




Cite this: DOI: 10.1039/c8ay00176f

Highly selective preconcentration of ultra-trace amounts of lead ions in real water and food samples by dispersive solid phase extraction using modified magnetic graphene oxide as a novel sorbent

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A simple and rapid dispersive solid-phase extraction method coupled with furnace atomic absorption spectrometry detection was developed for selective separation and preconcentration of ultra-trace amounts of lead ions using modified magnetic graphene oxide such as the pseudo imprinted polymer sorbent in real water and food samples. Some effective parameters in the extraction of lead were selected and optimized. The optimum experimental conditions of the proposed method were: pH, 5.0; amount of adsorbent, 1 mg; eluent type and its volume, 50 μL of 0.4 mol L^{-1} hydrochloric acid; sample solution volume, 30.0 mL. Under the optimum conditions, a high preconcentration factor of 600 was obtained for 30.0 mL of sample solution. The relative standard deviation for seven 20 ng L^{-1} replicates of lead was 2.4% and the detection limit was 0.18 ng L^{-1} . The proposed method was applied for the determination of lead ions in real water and food samples, and its accuracy was assessed through the analysis of a certified reference water (ERA 1340) and recovery experiments.

Received 24th January 2018

Accepted 31st March 2018

DOI: 10.1039/c8ay00176f

rsc.li/methods

1. Introduction

The pollution of the environment by heavy metals has been received considerable attention over the last few years. Lead pollution is one of the most significant environmental problems due to its stability at the contaminated sites, the reduction of enzymatic activities, and several other complications in humans, plants, and animals.¹

This metal is usually present at low concentrations ($\mu\text{g g}^{-1}$ or ng g^{-1}) in environmental, biological and food samples, and thus its measurement requires high sensitivity detection techniques and/or efficient sample preparation methods before analysis. Several methods have been proposed for extraction and preconcentration of trace amounts of Pb(II) including liquid-liquid extraction (LLE),² solid-phase extraction (SPE),³ cloud point extraction (CPE),⁴ and liquid-phase microextraction (LPME).⁵ Although, these methods are very suitable for separation and preconcentration of Pb(II), the important problem with them is the matrix effects, especially in the presence of interfering species that may highly affect the analysis results in real samples. Therefore, it is clear that a sample preparation is needed to reduce the effect of the interfering species and to increase the selectivity, accuracy and precision of lead analysis.⁶ One of the most selective SPE sorbents is imprinted polymers.

Molecular imprinting is a method that enables the formation of tailor-made recognition materials by copolymerization of suitable monomers in the presence of a desired imprint molecule. Recently, there have been some reports on the application of imprinted technique for separation and enrichment of heavy metal ions.⁷

Magnetic dispersive solid-phase extraction (MDSPE) is a new mode of SPE based on magnetic sorbents and desorbed analytes under an external magnetic field without tedious centrifugation or filtration procedures, and adsorbent particles could be easily retrieved, which makes the sample pretreatment procedure more convenient, time-saving, and economical.⁸⁻¹⁰ A magnetic adsorbent dispersed in the sample solution can significantly increase the contact interface with analytes, and it was beneficial to facilitate the mass transfer.¹¹ The performance of the method can be improved by dispersing the sorbent into a solvent prior to injection into the sample solution because the extraction time and contact time between the SPE sorbent and analyte are greatly reduced and so, the selectivity of the method is increased. On the other hand, the possibility of extraction of species with low mass transfer onto the SPE sorbent decreases dramatically with reducing the extraction time.¹²

Graphene, as a new carbon material, has attracted great attention since its discovery in 2004.¹³ Graphene oxide (GO), a derivative of graphene, contains various reactive oxygen-containing functional groups, such as hydroxyl, epoxy and carboxylic groups,¹⁴ which make GO sheets ideal fundamental materials for the immobilization of diverse substances onto its

