensive and costly for the maintenance. CV-AAS has been widely used with the considerable merits such as high sensitivity and little interference effect but this method suffers. In some techniques, separation and preconcentration via methods such as liquid–liquid extraction, ion-exchange, co-precipitation, should be performed to determine extremely low concentration of mercury (10). Among the most useful methods, adsorbents are of benefit to trace the elemental preconcentration (11). The development of new sorbents and their application in preconcentration methods for determination of trace elements is a subject of great interest. Nanoparticles exhibit good adsorption efficiency especially due to higher surface area and greater active sites for interaction with metallic species (12).

In recent years, nanometer-sized alumina (13, 14) and nanometer-sized titania (15) have been proposed and applied in the preconcentration of trace metals. Aerogels, nanomaterials normally prepares by sol-gel polymerization and supercritical drying, have great potential for use as adsorbents (16). Silica aerogels is a highly porous, open cell, low-density foam. Furthermore, one of the most important properties of silica aerogels is also the possibility to modify their surface chemical nature with the incorporation of organic functional groups (17). Silica aerogel (SA) surface modifications with chelating agents for adsorption/ removal of metal ions have been reported in recent years, such as

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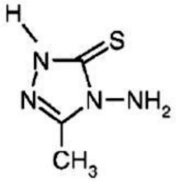
polyacramide (18), mercaptopropyl (19) were successfully incorporated. These materials have demonstrated ability to remove various heavy metal ions such as Cu^{2+}, Hg^{2+}. In this literature was used 4-amino-5-methyl-1, 2, 4-triazole-3(4H)-thion (AMTT) as metal chelating ligands (for structure see Scheme 1.) and its application for selective adsorption of Hg (II) ion.

In this work, silica aerogel (SA) nanoparticles adsorbent coupling with metal chelating ligands of AMTT was prepared and was applied to preconcentration of Hg (II) from hair samples.



Scheme 1. The structures of AMTT

EXPERIMENTAL

Materials and methods

Tetramethylortho silicate (TMOS) and methyltrimethoxysilane (MTMS) from Aldrich and another reagents used in the present study were of analytical grade from E.Merk. 1000 µg mL^{-1} of Hg(II) stock solution was prepared by dissolving 1.354 g of $Hg(Cl)_2$ in 10mL 1 M HNO_3 and dilute to by deionized water. Diluted HNO_3 and NaOH solutions were used for adjusting the initial pH of solutions. A Perkin-Elmer 4100 (Australia) atomic absorption spectrometer (equipped with VGA77) was used for all absorption measurements. A mercury hollow cathode lamp was used as light source. An infrared spectrum was obtained using a FT-IR (Bruker, model vertex vo) and Scanning electron microscopy (SEM) was performed to measure the particle size (SEM-EDX, XL30 and Philips Netherland). The thermal behaviour of the dried materials was examined using TGA (Mettler-851e). The pH values were controlled with a Mettler Toledo 320-S pH meter (Shanghai, China) supplied with a combined electrode. A Band line Sonorex D-12207 ultrasonic cleaning bath +(Berlin, Germany) programmable for temperatures, ranging from 0 to 90ºC, and times, up to 15 min, and with a frequency of 35 kHz for the ultrasound energy, was used to induce the acid-leaching process.

Adsorbents synthesis

The 5.02 mL TMOS was diluted with 44.2 mL of methanol, then 1.5 mL of MTMS was added and finally 1.2 mL NH_4F (0.1 $molL^{-1}$) solution was added to mixture. Then the mixture was stirred at 20°C for 30 minutes. After the intermediate product was homogenisation by homogeniser (20000 rpm) and during the homogenisation 0.033 g AMTT was added to mixture. The mixture was poured into a Teflon beaker where the sol aged into hydrogel with in about 10 min. After gelation, the gel was left for one day. Subsequently, the product was thoroughly immersed in to methanol for 24h and dried at room temperature for 5 days and finally the SA–AMTT adsorbent was obtained.

Sample Collection

A number of hair samples were collected from west of Tehran. Individuals were invited to answer a small questionnaire designed to obtain information about age, sex, food ingestion (home grown fruits and vegetables, fish, and animals, breeding cattle and canned food), source of drinking water, smoking habits, alcohol consumption, health condition, medication, and workplace. The first step in the analysis was sampling. It is very important to use a tool that does not contaminate the samples with the trace elements to be examined. Samples were taken from the same site in all individuals, namely, from the back of the head, because it is relatively protected against environmental exposures and cosmetics. The collected samples were stored individually in sealed plastic bags at room temperature.

