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Aspartic acid-modified magnetic nanoparticles as an ideal sorbent for solid phase extraction of Pb in water samples prior to ICP-OES determination

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ABSTRACT

The present study will consider the application of aspartic acid-coated Fe_3O_4 as a sorbent for solid-phase extraction of trace amounts of Pb using inductively coupled plasma optical emission spectrometry. Magnetic nanoparticles (MNPs) of Fe_3O_4 possess a high potential for modification with different organic and inorganic compounds. Using an amino acid (in this case, aspartic acid) as a nontoxic modifier, without an organic solvent, could provide a number of environmentally friendly applications in the field of green chemistry. By using modified MNPs as a sorbent, the separation of metal ions from an aqueous sample solution was easily performed by an external magnet without centrifuging or filtering. An elution step was accomplished by using a 2 mol L^{-1} nitric acid solution for introducing the desorbed analyte to ICP-OES. Different parameters influencing on the extraction efficiency, such as pH, volume of the modifier, extraction and elution time, types and concentrations of eluent were investigated and optimized. Under the optimized conditions, the detection limit for Pb was 0.6 μg L^{-1} and the calibration curve showed linearity in the range of 1–600 μg L^{-1}. The relative standard deviation (RSD, $C = 300$ μg L^{-1}, $n = 5$) was 2.8%. The sorption capacity of the sorbent was found to be 19.9 mg g^{-1}. The sorbent exhibited good stability and high adsorption capacity for lead ions. The applicability of the sorbent was examined by a real sample and the results were satisfactory.

Keywords: Fe_3O_4 magnetic nanoparticles; Solid-phase extraction; Lead; Water samples

1. Introduction

Pollution related to heavy metals can produce severe toxicological effects on living organisms. The direct determination of metals would appear to be difficult due to their low concentrations. Sample preparation and pre-concentration methods can, however, solve this problem. Lead is reported to be a highly toxic and hazardous element to human health [1]. According to the US Environmental Protection Agency, the action level of lead in drinking water is 0.015 mg L^{-1} [2]. Therefore, sensitive determination methods should be designed to control the trace amount of lead in diverse samples. Different sample preparation methods such as cloud point extraction, liquid extraction and solid-phase extraction (SPE) are proposed for the separation and preconcentration of different heavy metals [3–9]. Application of these methods prior to instrumental analysis, such as inductively coupled plasma-optical emission spectrometry (ICP-OES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic

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absorption spectrometry (AAS), overcomes some limitations such as low concentrations of analytes and complexity of matrices [10,11]. As a routine extraction method, SPE has some significant advantages such as the consumption of small volumes of organic solvents and a high enrichment factor [12]. The choice of sorbent is a key factor in SPE because it can control many analytical parameters such as selectivity, affinity and capacity [13]. Different sorbents, such as silica gel, alumina, modified alumina, resins, meso-porous TiO_2, magnetic nanoparticles (MNPs), nanometer-sized Al_2O_3, multi-walled carbon nanotubes (MWCNTs), etc. [14–23], have been used as applicants in the SPE of heavy metals. Nanoparticles have received increasing attention in the past few decades due to their unique properties and are now widely used in different fields of science. These properties include large surface area, short diffusion route, lower sedimentation rate, high extraction capacity and efficiency. Also, the surface of nanoparticles can be easily modified to achieve selectivity in extraction, and there is no need for centrifuging and filtering for desorption of the analyte from the sorbent [24,25]. The special properties of MNPs arise from their finite size and surface effect that dominate the magnetic behavior of individual nanoparticles [26]. Superparamagnetic iron oxide nanoparticles with appropriate surface chemistry can be used for different applications. These nanometer-sized metal oxides are not target-selective and can easily form large aggregates that may alter their magnetic properties, so they are unsuitable for samples with complex matrices [27–29]. Coating the surface of MNPs with suitable and nontoxic compounds has been proven to be one of the most efficient ways for providing stability to the nanoparticles in solution [30]. In this study, a new application of Fe_3O_4 NPs is developed by physical modification with aspartic acid as a fast, simple, sensitive procedure for preconcentration of lead ions in different water samples prior to ICP-OES determination.

2. Materials and methods

2.1. Instrumentals

The measurements were carried out with a Varian (model: VISTA-MPX) inductively coupled plasma optical emission spectrometer (ICP-OES). The pH-meter model 713 (Herisau, Switzerland) supplied with a glass combined electrode and a universal pH indicator (pH values of 0–14) from Merck (Darmstadt, Germany) was used for pH measurements. An ultrasonic cleaning system from Hettich (Tuttlingen, Germany) with a voltage line of 230 V and frequency of 50–60 Hz was used for the synthesis of MNPs and also for performing adsorption/desorption(or elution) processes.