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surface.¹⁵ Due to their high adsorption capacity, graphene-based materials have been widely used to remove heavy metal cations and organic contaminants from water and waste water samples, and also applied as a unique sorbent for sample preparation, especially for SPE.¹⁶ One limitation of graphene oxide as a SPE sorbent is its low selectivity to extract the analyte in real samples, especially in the presence of interfering species. In order to overcome this disadvantage, the functional groups on the surface of graphene oxide are chemically modified with new and suitable functional groups,¹⁷ such as EDTA functionalized magnetic graphene oxide,¹⁸ magnetic graphene oxide¹⁹ and magnetic chitosan/graphene oxide,²⁰ for separation of metals. Also, other forms of carbon are used as SPE sorbents such as modified single-wall carbon nanotubes.²¹

In this work, MDSPE coupled with electrothermal atomic absorption spectrometry (ETAAS) was used for the extraction and determination of lead ions in real samples. A novel SPE sorbent, magnetic graphene oxide functionalized with 4-(2-pyridylazo)resorcinol (PAR) (GO-PAR@Fe₃O₄), was synthesized and applied for pre-concentration of ultra-trace amounts of lead ions. Characterization of GO-PAR@Fe₃O₄ was made by studying the FTIR spectrum and SEM image. Affecting factors in extraction and desorption of lead ions onto the sorbent were optimized. The accuracy of the proposed method was investigated using the analysis of a Certified Reference Material (CRM). The new sorbent shows high selectivity for extraction of lead ions in the presence of other metal ions. The method has the most advantages such as simplicity, high sensitivity and low cost. Finally, the SPE procedure was successfully employed for the extraction of lead ions in real water, fruit juice and rice samples and this indicates that the new sorbent was very efficient and selective for preconcentration of this metal ion in real samples.

2. Experimental

2.1 Apparatus and materials

An atomic absorption spectrometer, Shimadzu AA-7000 (Kyoto, Japan) with a deuterium background correction and a Pb hollow-cathode lamp as the radiation source for absorbance measurements at a wavelength of 283.3 nm, equipped with a graphite furnace atomizer and an autosampler, was used for this work. The furnace tube was a pyrolytic coated graphite tube. The furnace temperature programs applied were as recommended by the manufacturer. In order to characterize the new sorbent (GO-PAR@Fe₃O₄), scanning electron microscopy (SEM), S-3000N microscope (Hitachi, Japan), and Fourier transform infrared spectrometry (FT-IR), (Thermo Nicolet AVATAR, USA), were used. The sample injection volume was 20 μ L in all experiments. All chemicals used were of GC grade and obtained from Merck Company.

2.2 Synthesis of graphene oxide

Graphene oxide was prepared referring to previously reported procedures, Entezari *et al.*²² In this procedure, a mixture of graphite flakes (0.5 g) and NaNO₃ (0.5 g) was cooled to 0 °C in an

ice bath followed by drop-wise addition of 0.023 L of concentrated H₂SO₄. 3.0 g of KMnO₄ was gradually added to the mixture and the temperature of the suspension was kept below 20 °C. The suspension was ultrasonically treated for 20 min at room temperature and diluted with 0.04 L of deionized water. In order to remove any excess of KMnO₄, a mixture of 0.03 L H₂O₂ (30%) and 0.1 L de-ionized water was finally added drop-wise to the suspension until the color of the suspension changed from dark brown to yellow. The resulting product was washed several times with 5% HCl aqueous solution and distilled water to remove any metal ion impurities, sulfate ions and the excess of acid, respectively. After filtration, graphene oxide was dried under vacuum at 80 °C for 24 h.

2.3 Preparation of modified graphene oxide

First, 1.7 g of GO was dispersed by sonication in 0.1 L of dimethylformamide (DMF) for 1 h. Thionyl chloride (0.025 L) was then added to the suspension. The mixture was transferred to a water bath (70 °C) and refluxed for 24 h to carry out the reaction. The excess of thionyl chloride was removed using a distillation procedure. Finally, the products (GO-Cl) were dried at 70 °C overnight in a vacuum.

To prepare GO-PAR, 1.0 g of GO-Cl and 0.15 g PAR were ultrasonically dispersed in 0.1 L of ethanol for 30 min. The mixture was then refluxed at 70 °C for 24 h. The obtained GO-PAR was washed several times with ethanol and high purity water. The composite was then dried in an oven at 60 °C for 12 h.

