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Graphene-silica hybrid in efficient preconcentration of heavy metal ions via novel single-step method of moderate centrifugation-assisted dispersive micro solid phase extraction

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ABSTRACT

Novel nanoadsorbent of graphene-silica hybrid was synthesized via chemical vapor deposition (CVD) method. Graphene sheets were catalytically grown on a silica-based substrate and after being characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM), their high efficacy in adsorption of metal ions (lead, cadmium, and chromium) was examined. It was found that the presence of silica within the G-SiO₂ structure imparts an amphiphilic property to the hybrid that enables it to interact with both free and bounded metal ions present in the biological samples. Utilization of the innovative method of moderate centrifugation-assisted dispersive micro solid phase extraction (MCD_μSPE) coupled with electrothermal atomic absorption spectrometry (ETAAS), not only facilitated absolute separation of the fabricated nanoadsorbent from the solvent, but also helped complete recovering of the scant volume of desorbed supernatant. Thus, microliter amount of desorption solvent can be regained completely by MCD_μSPE method without sorbent loss. Various parameters affecting the extraction efficiency were investigated and admirable linearity from 0.012 to 12.5 μg L⁻¹ and favorable detection limits (LOD) could be recorded. Intra day precision (RSD, *n* = 10) ranged from 3.1 to 3.8%, whereas inter day precision (RSD, *n* = 5) ranged from 6.3 to 7.2%.

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1. Introduction

Accumulation of toxic and detrimental heavy metals ions such as cadmium, lead, and chromium in soft tissues of animals or human body even at trace levels is a great concern as they are not metabolized and may cause serious hurt and even cancer [1,2]. Several detection techniques have been practiced for determination of heavy metals, including inductively coupled plasma mass spectrometry (ICP-MS) [3], inductively coupled plasma optical emission spectrometry (ICP-OES) [4,5], electrothermal atomic absorption spectrometry [6–8], and flame atomic absorption spectrometry (FAAS) [9,10]. Although all these detection strategies have been useful in tracing free ions and have many advantages such as multi-elemental analysis capability, large dynamic linear range, low detection limits, and high productivity; direct determination of heavy metal ions in biological fluids is still limited

due to their low level of concentration and matrix interferences. New separation and preconcentration techniques as the pre-requisite steps for elimination of any matrix components and consequently improving the detection limit are of significant importance. Solid phase extraction (SPE) as a well-renowned method of separation and preconcentration [11,12], has been developed and widely used [13,14]. It is simple, rapid, inexpensive, and needs low amounts of reagents [15]. Its miniaturized format, called micro solid phase extraction (μSPE) has been recently attracting attentions as it further reduces both solvent and sorbent consumption and facilitates sample handling [16,17]. In dispersive μSPE (D-μSPE), the extraction time is further reduced and channeling and blocking of the cartridge or disk-SPE are avoided. Different nanoparticles can be applied in D-μSPE for adsorption of target analyte in various matrixes.

Graphene, the single-layer sheet of sp² hybridized carbon atoms arranged in a honeycomb lattice [18,19] possessing ultra-high specific surface area [20], fast mobility of charge carriers, good thermal conductivity, and high values of Young's modulus

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and fracture strength [21] has been reported to have high adsorption capacity [22]. Graphene performance as an adsorbent in SPE is better than carbon nanotubes [22–25]. This is due to the special morphology of graphene in which both sides of its planar sheets are available for molecule adsorption and leads to fast adsorption equilibrium and analyte elution [22,26]. Metal ions in biological fluid are in both forms of free ones and bonded to proteins. Although the highly hydrophobic surface of graphene imparts it as a favorable nanoagent in separation of organic chemicals through π - π interaction [27,28], separation of metal ions by graphene has been rarely reported. To this end, a chelating agent was used to form a stable complex in a study [29,30].

In the present research, fabrication of a new nanoadsorbent with both hydrophilic and hydrophobic properties is introduced for the first time that is capable of interacting with both categories (the free ions and the bonded ones) of metal ions in biological fluids. Mineral silica was used for CVD synthesis of graphene-based hybrid, since the residual impurities of copper and nickel (the famous catalysts for graphene growth) present in natural silica are the keynote of the hybrid fabrication. Having both properties of graphene nanosheets and porous silica, not only it can adsorb the free metal ions with ionic properties, but even the metal ions bonded to proteins, thanks to its hydrophobic properties. Graphene-silica hybrid was used for preconcentration of lead, cadmium, and chromium from saliva and urine samples via the novel procedure of moderate centrifugation-assisted dispersive micro solid phase extraction (MCD μ SPE). Sample clean-up and the extraction step are simultaneously performed, hence it is suitable for the extraction in complex matrices. It is worthy of notice that only a small volume of sample is needed for the MCD μ SPE method making this procedure ideal for the cases when the amount of the biological sample is very limited. With the aid of centrifuge filtration method, even small volumes of desorption solvent can be recovered completely, consequence of which highly increased the enrichment factor of the proposed MCD μ SPE method.