2.2. Materials

All chemicals used in this work were of analytical grade purchased from Merck Chemicals (Darmstadt, Germany). All solutions were prepared in double-distilled deionized water. A stock standard solution of lead at a concentration of 1000 mg L^{-1} was prepared by dissolving the appropriate amounts of $Pb(NO_3)_2$ in 0.1 mol L^{-1} nitric acid. Dilute solutions were prepared by dilution of the stock solution in doubly distilled water. A solution of 10^{-2} mol L^{-1} aspartic acid was prepared by dissolving the appropriate amounts of it in distilled water. Nitric acid (0.1 mol L^{-1}) and aqueous ammonia (0.1 mol L^{-1}) solutions were used to adjust the pH. The pipettes and vessels used were kept in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water before use.

2.3. Synthesis of MNPs

The MNPs were prepared according to the method used by Suleiman et al. [30]. Magnetite was precipitated by dissolving 5.6 g $FeSO_4{\cdot}7H_2O$ and 10.8 g $FeCl_3{\cdot}6H_2O$ in 300 mL demineralized water, heating it to 80℃ and adding 200 ml 25% NH_4OH while being vigorously and continuously stirred. The produced black powder was washed several times with deionized water until it reached neutral pH and then the supernatant was removed by decantation using a permanent magnet to control the magnetic precipitate. The MNPs were dark-brown colored. They exhibited visible magnetic properties in the presence of a permanent magnet and were stable up to 6 months. Figs. 1 and 2 show a SEM image of the prepared Fe_3O_4 NPs and FTIR spectrum of Fe_3O_4 nanoparticles.

2.4. Recommended procedure

The procedure for magnetic SPE is presented in Fig. 3. A sample solution (100 mL) containing 300 μg L^{-1} of Pb ions was prepared in a vessel. 1,200 μL of aspartic acid (10^{-2} mol L^{-1}) was transferred to the solution and the pH was adjusted to 4.5 with nitric acid and aqueous ammonia solutions. 12 mg of MNPs were then added, and the solution was ultrasonicated for 10 min to accelerate the adsorption of metal ions onto the nanoparticles. An external magnet was then used to separate the magnetic adsorbent and it was rapidly decantated. Afterward, the magnet was

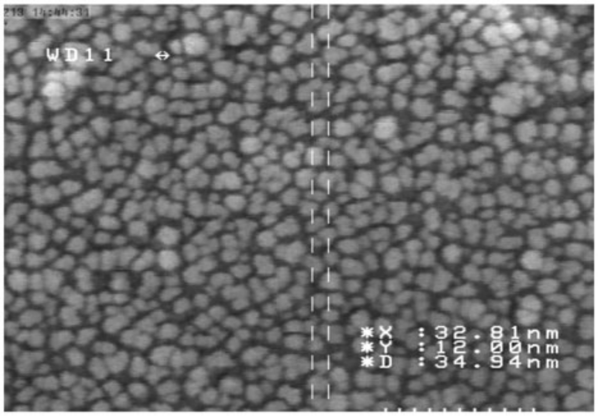

Fig. 1. SEM image of synthesized Fe_3O_4 nanoparticles.

removed, and a solution containing 2 mL nitric acid 2 mol L^{-1} was added as eluent and was ultrasonicated for 5 min. Finally, an external magnet was used to collect the nanoparticles and the remaining solution transferred into a test tube to allow analysis of the lead ions using ICP-OES.

3. Results and discussions

3.1. Effect of pH

The interaction between lead and aspartic acid-modified MNPs is seriously contingent upon the pH of the sample solution. The degree of the adsorption of ions on the sorbent surface is influenced by the surface charge of the sorbent. In this extraction system, the pH of the sample solution should be adjusted as the surface of the MNPs finds positive charges. The point of zero charge (PZC) of bare Fe_3O_4 nanoparticles is pH 6.8. Around this point, the surface charge density (Σ) is too small and the particles are no longer stable in water and flocculate. Playing on both electrostatic and steric stabilization is then necessary to obtain stable iron oxide nanoparticles [30]. At pHs < pH_{pzc}, the surface charge of Fe_3O_4 nanoparticles is positive, so an electrostatic repulsion occurs between the positively charged analyte and the sorbent. On the other hand, aspartic acid can become negatively charged at pH > 2.7 and have a strong interaction with metal. Carboxillic and NH_2 groups form part of the structure of amino acids, which can then become negatively or positively charged in different pH conditions. An iso electric point (IEP) is the pH at which a particular molecule carries no net electrical charges. The IEP of amino acids helps us to determine the structure of amino acid in acidic or alkaline solutions. In pH values higher than the IEP, the COOH group of amino acid changes to COO^- whereas in pH values lower than IEP the NH_2 group of amino acid changes to NH_3^+. For that reason, we had to adjust the pH of the sample solution according to these two points. Since the IEP of aspartic acid is