Finally, for the preparation of GO-PAR@Fe₃O₄, 1 g GO-PAR was added to 0.04 L of deionized water and dispersed for 1 h. Subsequently, FeCl₃·6H₂O (0.8 g) and FeCl₂·4H₂O (0.45 g) were added to the mixture. The solution was heated up to 80 °C under a nitrogen atmosphere with vigorous stirring (1000 rpm). Then, 0.002 L of ammonia solution (25 wt%) was quickly added to the mixture and a black precipitate was instantly formed. The mixture was left for 5 min in order to complete the precipitation of GO-PAR@Fe₃O₄. The precipitate was then collected using a strong magnet while the solution was decanted. The black precipitate was washed with double-distilled water and then dried in vacuum at 65 °C.

2.4 Extraction procedure

For the MDSPE procedure, 0.01 L of distilled water containing lead ions at pH 5 was introduced into a polyethylene conical bottom tube. 1 mg of G-PAR@Fe₃O₄ was then transferred to a glass vial containing 0.001 L of distilled water, ultrasonicated for 5 min, and injected rapidly into the sample solution using a 1 mL syringe. At this stage, a cloudy solution was instantaneously produced and the analyte was adsorbed onto the dispersed sorbent. The GO-PAR@Fe₃O₄ nanocomposite was subsequently separated from the solution through the application of an external magnetic field and the supernatant was discharged using a pipette in the presence of a strong magnet. The GO-PAR@Fe₃O₄ was washed with 2 mL of methanol-water (1 : 2, v/v) to remove any impurities and then 50 μ L of 0.4 M HCl was added into the tube as an eluent and the mixture was

ultrasonicated for 3 min. Finally, the adsorbent was separated through an external magnet and the supernatant was collected for the determination of lead by ETAAS.

3. Results and discussion

3.1 Characterization of sorbents

Scanning Electron Microscope (SEM) images of GO-PAR@Fe₃O₄ are shown in Fig. 1. FT-IR was employed to examine the surface functional groups of GO, GO-Cl, GO-PAR and GO-PAR@Fe₃O₄ nanocomposites, and the obtained FT-IR spectra are shown in Fig. 2. In the FT-IR spectrum of GO, the bands located at 3300 cm⁻¹ and 3199 cm⁻¹ correspond to the stretching vibrations of hydroxyl groups removed or decreased in other spectra due to the reaction with thionyl chloride in GO-Cl. The stretching vibrations of C=O and C-O functional groups for GO were detected clearly at 1720 cm⁻¹ and 1051 cm⁻¹, respectively, with a band shifted from 1720 cm⁻¹ to shorter wavelengths in GO-Cl. The peak located at 1226 cm⁻¹ for GO is mostly often related to the vibration of the epoxy group. The spectrum of GO also shows a C=C peak at 1618 cm⁻¹ corresponding to the remaining sp² character. The peaks located at 1169 cm⁻¹, 1060 cm⁻¹ and 837 cm⁻¹ in the GO-Cl spectrum are related to C-Cl. The peak at 1552 cm⁻¹ is due to the N=N stretching vibration of PAR, the peak at 1173 cm⁻¹ is the C-N stretching vibration for the benzenoid unit in PAR (no. 3, Fig. 2). Obviously, Fe₃O₄ displayed the characteristic peaks of Fe-O at 574 cm⁻¹ as shown in no. 4 Fig. 2.

3.2 Optimization of the extraction conditions

In order to obtain the highest adsorption efficiency, precision and high enrichment factor, different effective parameters in the extraction conditions were optimized.

3.2.1 Effect of pH. The pH of the sample solution is the main parameter and plays a very important role in metal chelate formation and subsequent extraction. The influence of pH on adsorption efficiency was studied over the pH range from 3 to 8. As indicated from the results (Fig. 3), the adsorption efficiency increases with increasing of the pH of the solution to 5 and decreases with pH over 6. This could be explained by the fact that at low pHs the amine groups on the surface of the adsorbent can be easily protonated. Also, at higher pHs, due to the formation of the metal hydroxide and its precipitation, the adsorption efficiency of Pb(II) onto the sorbent decreased. An optimum pH value of 4.8–5.2 is needed for adsorption of Pb(II) ions, and a pH value of 5 was chosen for the adsorption experiments presented in this study.

