ORIGINAL ARTICLE

Preconcentration of trace amounts of lead in water samples with cetyltrimethylammonium bromide coated magnetite nanoparticles and its determination by flame atomic absorption spectrometry

Mohammad Faraji [a], Shahab Shariati [b,*], Yadollah Yamini [c], Mahnaz Adeli [d]

[a] Young Researchers Club, Rasht Branch, Islamic Azad University, Rasht, Iran
[b] Department of Chemistry, Rasht Branch, Islamic Azad University, Rasht, Iran
[c] Department of Chemistry, Tarbiat Modares University, Tehran, Iran
[d] Knowledge Development & University Relationship Department, Iran Khodro Company, Tehran, Iran

Abstract A sensitive and simple magnetic solid phase extraction procedure was presented for the preconcentration of lead ions in environmental water samples. In the present study, lead ions form complexes with 1-(2-pyridilazo)-2-naphthol reagent (PAN) in basic medium, and then are quantitatively extracted to the surface of cetyltrimethylammonium bromide (CTAB)-coated magnetite nanoparticles (Fe$_3$O$_4$ NPs). After magnetic separation of adsorbent, the adsorbent was eluted with 0.5% (v/v) HCl in methanol prior to its analysis by flame atomic absorption spectrometry (FAAS). The pH of sample, concentrations of PAN, amounts of CTAB and Fe$_3$O$_4$ NPs, sample volume and desorption conditions were optimized. Under optimum conditions, the calibration curve was linear in the range of 0.05–100 ng mL^{-1} with $R^2 = 0.9996$. Detection and quantification limits of the proposed method were 0.005 and 0.05 ng mL^{-1}, respectively. Enhancement factor of 1050 was achieved using this method to extract 1000 mL of different environmental water samples. Compared with conventional solid phase extraction methods, the advantages of this method still include easy

* Corresponding author. Tel.: +98 131 4224343; fax: +98 131 4224949.
E-mail address: shariaty@iaurasht.ac.ir (S. Shariati).

preparation of sorbents, short times of sample pre-treatment, high extraction yield, and high break-through volume. It shows great analytical potential in preconcentration of lead from large volume water samples.

1. Introduction

Lead enters food and drinks, contaminating them and therefore, it is a serious health hazard for everybody (Mosquera, 1999). Lead is particularly harmful, but even at high levels it is considered innocuous in the past (Ladron de Guevara, 1995). Water is one of the main sources of lead contamination for the general public. Even though the lead quantity in these samples is low, its introduction in the daily diet may have significant physiological effects (Cabrera, 1994). Determination of lead at trace levels in water samples requires the use of highly sensitive and reliable analytical techniques (Mena et al., 1997). Only few techniques such as electrothermal atomic absorption spectrometry (ET-AAS) (Bruno et al., 1994; Jorhem and Sundström, 1995), or anodic stripping voltammetry with microelectrodes (Baldo et al., 1997) have enough sensitivity to directly determine the low quantities of lead. Flame atomic absorption spectrometry (FAAS) is available in most laboratories and is normally less subjected to interferences, but it requires a preconcentration step in order to increase the lead concentration because of lead concentrations in environmental water samples are typically below the FAAS detection limit. Preconcentration and separation procedures coupled with FAAS offer the possibility of using a relatively simple and cheap detection system (Naghmush et al., 1995; Ferreira et al., 2001).

Several methods have been proposed for separation and preconcentration of trace amounts of lead such as dispersive liquid–liquid microextraction, cloud point extraction, liquid–liquid extraction, and solid-phase extraction (SPE). Such systems improve the sensitivity and the selectivity of FAAS allowing the determination of traces of lead in water samples, and could represent an alternative to ET-AAS (Ferreira et al., 2001). Among these techniques, the SPE procedures, either off- or on-line, are considered superior to the other procedures for their simplicity, consumption of small volumes of organic solvents, capability to eliminate undesirable matrix components, and their ability to achieve a higher enrichment factors (Fang et al., 1991).

More recently, the use of magnetic NPs for sample extraction and preconcentration is gaining researchers interest (Huang and Hu, 2008a,b; Zhao et al., 2008a,b; Suleiman et al., 2009; Zargar et al., 2009; Sun et al., 2009; Faraji et al., 2010a). Compared with micrometer-sized particles used in the SPE, the NPs offer a multitude of benefits that make them a better choice. They have significantly higher ratio of surface area-to-volume and a short diffusion route, resulting in higher extraction capacity; rapid dynamics of extraction and higher extraction efficiencies (Moeller et al., 2007). Moreover, by using superparamagnetic NPs such as Fe_3O_4 a shorter analysis time can be achieved, due to the magnetically assisted separation of these particles from the sample solution. These particles are attracted to a magnetic field but retain no magnetic charge after the field removal. This property makes them particularly suitable for sample preparation because in comparison with non-magnetic adsorbents no centrifuging or filtration of the sample is needed after extraction.

The aim of the present study was to develop a NP-based method for the preconcentration and determination of trace amounts of lead. The method is based on the extraction of lead as hydrophobic complexes of lead-PAN on cetyltrimethylammonium bromide (CTAB) – coated Fe_3O_4 NPs. The level of lead in extracted phase was then determined by FAAS. To the best of our knowledge, this method has not been employed previously in the extraction and determination of trace amounts of lead from aqueous samples.

2. Experimental

2.1. Instrumentation

A Varian (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer model SpectrAA 110, with an air-acetylene flame was used for lead determinations. Absorbance measurements were carried out at 217.0 nm using lead hollow cathode lamp (from Varian) operated at 4.0 mA with deuterium background correction (at 10 mA). The instrumental parameters were used according to the manufacturer's recommendations. All measurements were based on peak height. The pH of the solutions were measured with a WTW pH meter (Inolab, Germany) which was supplied with a combined pH electrode. TEM images were obtained with an H-800 transmission electron microscope (Hitachi, Japan) and magnetic properties were analyzed using a vibrating sample magnetometer (VSM, LDJ9600).

2.2. Reagents

All chemicals used were of analytical reagent grade. Ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$), sodium hydroxide, 1-(2-pyridilazo)-2-naphthol (PAN), lead nitrate ($Pb(NO_3)_2$), CTAB, methanol, acetone, and 1-propanol, hydrochloric acid were all purchased from Merck (Darmstadt, Germany). The stock solution of lead ($1000 \mu g \, mL^{-1}$) was prepared by dissolving the appropriate amounts of $Pb(NO_3)_2$ in doubly distilled water. A solution of $1 \times 10^{-3} \, mol \, L^{-1}$ PAN was prepared by dissolving the appropriate amount of this reagent in methanol.

2.3. Synthesis of Fe_3O_4 NPs

Fe_3O_4 NPs were prepared by chemical co-precipitation method via a reactor which was designed in our previous work (Faraji et al., 2010b). Briefly, 10.4 g of $FeCl_3 \cdot 6H_2O$, 4.0 g of $FeCl_2 \cdot 4H_2O$ and 1.7 mL of HCl ($12 \, mol \, L^{-1}$) were dissolved in 50 mL of deionized water in order to prepare stock solution of ferrous and ferric chloride in a beaker which was then degassed with nitrogen gas for 20 min. Simultaneously, 500 mL