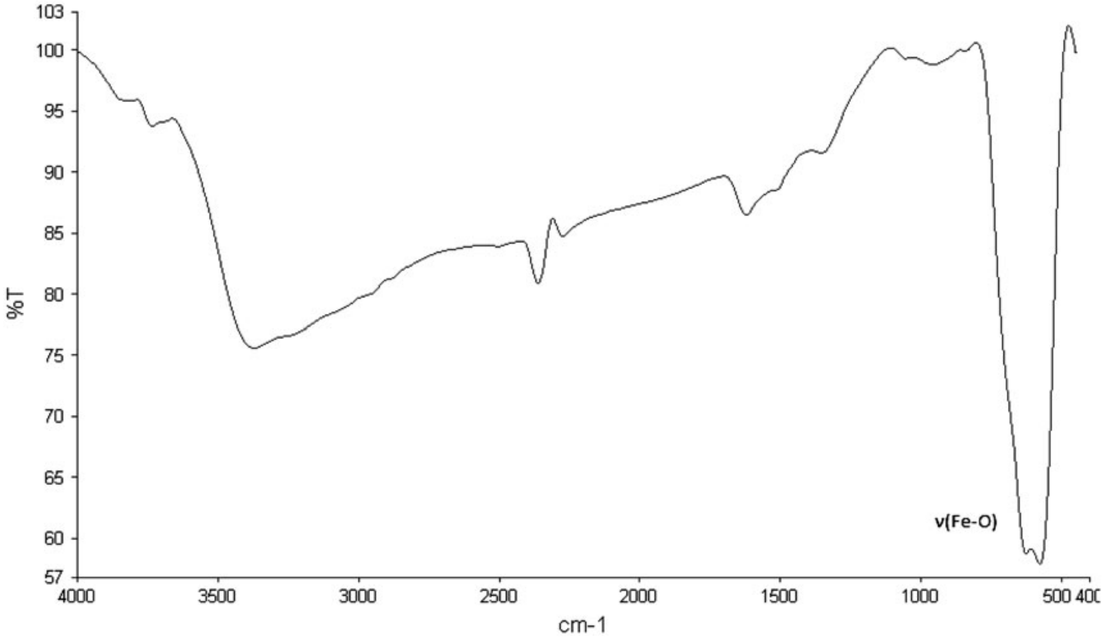

Fig. 2. FTIR spectrum of Fe_3O_4 nanoparticles between 500 and 3,500 cm^{-1} showing absorption peaks at around 600 cm^{-1}, which are assigned to the Fe–O stretching modes.

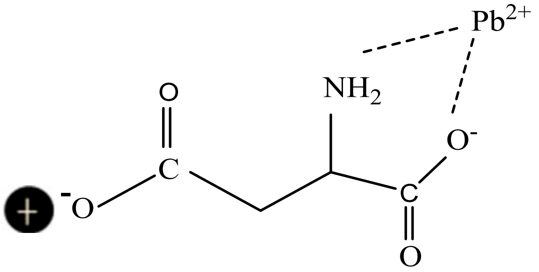

Fig. 3. Schema of sorbent in sample solution.

2.77, a series of experiments were performed by adjusting the pH from 3 to 6. The results for this study are displayed in Fig. 4. It reveals that the recovery of Pb ions is increased up to pH 4.5 and decreased in the higher pH. At higher pH, the density of the positive charges on magnetic particles decrease, while at the lower pH values, the density of negative charges on amino acid decrease. Both those phenomena have a negative impact on extraction efficiency. Therefore, pH 4.5 was selected for subsequent work enquiry.