3.2.2 Effect of sorbent amount. The influences of various amounts of sorbent on the adsorption of lead ions were investigated in the range of 0.5–5.0 mg. The increase of adsorption efficiency was attributed to more available adsorption sites which could be obtained at higher amounts of sorbents. The least amount of sorbent (1.0 mg) was selected for high adsorption efficiency in this study.

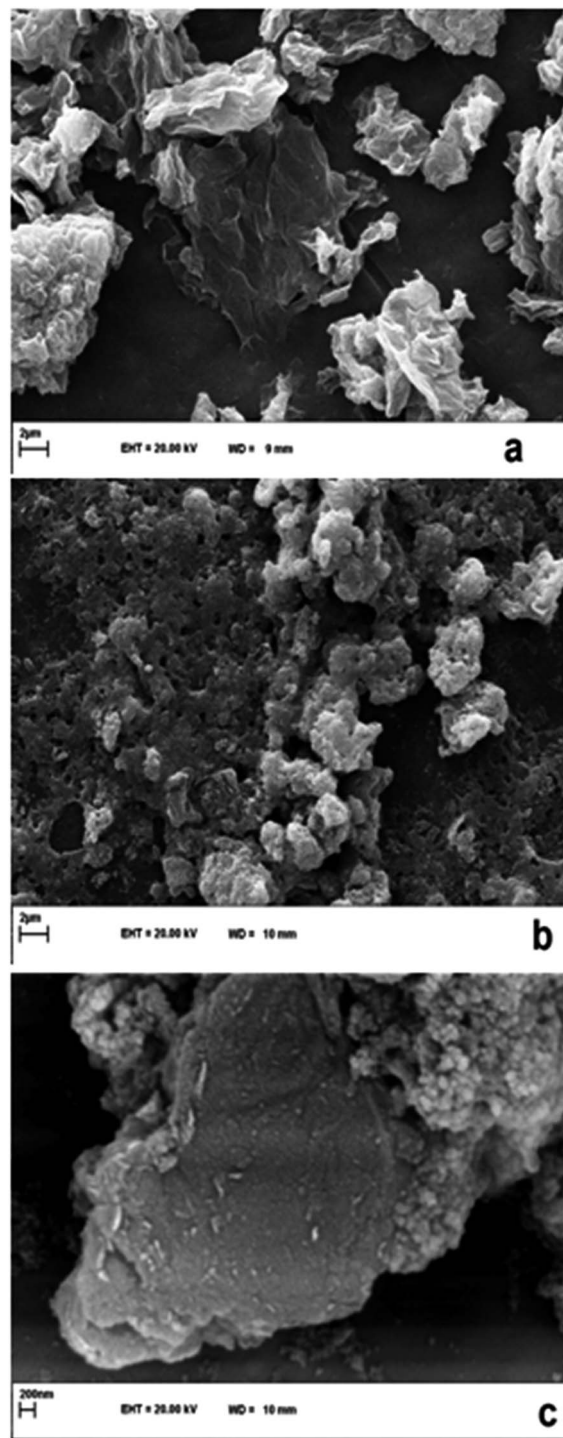


Fig. 1 SEM images of GO (a) and GO-PAR@Fe₃O₄ (b and c).

3.2.3 Influence of desorption conditions. The desorption solution must have high affinity towards the target analyte and fast kinetics for its quantitative recovery in a short time. The optimization of desorption conditions was performed using a series of aqueous desorption solutions including HCl, HNO₃, and CH₃COOH (Fig. 4). The results show that hydrochloric acid solution with the extraction recovery of 97.2% ± 1.7% provides the best result for desorption of lead ions from the sorbent