2. Experimental

2.1. Reagents and materials

The analytical grade of chemical solvents such as nitric acid 65% (w/v), hydrochloric acid 37% (w/v), glacial acetic acid, sodium hydroxide, lead nitrate Pb(NO₃)₂, cadmium nitrate Cd(NO₃)₂, chromium nitrate Cr(NO₃)₃, magnesium nitrate (Mg(NO₃)₂), and nitrate salts of interferences were purchased from Merck (Darmstadt, Germany; <http://www.merckgroup.com>). The stock standard solutions of investigating ions (1000 mg L⁻¹) were prepared by dissolving appropriate amount of their salts in 100 mL deionized (DI) water. The working standard solution of metal ions was prepared daily by suitable dilution of their stock standard solution. The salt of Magnesium nitrate (Mg(NO₃)₂) was used as a chemical matrix modifier for determination of Pb(II), Cd(II), and Cr(III) by ETAAS. The Magnesium nitrate solution was prepared by dissolving appropriate amount of magnesium nitrate salt in DI water. Silica was prepared from Iran natural mines.

2.2. Apparatus

The evaluation and determination of cadmium, lead, and chromium were performed using GBC electro-thermal atomic absorption spectrometer (Plus 932, Australia) with a graphite furnace module (GF3000) equipped with a hollow cathode lamp and a deuterium background correction. Instrumental condition and the graphite furnace temperature program for Pb, Cr, and Cd are summarized in Table 1 and Table 2. The catalytic chemical

Table 1

The ETAAS conditions for determination of mentioned metal.

Parameter	ETAAS		
	Cd	Pb	Cr
Wavelength (nm)	228.8	283.3	357.9
Slit (nm)	0.5	0.5	0.2
Lamp current (mA)	3	5	6
Volume Injection (μ L)	20	20	20
Mode	Peak Area	Peak Area	Peak Area
Gas	Argon	Argon	Argon

vapor deposition (CCVD) technique was carried out in a horizontal furnace consisting of a quartz tube with 45 mm in diameter and 150 cm in length. XRD pattern of samples was obtained with an INEL EQUINOX 3000 X-ray diffractometer (INEL, France), using Cu-K α radiation ($\lambda=1.541874$ Å), (40 kV and 45 mA conditions). The morphology of the graphene-silica hybrid was analyzed via scanning electron microscope (VEGA//TESCAN). Thermo-gravimetric analyses (TGA) were conducted with a LINSEIS model STS PT 16000 thermal analyzer at a heating rate of 5 °C min⁻¹.

2.3. Synthesis of graphene-silica hybrid

Graphene-silica hybrid was synthesized via CVD method in which silica was used as the catalyst and support. To summarize, milled silica (10 g) was loaded in a quartz boat placed in a quartz tube. The reactor was purged with hydrogen stream (at a flow rate of 300 mL min⁻¹) for 180 min while it reached from ambient temperature to the reaction temperature. The reaction was started using methane as the carbon source with a flow rate of 50 mL min⁻¹ and hydrogen as carrier gas with a flow rate of 250 mL min⁻¹ at 1000 °C for 30 min. Finally, the furnace was allowed to cool to room temperature under nitrogen atmosphere. Thus, upon completion of the reaction, a black product was formed. Yield of graphene growth was calculated by TGA curve (Fig. S1) about 36%. Repeatability of G-SiO₂ hybrid was checked upon which same results and structure were achieved in each batch.

2.4. Sampling

Laboratory glassware and vessels were cleaned by soaking in 10% (v/v) nitric acid for at 24 h and rinsing with DI water prior to use. (Important: since cadmium, lead, and chromium concentrations in whole urine and saliva are very low, even minor contamination at any stage of sampling, sample storage and handling, or analysis has the potential of severely affecting the accuracy of the results). Saliva samples were taken in the morning before breakfast. The participants were asked to rinse their mouth for 1 min with 10 mL of sterilized distilled water and immediately after the rinsing about 6 mL of saliva was collected for 10 min with the mouth closed and were introduced into polypropylene tubes. The first mL of saliva was discarded and it was immediately centrifuged at 5000 rpm for 5 min in order to precipitate cellular debris and then it was stored at -20 °C before being processed. Urine samples after collection were centrifuged at 5000 rpm for 10 min and the sediments were discarded. Saliva and urine samples were collected from normal and healthy human. The supernatants were stored at 4 °C until analysis. River water samples were collected from Kan River, Tehran, Iran. The water sample was filtered with 0.45 μ m membrane filter to remove particles and stored at 4 °C until analysis. A 0.45 μ m nylon centrifuge filter (1.5 mL) prepared from Whatman (USA) was used for separation of nanoadsorbents from solution.

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