Nano-alumina coated with sodium dodecyl sulfate and modified with 4-(2-Pyridylazo) resorcinol for extraction of heavy metals in different matrixes

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ABSTRACT

A green, novel and efficient solid phase extraction method based on the use of nano-alumina (nano-Al_2O_3) coated with sodium dodecyl sulfate (SDS) and modified with 4-(2-Pyridylazo) resorcinol (PAR) as a new adsorbent was developed for separation and preconcentration of trace amounts of Ni, Pb, Cu and Zn ions prior to determination by inductively coupled plasma-optical emission spectrometry (ICP-OES). Under the optimum conditions (eluent: HNO_3, 4.0 mL, 3.0 mol L^{-1}; adsorbent: 0.8 g of nano-Al_2O_3, 40 mg of SDS, 8.6 mg of PAR; and sample: pH 6, flow rate 2.0 mL min^{-1}), adsorption capacity of nano-Al_2O_3-SDS-PAR, enrichment factors and limits of detection for the analytes were 8.7–12.9 mg g^{-1}, 125–250, and 0.12–0.71 $\mu g\,L^{-1}$, respectively. The proposed method presented excellent repeatability with relative standard deviations less than 1.6% ($n = 10$), and calculated calibration curves gave good level of linearity with correlation coefficient values between 0.989 and 0.999. Finally, the feasibility of the method was evaluated by extraction and determination of Ni, Pb, Cu and Zn ions in rice seed, apple juice, coriander, lettuce and tap water samples.

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1. Introduction

One of the most important challenges in the environmental and medical sciences is the study of carcinogenic and mutagenic effects of released heavy metals, such as Ni, Pb, Cu and Zn ions, through industrial effluents on human beings and environment [1,2]. Therefore, determination of these ions in environmental systems and other real samples, such as vegetables, beverage and fruit, is crucial and could be help to healthcare. However, concentration of these ions in the environmental and mentioned real samples is low and in order to determine these ions, an extraction or a preconcentration step is necessary.

Different methods such as, membrane filtration [3], cloud point extraction (CPE) [4], co-precipitation [5], supercritical fluid extraction (SFE) [6], pressurized liquid extraction (PLE) [7], ultrasonic extraction (UE) [8], microwave-assisted extraction (MAE) [9] and solid phase extraction (SPE) [10–13], have been used for the preconcentration and determination of trace amounts of metal ions in different real samples. Among these methods, because of its high enrichment factor and recovery, low cost, and compatibility with analytical instruments for on-line determina-

tion, SPE is still a good choice for separation and preconcentration of metal ions in various real samples. In this way, ion exchange resins [14], molecular imprinted polymers (MIPs) [15], functionalized activated carbon [16,17], chemically bonded multiwalled carbon nanotubes [18], metal oxides [19], metal oxide nanoparticles (such as titania, zirconia, silica and alumina [20]) and biomaterials [21] have been widely employed as SPE sorbent materials.

Nano-alumina, because of its versatile properties including excellent mechanical strength, inertness to most acids and alkalis [22], high adsorption capacity [23], large specific surface area [24–26] and absence of internal diffusion resistance [27] have been successfully applied for the separation and preconcentration of trace heavy meal ions. Furthermore, functional groups such as oxygen, nitrogen, phosphorus and sulfur are able to form the selective binding with both nano-alumina and certain metal ions [24].

Electrostatic attractive interactions between the head group of ionic surfactants and oppositely charged groups on the nano-alumina result in the formation of mixed hemimicelles assemblies. Besides, ligand can be effectively adsorbed on the formed hemi- and ad-micelles on the nano-alumina surface, through the hydrophobic interactions between hydrocarbon tail-groups of surfactant and hydrocarbon groups of ligand, which give a number of advantages, such as high selectivity, high breakthrough

volumes, easy elution of analytes and high flow rate for sample loading [28,29]. Several analytical techniques such as flame atomic absorption spectrometry (FAAS), electro thermal atomic absorption spectroscopy (ETAAS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) can be used for trace analysis of metal ions [30]. Among these techniques, because of its high sensitivity and wide dynamic range, ICP-OES is a powerful analytical technique for the determination of trace elements in the various environmental and biological samples.

Due to low concentration of metal ions and high matrix effects, there is a great necessity for good preconcentration and sensitive determination of these analytes in real samples. To achieve this purpose, nano-alumina (nano-Al_2O_3) was coated with sodium dodecyl sulfate (SDS) and after modification with 4-(2-Pyridylazo) resorcinol (PAR) was used as a new adsorbent for separation and preconcentration of Ni, Pb, Cu and Zn ions in rice seed, apple juice, coriander, lettuce and tap water samples prior to determination with ICP-OES. This method is simple, rapid, efficient, and in comparison with other traditional SPE methods it does not require any organic solvent at steps of experiment. Also, the proposed method shows great analytical potential in processing of complex real samples.