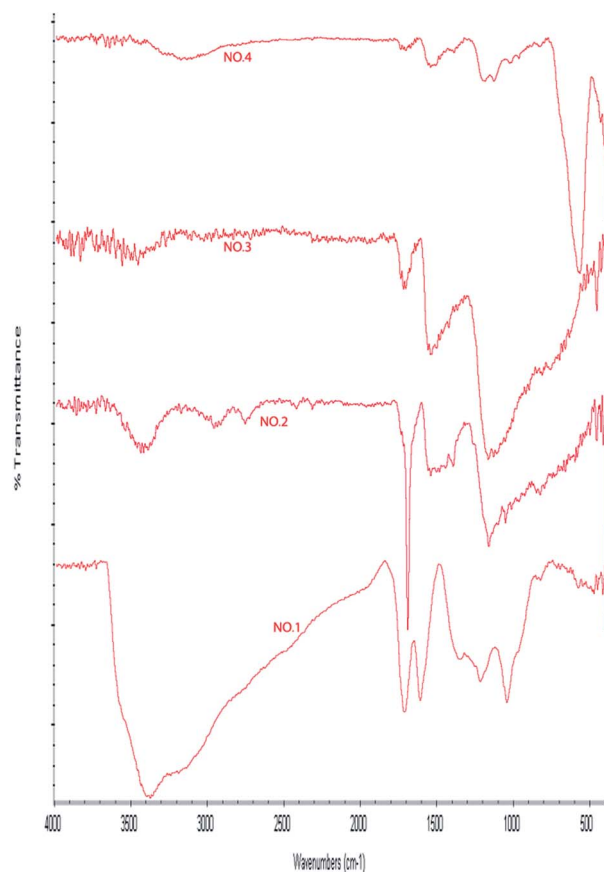


Fig. 2 FTIR spectra of GO (1), GO-Cl (2), GO-PAR (3) and GO-PAR@Fe₃O₄ (4).

surface. The concentration of the HCl solution was then varied from 0.4 to 3 mol L⁻¹. It was found that the recovery of lead ions was high and maximum when the HCl concentration was 0.4 mol L⁻¹ or higher. Furthermore, the effect of the volume of desorption solution was studied in the range of 30–500 μL. The results indicated that 50 μL of eluent is sufficient for complete extraction recovery of lead ions and injection to ETAAS.

The effect of ultrasonic time on desorption of lead ions from the sorbent surface was also examined. The minimum time for desorption of lead ions (3 min) was selected to reach high extraction recovery in this study.

3.2.4 Effect of sample volume. In order to examine the possibility of enriching low concentrations of analyte from large volumes, the effect of sample volume on the recovery of lead was studied. The effect of the sample volume (0.01–0.1 L) on the extraction of 50.0 ng L⁻¹ of lead was studied. The results indicated that the maximum absorbance for complete extraction recovery of lead ions is obtained for 0.03 L of sample solution. Therefore, 0.03 L of sample solution volume was selected for further studies.

3.2.5 Adsorption isotherms. The capacity of GO-PAR@Fe₃O₄ for adsorption of lead ions was examined by measuring the initial and final concentrations of lead ions. To investigate the adsorption capacity of the sorbent, 1 mg of GO-PAR@Fe₃O₄ sorbent was dispersed in 0.03 L of the solution

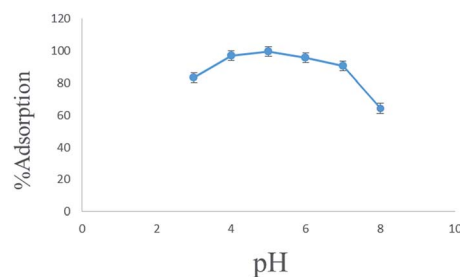


Fig. 3 Effect of pH solution on adsorption of lead using MDSPE-ETAAS.

containing different concentrations of lead ions. After the extraction, the concentration of lead ions in the sample solution was determined by ETAAS. Both Langmuir and Freundlich adsorption isotherms were used to normalize the adsorption data. The results showed that the Langmuir model fitted better ($R^2 = 0.999$) than the Freundlich model ($R^2 = 0.9377$), demonstrating that the adsorption of lead ions onto GO-PAR@Fe₃O₄ can be considered to be a monolayer adsorption process. This may be due to the formation of a monolayer strong complex between the PAR on the surface of the adsorbent and lead ions which covers the surface of GO-PAR@Fe₃O₄. The Langmuir isotherm equation was used to describe the relationship between the amount of Pb adsorbed and its equilibrium concentration in solutions (Fig. 5). The adsorption capacity (q_m , mg g⁻¹) was calculated using the following equation:

$$\frac{c}{q} = \frac{1}{Kq_m} + \frac{c}{q_m}$$

where c (mg L⁻¹) is the equilibrium concentration of Pb(II) in the solution, q (mg Pb per g adsorbent) is the equilibrium adsorption amount of Pb(II), q_m is the maximum adsorption amount of Pb(II) per milligram of sorbent (mg g⁻¹) and K is the Langmuir adsorption equilibrium constant in liter per mg of sorbent (L mg⁻¹). The capacity of GO and GO-PAR@Fe₃O₄ (Fig. 5) as sorbents for extraction of lead ions under the optimized conditions was evaluated and found to be 87 and 133 mg g⁻¹, respectively. As seen from Fig. 1 (SEM images of GO and GO-PAR@Fe₃O₄) after the combination of GO with PAR and Fe₃O₄ to form the GO-PAR@Fe₃O₄ nanocomposite, the sorbent had a much rougher surface due to increased adsorption capacity of the sorbent.

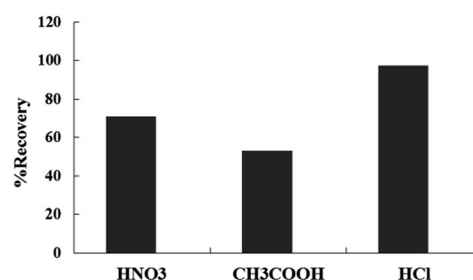


Fig. 4 Effect of the kind of desorption solvent using MDSPE-ETAAS.

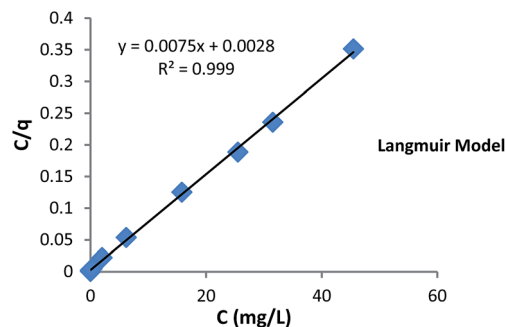


Fig. 5 The plot of c/q versus c (mg L^{-1}) at 25°C and $\text{pH} = 5.0$ with Langmuir model fit of the data.

3.2.6 Effect of interfering ions. The effects of cations and anions on the determination of lead ions were investigated under the optimum conditions. The results for this study are given in Table 1. The tolerance limit was defined as the ion concentration causing a relative error smaller than $\pm 5\%$ in the determination of lead. According to these experimental results, it can be concluded that the large numbers of ions studied have no considerable effects on the determination of lead.

3.3 Analytical performance

The analytical characteristics of the optimized method, including the limit of detection, linearity, repeatability and preconcentration factor, are summarized in Table 2. The total time of furnace temperature programs was 1 minute. The limit of detection (LOD), calculated as $3S_b/m$ (S_b : standard deviation of the blank signals, m : slope of the calibration curve after preconcentration), was equal to 0.18 ng L^{-1} . The precision (relative standard deviation, RSD) for seven replicate measurements of $20 \text{ ng L}^{-1} \text{ Pb(II)}$ was 2.4%. A good linearity of Pb(II) was obtained in the concentration range of 0.5 to 100.00 ng L^{-1} , with a linear

Table 1 Effect of interfering ions on the recovery of $20 \text{ ng L}^{-1} \text{ Pb(II)}$ in water samples using MDSPE-ETAAS

Ion	Mol ratio (ion/lead)	Recovery (%)
Na^+	10 000	96.1
K^+	10 000	96.8
PO_4^{2-}	10 000	97.1
NO_3^-	10 000	96.3
NO_2^-	10 000	95.8
Ba^{2+}	10 000	95.1
F^-	10 000	96.8
Ca^{2+}	10 000	95.3
Mg^{2+}	10 000	96.7
AS^{3+}	1000	95.6
Ni^{2+}	1000	96.1
Cd^{2+}	1000	96.5
Zn^{2+}	1000	94.2
Mn^{2+}	1000	95.8
Se^{2+}	1000	97.9
SO_4^{2-}	1000	96.9
Cr^{3+}	100	95.2