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Samples preparation

The risk of sample contamination during the sampling and digestion was minimized. Prior to analysis, hair samples were washed with acetone, water, and acetone again (20). To optimize the washing procedure, each hair sample was weighed directly into a conical sample tube, 25 mL of the washing solution was added and the tube was capped. The container was shaken on a mechanical shaker for 1 h at 20 ˚C. Then the supernatant was pipetted-off. The hair sample was oven– dried at 70 ˚ C for 6 hs and then digested the next day.

About 0.1 g of hair samples were accurately weighed in to conical tubes. Then, 4 mL of 6mol L^{-1} HCl is added to the samples, sonicated at 80 min, the residue was extracted again and then further diluted deionized water.

General procedure

Sample solutions were adjusted to the desired pH value 6 with 0.1molL^{-1} NH_3 and HCl before use. Then in flasks, 0.16 g SA–AMTT added to sample solutions. The flasks were kept for shaking at 200 rpm in an orbital shaker (GFL 3005 German) for 6h. Then the samples were centrifuged at 2500 rpm for 5 min to separate the adsorbent. The retained analytes were eluted with 4.0mL of 1.0 mol L^{-1} KBr solution and determined by CV-AAS.

RESULTS AND DISCUSSION

Characterization of adsorbents

Fig .1 (a, b), shows the SEM micrographs of the SA and SA–AMTT. The result of TGA shows that there is a very little weight loss up to a temperature of 300 ºC. A further increase of temperature causes weight loss along with exothermic peaks corresponding to the oxidation of surface organic (CH_3) groups.

In Fig. 2, the FTIR investigation of silica aerogels modified with AMTT are shown in comparison to unmodified silica aerogel. The silica aerogel exhibits bands in the 1250–1050 cm^{-1} region and 800 cm^{-1} and 457 cm^{-1} easily attributed to the Si–O–Si asymmetric and symmetric stretching vibrations of the silica network respectively (21, 22). As expected for SA–AMTT samples, a new but weak and sharp peak appeared at 2560 cm^{-1} due to sulphur containing groups. Also, a new but weak and sharp peak appeared at 1560.22 cm^{-1} due to NH_2 groups, 754cm^{-1} due to C=S groups (23). This peak is not observed for silica aerogel. The above FTIR data indicates that strong interaction exists on the interface of silica aerogel and SA–AMTT, and silica aerogel is successfully modified by AMTT.