3.2. *Effect of volume of aspartic acid*

The effect of the volume of aspartic acid on the extraction efficiency was studied by using various volumes of aspartic acid ranging from 100 to 1500 µL. The results illustrated in Fig. 5 show that the extraction efficiency is increased by increasing aspartic acid volume up to 1,200 µL, and then remains constant. As a result, 1,200 µL of 1×10^{-2} mol L^{-1} aspartic acid was chosen in order to achieve a high level of Pb^{2+} extraction.

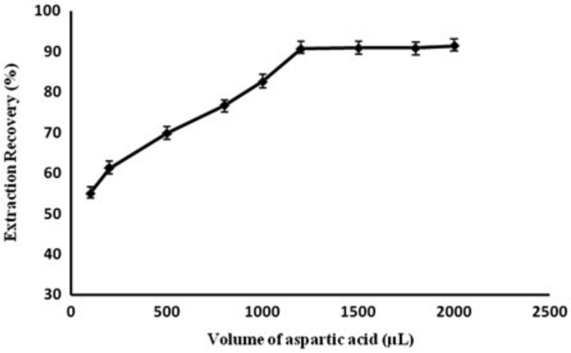

Fig. 5. The effect of aspartic acid volume on extraction recovery. The conditions: 100 mL of sample solution containing 300 µg L^{-1} lead ions, pH 4.5, and 12 mg sorbent at different volumes of aspartic acid (1×10^{-2} mol L^{-1}). 2 ml nitric acid (2 M) was used as eluent.

3.3. *Effect of the amount of sorbent*

The amount of modified MNPs sorbent was studied in the range of 5–20 mg. Results reported in Fig. 6 show that by increasing the amount of nanoparticles up to 12 mg, the extraction efficiency increases up to 93.5% and remains constant in larger amounts of the sorbent. So 12 mg of MNPs was adequate for quantitative extraction of Pb^{2+} in further experiments.

3.4. *Effect of sample volume*

In order to obtain a high enrichment factor, the SPE procedure was performed by using different volumes of sample solutions. About 20–500 ml of sample solutions containing 300 µg L^{-1} of Pb^{2+} was used. The quantitative extraction was achieved by using a

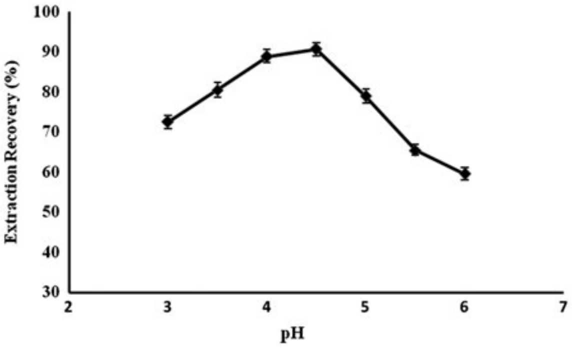

Fig. 4. The effect of pH on extraction recovery. The conditions: 100 mL of sample solution containing 300 µg L^{-1} lead ions, 12 mg sorbent, and 1,200 µL aspartic acid (1×10^{-2} mol L^{-1}) at different pH. 2 ml nitric acid (2 M) was used as eluent.

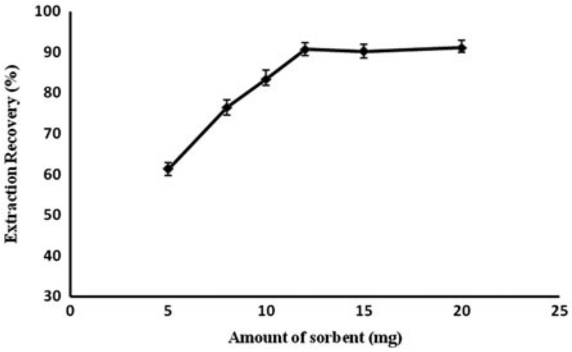

Fig. 6. The effect of Fe_3O_4—NPs amount on extraction recovery. The conditions: 100 mL of sample solution containing 300 µg L^{-1} lead ions, pH 4.5, and 1,200 µL aspartic acid (1×10^{-2} mol L^{-1}) at different amount of sorbent. 2 ml nitric acid (2 M) was used as eluent.

sample volume up to 200 ml and the elusion was performed with 2 ml of eluent. Consequently, an enrichment factor of 100 was obtained via this method. Finally, an amount of 100 ml of the sample solution was selected for routine daily analysis.