2. Experimental

2.1. Instrumentation

The heavy metal ions were measured with a simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES), Vista PRO model from Varian Company (Springvale, Australia) coupled to V-groove nebulizer and Scott spray chamber made from quartz glass and equipped with a charge coupled device (CCD) detector. The optimal instrumental conditions (including RF generator power, viewing height, nebulizer pressure and pump rate, ...) via ICP-OES are shown in Table 1. The emission lines which were used for determination of the metal ions were Ni 231.604 nm, Pb 227.353 nm, Cu 324.754 nm and Zn 213.857 nm. A silicon tube (L = 4.0 cm, I.D. = 2.52 mm) was used as a loop and was connected to a six-port two-position injection valve to introduce the final solution to ICP-OES. The pH of solutions was measured by a PHS-3BW model pH-meter (Bell, Italy). A LAMBDA CZs.ro multi flow peristaltic pump (LAMBDA, Switzerland) and a PTFE (poly tetrafluoroethylene) column (30 mm × 4.0 mm i.d.) were used with small natural cotton (Kave Company, Iran) at both ends.

2.2. Chemicals and reagents

All chemicals used in this work, were of analytical reagent grade. Stock solutions (1000 μg L^{-1}) of the elements were prepared by dissolving appropriate amount of their ultrapure salt from Merck (Darmstadt, Germany) in HNO$_3$ (1.0 mol L^{-1}). Working standard solutions were prepared daily by suitable stepwise dilution of stock solutions with distilled deionized water. Nano-alumina (nano-Al_2O_3, gamma, purity 99.5%, 45–55 nm) were obtained from Alfa Aesar GmbH & Co KG A Johnson Matthey

Table 1
ICP-OES operating conditions.

Parameters	Value
RF generator power	1.4 kW
Torch mode	Axial
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.5 L min^{-1}
Viewing height (above coil)	6 mm
Nebulizer pressure	160 kPa
Pump flow rate	1.4 mL min^{-1}

Company (Karlsruhe, Germany). The sodium dodecyl sulfate (SDS) and 4-(2-Pyridylazo) resorcinol (PAR) were purchased from Merck (Darmstadt, Germany) and their solutions were prepared by dissolving certain amounts of these compounds with double distilled water in 100 mL volumetric flask and stored at 4 °C. A buffer solution of acetate-acetic acid (pH 5.0-6.0) was used and the pH was adjusted by addition of nitric acid (0.1 mol L^{-1}) and sodium hydroxide (0.1 mol L^{-1}) solutions. Before the performance of experiments, all laboratory glassware were washed with a 5.0% (v/v) HNO$_3$ solution and rinsed with double deionized water.

2.3. Preparation of adsorbent

2.3.1. Adsorbent modification

In order to activation of nano-Al_2O_3 surface (0.5 g), 5.0 mL nitric acid (4.0 mol L^{-1}) was added and the mixture was stirred for 5 min. The excess acid was removed with double distilled water (pH 3.0). After activation, while the mixture was stirring, firstly SDS solution (20.0 mg L^{-1}) was added to the adsorbent and PAR solution (10.0 mg L^{-1}) was then added and stirred for 15 min. Finally, supernatant was removed and the adsorbent was rinsed with double distilled water.

2.4. SPE procedure

pH adjusted sample solutions of metal ions were passed through the column containing of modified nano-alumina at a flow rate of 2.0 mL min^{-1}. Afterwards, the absorbed analytes on the modified adsorbent was eluted with nitric acid solution and were determined by ICP-OES.

2.5. Sample preparation

The proposed method was applied to different samples such as rice seed, apple juice, coriander, lettuce and tap water samples.

2.5.1. Apple juice and water samples

The apple juice and water samples were collected from Semnan, Iran, and filtered through a 0.45 μm pore size cellulosic membrane filters. Firstly, in the presence of H$_2$O$_2$ (1.0%, (w/v)) and addition of concentrated nitric acid, the organic content of the apple juice samples was oxidized and the resultant was filtered and stored at 4 °C in the dark [24]. After dilution, the pH of water sample and the resultant were adjusted at 6.0 and the proposed solid phase extraction was performed.

2.5.2. Rice seed samples

Rice seed samples were collected from Mazandaran, Iran. 1.0 g of the rice seed sample was weighed and powdered. 15 mL of concentrated HNO$_3$ was added to the powdered sample and was kept over the night. The mixture was then evaporated near to dryness, on a hot plate at about 130 °C for 3 h, and the residue was dissolved in 0.5 mol L^{-1} HNO$_3$ solution. After filtration, the obtained clear solution was diluted to 50.0 mL with distilled water and the proposed solid phase extraction was performed.

2.5.3. Coriander and Lettuce samples

Coriander and Lettuce leaves were collected from Semnan, Iran. The leaves were rinsed with double deionized distilled water and, after drying, were taken in small mesh. 50.0 g of small mesh samples were digested with 20.0 mL of concentrated HNO$_3$ in silica crucible for 3 h, on a hot plate to near dryness. 1.0 ml of concentrated HCl was then added to ensure complete digestion and the residue was transferred to a furnace at 600 °C for 4 h, to decompose organic matter completely. The final residue was treated with the mixture of 3.0 mL concentrated HCl and