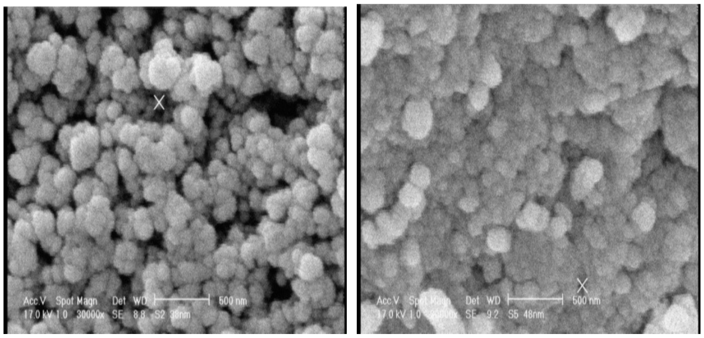

Fig. 1. *The SEM image of SA (left) and SA–AMTT nanoparticles (right)*

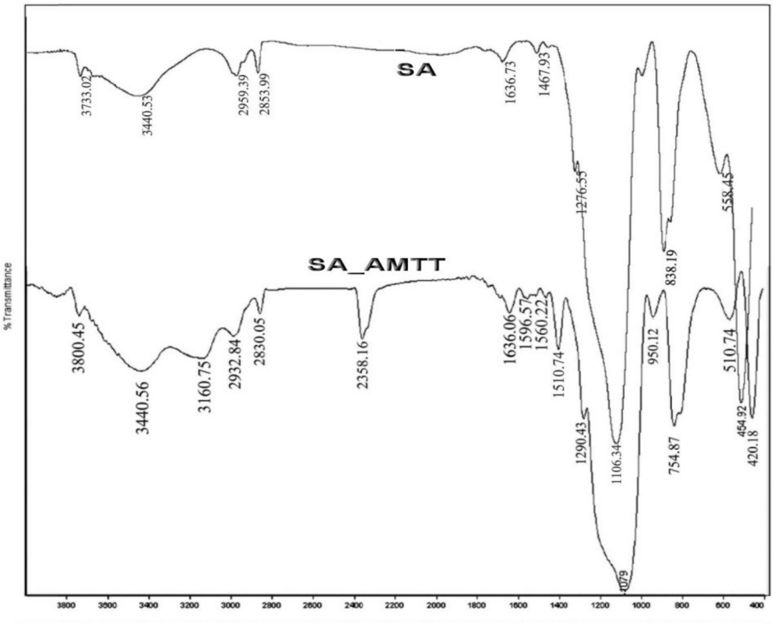

Fig. 2. FTIR absorption spectra of SA and SA–AMTT

Adsorption studies

Effect of pH on the adsorption: The influence of pH on the preconcentration of Hg(II) on a SA–AMTT nanoparticles was studied by adjusting the pH values of sample solutions containing 0.1 $mgmL^{-1}$ from 2 to 10. The experimental results indicated that quantitative adsorption (>90%) could be obtained in the pH range of 5–6. Hence, pH 5–6 was selected as the optimum pH for all subsequent studies.

Effect of contact time: The sorption of Hg(II) by SA–AMTT at various contact times ranging from 5 min to 20 h was performed. According the results, it was set a contact time of 6 h in order to ensure that equilibrium conditions are attained.

Effect of eluent: 0.1g of SA–AMTT was used for adsorbing in 20 mL of Hg(II) solution (20.0 mgL^{-1}) at pH 6.0. Then the obtained solid-phase mass was shacking to 4 mL 1M of KBr, KSCN, $(NH_2)_2CS$, DDTC for 8h. The highest desorption was observed for the KBr solution as the effluent (98%).

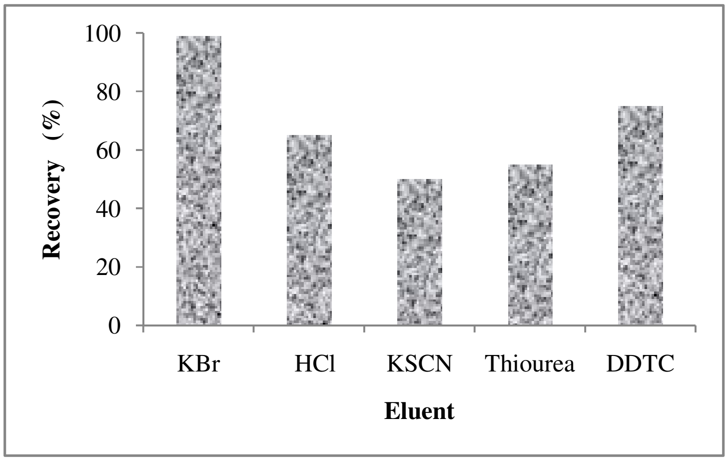

Fig. 3. Percentage of mercury recovered by using different eluant.

([eluant] = 1M ; eluant volume = 20 mL; t = 24 h ; 20 ^{0}C)

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The effect of real matrix: Along with the samples, several known amounts of Hg(II) were spiked to examine the reliability of the method. Weight of 500 mg of hair was initially digested and then the prepared solution was subjected to the proposed method. The recovery of the spiked amounts as shown in Table 1 was in the range of 90–94% which demonstrates that the proposed method exhibits a good reliability.

Table 1.The effect of real matrix in preconcntration of Hg(II) by 0.1g SA–AMTT.

Sample	Added (mg L^{-1})	Removal %
Hair 1	1.00	92.43
	10.0	90.22
Hair 2	1.00	93.34
	10.0	91.67
Hair 3	1.00	94.21
	10.0	90.37

Regenerability: Investigate the reusability of the SA–AMTT, three adsorption–desorption cycles were carried out under optimum conditions. The result reveals that SA–AMTT has excellent reuse potential and only 4% reduction in Hg(II) uptake capacity was observed at the end of the third cycle (data not shown), which reveals its great potential to be used as reusable adsorbent for the removal of Hg(II).

***Enrichment factor*:** 25 mL of sample solution was adopted for the preconcentration of Hg(II). And a high enrichment factor of 150 was obtained because 4.0 mL of 1.0 mol L^{-1} KBr was used as eluent in these experiments.

CONCLUSIONS

In this study, modified silica aerogel with AMTT, an Hg adsorbent was synthesized and the adsorption of Hg was investigated in batch technique. The FTIR, SEM and TGA were used to characterize the as-prepared SA–AMTT. The optimum pH was found to be in the range of 6 and the equilibrium time was reached with in 6h The possibility of using nanoparticles SA–AMTT as an adsorbent material for the preconcentration of Hg(II) and their determination by CV-AAS in hair samples has been explored, and the results obtained were satisfactory. The advantages of the proposed method are:

(i) High enrichment factors

(ii) Low consumption of analytes

(iii) Good regenerability

The proposed method is sensitive, selective, reproducible and can be applied to the preconcentration of Hg (II) ions in hair samples.

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