Table 2 Analytical performance of the proposed method

Parameter	Analytical feature
Limit of detection (ng L^{-1}) ($n = 7$)	0.18
Linear range (ng L^{-1})	0.5–100
Repeatability (RSD) ($n = 7$)	2.4%
Enhancement factor	600
Correlation coefficient (r^2)	0.9989
Sorbent capacity (mg g^{-1})	133

correlation coefficient of 0.9979 under the optimum conditions. The enhancement factor for the developed method was calculated to be 600 based on the volume ratio of the sample solution (0.03 L) to the desorption solution ($50 \mu\text{L}$) with the extraction recovery of $95\% \pm 2.0\%$. The validation of the presented procedure was performed by analysis in a CRM clean water sample ERA 1340.lot:210815 in Table 3. The results showed that the extraction recovery for the lead ions in the CRM was in good agreement with the certified value ($98.8\% \pm 1.7$).

3.4 Affinity of lead in the certified reference material (CRM)

In order to confirm the selectivity of the method for separation of lead ions in the presence of other metal ions, the extraction recovery from some metal ions in a clean water sample ERA 1340 was studied. For this purpose, 0.01 L of certified reference material (ERA 1340) at $\text{pH} 5$ was introduced into a polyethylene conical bottom tube. Then 1 mg of dispersed sorbent was

Table 3 Analytical results of the determination of some metal using the proposed method in a certified reference material (CRM) clean water (ERA 1340)

Metal	Certificate value	Determined value	Recovery (%)
Lead	$11/6 \pm 0.5\%$	11.5	98.8 ± 1.7
Cadmium	$14/6 \pm 0.5\%$	2.5	17.1 ± 2.1
Chromium	$7/74 \pm 0.5\%$	2.3	30.0 ± 1.3
Cobalt	$33/2 \pm 0.5\%$	1.7	5.0 ± 1.7
Copper	$334 \pm 0.5\%$	97.2	29.1 ± 1.5
Manganese	$23/8 \pm 0.5\%$	0.24	1 ± 0.2
Nickel	$8/19 \pm 0.5\%$	0.1	1.3 ± 0.1
Selenium	$7/11 \pm 0.5\%$	0.1	1.4 ± 0.1
Zinc	$115 \pm 0.5\%$	13.9	12.1 ± 1.1
Iron	$342 \pm 0.5\%$	15	4.4 ± 0.9
Arsenic	$12/9 \pm 0.6\%$	1.7	13.3 ± 1.3

Table 4 Effect of SPME sorbents on the extraction recovery of lead

SPME sorbent	Recovery	
	Spiked (80 ng L^{-1})	CRM
GO	69.3%	67.1%
GO-Cl	40.1%	37.9%
GO-PAR	95.1%	95.8%
GO-PAR@ Fe_3O_4	98.3%	98.8%

Table 5 Determination of lead ions in different real water samples^a

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water	0	ND	—
	20	19.2 ± 0.9	96
River water	0	3.2 ± 0.8	—
	20	22.1 ± 1.1	95.2
Well water	0	2.9 ± 0.7	—
	20	20.9 ± 1.2	94.3
Iranian rice	0	11.4 ± 0.6	—
	20	32.3 ± 1.3	103
Apple juice	0	5.2 ± 0.41	—
	20	27.1 ± 0.89	107
Pineapple juice	0	7.8 ± 0.43	—
	20	28.4 ± 0.85	102

^a ND: not detected.

injected rapidly into the CRM solution. Subsequently, the sorbent was separated from the solution using an external magnetic field. The sorbent was then eluted with a desorption solvent and diluted for the determination of lead and other metal ions using ETAAS under the standard instrumental conditions for each metal ion. As the results showed (Table 3), the extraction recovery for lead ions was 98.8%; however, for other metals it was smaller than 30%. These results indicate the high selectivity of the sorbent for extraction of lead ions. PAR is not a selective analytical agent. However, we have demonstrated that by combining PAR with GO and Fe_3O_4 nanoparticles a highly selective procedure for the extraction of lead ions is obtained compared with imprinted polymers. As shown in Fig. 1a and b, the structure of the $\text{GO-PAR@Fe}_3\text{O}_4$ is completely porous with cavities which are caused by the orientation of modified graphene oxide sheets and nanoparticles of iron. Although, the radius of the lead ion is larger than those of other metal ions in the CRM solution, but due to its more suitable interaction with the functional groups in $\text{GO-PAR@Fe}_3\text{O}_4$ than other metal ions, the extraction recovery of lead ions is the highest.