3.5. Selection of eluent type and volume

The type and concentration of eluent are two important factors affecting the extraction efficiency and preconcentration procedure at the quantitative desorption stage. Some experiments were carried out by using different concentrations of nitric acid and hydrochloric acid in the range of 0.5–2 mol L^{-1}. The results (Table 1) revealed that 2.0 ml of nitric acid 2.0 and 4.0 mol L^{-1} could accomplish stripping of Pb quantitatively. So, in order to achieve a higher enrichment factor, 2.0 mL of nitric acid (2.0 mol L^{-1}) was selected as the eluent for desorption of lead ions.

3.6. Effect of ultrasonic time for sorption and elution steps

In order to minimize the necessary time for the adsorption and elution stages, the required time for ultrasonication was optimized. The time duration that the solution and sorbent were exposed to the sonication waves was examined in the range of 2–20 min. The experimental results indicated that a quantitative recovery of analyte ions was achieved by ultrasonication of the solution for an optimum of 10 min. For the stripping step, 2.0 ml of nitric acid (2.0 mol L^{-1}) was added to the sorbent and was sonicated for 8 min to desorb lead ions. So in this study, the analyte could be separated rapidly from the sorbent by using an external magnetic field. The results are reported in Fig. 7.

Table 1
The effects of type, concentration, and volume of eluent on the extraction recovery

Eluent	Concentration[a] (mol L^{-1})	Volume (mL)	Recovery (%)
HNO_3	1	1	71.5 (2.3)
		2	78.9 (2.8)
HNO_3	2	1	85.5 (3.2)
		2	93.5 (2.8)
HNO_3	4	2	92.1 (3.2)
HCl	1	2	64.8 (3.4)
HCl	2	2	78.7 (2.8)
HCl	4	2	86.3 (2.3)

[a] Mean ± SD.

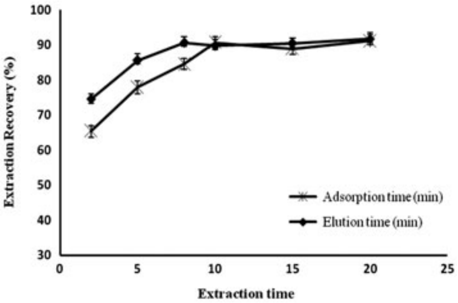

Fig. 7. The effect of adsorption and elution time on extraction recovery. The conditions: 100 mL of sample solution containing 300 μg L^{-1} lead ions, pH 4.5, and 1200 μL aspartic acid (1 × 10^{-2} mol L^{-1}). 2 ml nitric acid (2 M) was used as eluent.

3.7. Sorption capacity study

The capacity of the sorbent is a factor that determines how much sorbent is required to remove a specific amount of metal ions from the solution quantitatively. In order to study the sorption capacity of modified MNPs, 50 mg of sorbent was added to different concentrations of Pb^{2+} solutions. After shaking for 1 h, the mixture was filtered and the supernatant aspirated to ICP-OES. The sorption capacity (a_E, mg g^{-1}) was calculated as:

$$a_E = (C_0 - C_E)Vm^{-}$$

where C_0 and C_E are the initial and equilibrium concentrations (mg L^{-1}) of analyte ions in the solution, respectively. V is the volume of sample solution and m indicates the milligrams of sorbent used. The results in Fig. 8 show that the maximum amounts of Pb^{2+} ions that can be sorbed by the sorbent were found to be 19.9 mg g^{-1}.

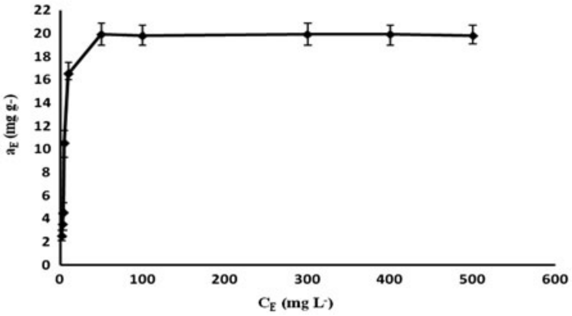

Fig. 8. The results of the investigation on sorbent capacity in different concentrations of lead.

Table 2
Tolerance limits for coexisting ions in preconcentration and separation of lead

Coexisting ion	Ratio [Coexisting ion]/[Pb]	Relative recovery (%)
Na^+	5,000	97.2 (3.4)
K^+	5,000	99.1 (3.2)
Ca^{2+}	1,000	95.6 (1.9)
Co^{2+}	1,000	98.2 (3.3)
Cr^{3+}	1,000	89.8 (3.4)
Al^{3+}	1,000	97.3 (2.7)
Ag^+	500	98.5 (2.8)
Pd^{2+}	500	94.3 (2.8)
Ni^{2+}	500	92.1 (1.9)
Cu^{2+}	50	97.8 (3.4)
Zn^{2+}	30	90.8 (2.4)
Cd^{2+}	30	91.5 (3.2)

3.8. Interference effects

To study the effect of foreign ions on the extraction efficiency of Pb^{2+}, the sample solutions containing 300 μg L^{-1} of Pb(II) ions and different concentrations of foreign ions were studied. The tolerance limits of different cations are shown in Table 2. The tolerance limit was considered if it resulted in a ±5% variation in sorption efficiency of Pb(II). The results showed that the recovery of Pb(II) was almost quantitative in the presence of foreign ions and the method proved its reliability for real sample analysis.

3.9. Quality parameters of the method

The analytical characteristics of the method under optimum experimental conditions are as follows: the limit of detection (LOD) was calculated as 3 Sd/m (Sd, standard deviation of the blank signals and m, slope of calibration curve after pre-concentration) which was 0.6 μg L^{-1}. A good correlation coefficient was obtained and the relative standard deviation (RSD) for five replicate measurements of 300 μg L^{-1} Pb(II) was 2.8%. The linearity of calibration curves was from 1 to 600 μg L^{-1}. The amounts of Pb ions in a 200 ml sample solution were measured after recovering into nearly 2 ml of eluent solution. The solution was concentrated by a factor of 100. A comparison between the method presented here and other SPE methods with different sorbents is given in Table 3. According to the reported table, the use of MNPs as a SPE sorbent could successfully determine the concentration of Pb in water samples. In addition, the higher sorption capacity of used sorbent compared to other sorbents could lead to higher extraction efficiency. These results can be expected due to the unique properties of nanomaterials that make them ideal as sorbents. The high enrichment factor and low LOD obtained in this research demonstrates that the practicality of this sorbent is similar to that of graphene in the determination of lead. However, as explained earlier, using magnetic sorbents facilitates and quickens the extraction process in comparison with other common sorbents by dispensing with the need for filtering and centrifuging.

4. Real sample analysis

Due to the low concentration of metal ions in water samples, the represented preconcentration method was applied to determine Pb ions in water samples for evaluating of the matrix effect. These real samples showed that the amount of lead was not detectable, so they were spiked by the standard solution. Table 4 shows that the recoveries obtained for real sample analysis with the mean value ($n = 3$) are in an acceptable range (96–102%).

Table 3
The comparison between the represented method and other SPE methods reported

Sorbent	Technique	Sorption capacity (mg g^{-1})	LOD (μg L^{-1})	EF[a]	Refs.
Silica gel	FAAS	19.76	0.51	300	[16]
SP70-benzoine oxime resin	FAAS	[b]	16	75	[31]
MWCNTs	FAAS	10.3	0.6	80	[32]
Modified silica gel	FAAS	12.63	0.58	200	[19]
Alumina	FAAS	13.3	2.8	63	[15]
Graphene	FAAS	16.6	0.61	125	[33]
p-DMABD-modified	ICP-OES	6.02	1.79	[b]	[34]
Bismuthiol silica coated	ICP-OES	9.4	0.085	87	[30]
Fe_3O_4 magnetic nanoparticles	ICP-OES	19.9	0.6	100	This work

[a] Enrichment factor.

[b] Data not available.

Table 4
Analytical results for real water samples

Samples	Pb(II) ($\mu g\ L^{-1}$) Added	Founded	Recovery (%)	RSD (%)
Mineral water (I)	–	–	–	–
	10	10.1	101	2.3
Mineral water (II)	–	–	–	–
	5	4.98	99.6	1.8
Tap water	–	–	–	-
	10	9.6	96	2.5
Spring water	–	–	–	–
	10	10.2	102	2.3

5. Conclusion

This paper has outlined the successful development of a SPE method when analyzing the presence of lead in water samples. Fe_3O_4 nanoparticles were modified physically by the introduction of aspartic acid molecules, with adjustments made to the pH value. This sorbent exhibited not only a fast adsorbtion/elution rate, but also a high capacity for the preconcentration and separation of lead ions. The analytical performance of the method reported here is comparable with other similar SPE systems. The advantages of this method include a high level of accuracy, a wide linear dynamic range, as well as a short analysis time and low detection limits. As no organic solvents were required in the process, the method described in this paper has shown to be potentially very useful in the investigation and determination of lead ions in water samples.

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