3.5 Effect of functional groups on the efficiency of the adsorbent

In order to confirm the effect of functional groups, the extraction recovery of lead ions in the spiked solution (80 ng L^{-1}) and the CRM solution for GO, GO-Cl, GO-PAR and $\text{GO-PAR@Fe}_3\text{O}_4$ was compared (Table 4). The high extraction recovery of GO can be related to the fact that the surfaces of the planar sheets of GO are accessible to metal ions. The extraction recovery of other metals for GO gave the same result but they are not mentioned here. The low extraction recovery of GO-Cl is related to the reduction of available OH sites for lead ions. In GO-PAR and $\text{GO-PAR@Fe}_3\text{O}_4$, the lead ion interacting with the functional groups (azo and OH groups) of PAR is the cause of increase in extraction recovery.

3.6 Application to real samples

This procedure was applied for the determination of lead in real water and food samples. Real water samples (tap, well and river water) were directly analysed while fruit juices and Iranian rice samples were analysed after wet acid digestion.²³ Tap and well water samples were obtained from the outskirts of Mashhad (Iran). River water samples were collected from the Golestan River (Torghabeh, Iran) in August 2017. The real fruit juice samples (Sunich brand, Alifard Co.) were purchased from a supermarket in Mashhad (Iran). For the present study, commercially available fruit juice samples of two different types (apple and pineapple) and Iranian rice samples were used. The results are presented in Table 5. The recoveries of the obtained results were in the range of 94.3–107% with a standard deviation smaller than 7%. In all cases, the spiked recoveries confirmed the reliability of the proposed method.

3.7 Comparison of analytical performance with other reported approaches in the literature

Comparison of the proposed method with other reported approaches in the literature for preconcentration and separation of lead is represented in Table 6. The present technique

Table 6 Comparison of the analytical performance of the proposed method for lead with other reported approaches in the literature^a

Sorbent	Determination technique	LOD ($\mu\text{g L}^{-1}$)	Capacity	EF	% RSD	Ref.
Chelating resin	FAAS	16		75		25
Modified silica gel	FAAS	22.5		27		6
Multiwalled carbon nanotubes	FAAS	8.9	20			26
5-Br-PADAP/Triton X-1 14	ETAAS	0.08		50	2.8	4
Amino-functionalized $\text{Fe}_3\text{O}_4@SiO_2$ magnetic nanomaterial	FAAS		76.6			27
Graphene	FAAS	0.61	16.6	125	3.56	28
Gallic acid-modified silica gel	FAAS	0.58	12.63	200	0.96	29
Oxidized carbon xerogel	UV	0.9	50		7.8	30
Polymer-modified magnetic nanoparticles	FAAS		166.1			24
Magnetic chitosan/graphene oxide	FAAS		76.94			20
$\text{GO-PAR@Fe}_3\text{O}_4$	ETAAS	0.00018	133	600	2.4	This work

^a EF: enhancement factor. FAAS: flame atomic absorption spectrometry. UV: UV-visible spectrophotometry.

provides a very good detection limit and high preconcentration factor in comparison with other methods. Also a suitable relative standard deviation is another advantage of this method. The results show that the adsorption capacity of the adsorbent is higher than that in previous studies except for polymer-modified magnetic nanoparticles but it has long extraction time.²⁴ The main advantage of the proposed method over the previous methods is the high affinity of sorbents, such as imprinted polymers, for lead ions.

4. Conclusion

In summary, a modified magnetic graphene oxide sorbent has been developed for selective separation and preconcentration of lead ions from contaminated water. The parameters such as the solution pH, initial lead ion concentration, amount of adsorbent and desorption conditions have been optimized for adsorption. The proposed procedure was successfully applied for the extraction and determination of lead at low concentrations with high selectivity in water and food samples. The main advantages of the proposed procedure are simplicity, rapidity, good detection limits, high selectivity, increased enhancement factors and good precision.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors gratefully acknowledge the support of this research by the Ferdowsi University of Mashhad, Mashhad, Iran (No. 3/32788 dated 12/04/2014) and Central Lab Rural Water and Waste Water Company, Khorasan Razavi, Iran.

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