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Ultratrace determination of arsenic in water samples by electrothermal atomic absorption spectrometry after pre-concentration with Mg–Al–Fe ternary layered double hydroxide nano-sorbent

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ABSTRACT

A selective solid phase extraction method, based on nano-structured Mg–Al–Fe(NO_3^-) ternary layered double hydroxide as a sorbent, is developed for the pre-concentration of ultra-trace levels of arsenic (As) prior to determination by electrothermal atomic absorption spectrometry. It is found that both As(III) and As(V) could be quantitatively retained on the sorbent within a wide pH range of 4–12. Accordingly, the presented method is applied to determination of total inorganic As in aqueous solutions. Maximum analytical signal of As is achieved when the pyrolysis and atomization temperatures are close to 900 °C and 2300 °C, respectively. Several variables affecting the extraction efficiency including pH, sample flow rate, amount of nano-sorbent, elution conditions and sample volume are optimized. Under the optimized conditions, the limit of detection ($3S_b/m$) and the relative standard deviation are 4.6 pg mL^{-1} and 3.9%, respectively. The calibration graph is linear in the range of 15.0–650 pg mL^{-1} with a correlation coefficient of 0.9979, sorption capacity and pre-concentration factor are 8.68 mg g^{-1} and 300, respectively. The developed method is validated by the analysis of a standard reference material (SRM 1643e) and is successfully applied to the determination of ultra-trace amounts of As in different water samples.

1. Introduction

Arsenic (As) is a common element in the earth's crust which occurs naturally in soil and bedrock, and known as a toxic element. The main source of As in natural water is a result of dissolving eroded rocks and soils [1]. Arsenic contamination in natural water is a worldwide problem and has become a challenge for the scientists. The ingestion of As causes a variety of disorders, including skin lesions, respiratory system problems, nervous system effects, cancers of different organs, and reproductive effects [2]. In natural waters, As is found in the form of inorganic As(V) and As(III) as acids [3]. The maximum permissible limit for As in drinking water is 10 μg L^{-1} according to the World Health Organization recommendation [4]. In view of the above facts, the analysis of As is great interest in environmental and drinking water samples.

Various analytical techniques including electrothermal atomic absorption spectrometry (ETAAS) [5–7], hydride generation atomic absorption spectrometry [8,9], hydride generation atomic fluorescence spectrometry [10], inductively coupled plasma [11,12], high performance liquid chromatography [13,14], and electrochemical methods [15,16] were employed for the determination of As. Among these techniques, ETAAS appears an attractive option because it is a robust and sensitive technique, and is routinely used for the determination of trace impurities in a variety of matrices. However, quantification of As in real samples remains a challenge at the lower limit of detections. Therefore, combination of simple and selective separation/preconcentration techniques with ETAAS detection is necessary. A number of separation and pre-concentration methods including; co-precipitation [17], cloud point extraction [18,19], liquid phase micro-extraction [6,7,20], and solid phase extraction (SPE) [10–12,21–32] were applied for this purpose.

SPE has frequently proven as a suitable method for pre-concentrating of different organic and inorganic analytes, due to some merits including convenience, low cost, reduced organic solvent utilization, possible miniaturization and simple operation. It should be noted that the sorbent material plays a crucial role for SPE. Thus, the development of new sorbent material with high selectivity, stability and extraction efficiency for SPE is in demand. Numerous substances were used as SPE sorbents for the

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separation and pre-concentration of As, such as cigarette fiber [10], carbon nanofiber [11], resin [21,22], modified mesoporous TiO_2 [23], immobilized nanometer TiO_2 [24], PTFE turnings [25], modified silica [12,26], modified activated carbon [27], carbon nanotubes [28–30], ion imprinted polymer [31] and cellulose fiber [32]. Among these, in recent years, nanometer-size materials have drawn growing attention of scientists because of their unique structure and properties.

Layered double hydroxides (LDHs) are a family of synthetic two-dimensional nano-structured anionic layered materials, with general formula of $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{n-}_{x/n}mH_2O]^{x-}$, where M^{II} and M^{III} represent divalent and trivalent metal cations, respectively, and A is an exchangeable n-valent anion in the interlayer space, x is equal to the ratio $M^{3+}/(M^{2+}+M^{3+})$, and m is the number of water molecules in the LDH interlayer. Because of the presence of large interlayer spaces and the significant number of exchangeable anions, LDHs have the potential to be good ion-exchangers and adsorbents [33,34].

We developed simple SPE systems based on Ni–Al LDH with nitrate interlayer anion for the separation and pre-concentration of various organic and inorganic anions [35,36]. Although Mg–Al–Fe LDH with carbonate interlayer anion was recently synthesized by other researchers and some properties of the LDH along with its applications were reported [37–39], no attempt was made to apply the Mg–Al–Fe LDH in SPE procedures. Therefore, in the present work, Mg–Al–Fe LDH with nitrate interlayer anion is applied as a novel nano-sorbent for the extraction and pre-concentration of ultra-trace amounts of As prior to determination by ETAAS. For this purpose, the LDH is synthesized and structurally and morphologically characterized by X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FT-IR) and field emission scanning electron microscopy. The effects of various experimental parameters on the extraction efficiency are optimized. The presented method is also applied to the determination of total As in different water samples with satisfactory results.

2. Experimental

2.1. Instruments

Atomic absorption spectrophotometer (Model CTA 3000, UK) equipped with a heated graphite furnace atomizer is used for the determination of As. An As hollow cathode lamp (operated at 6 mA) is used as the radiation source at the wavelength of 193.7 nm with 0.4 nm spectral bandpass. All measurements are performed using integrated absorbance (peak area). Argon 99.999% (Roham Gas Co., Iran) is used as a purge gas at flow rate of 450 mL min^{-1}. Instrumental parameters and temperature program are given in Table 1. A 2 mL polypropylene cartridge (30 mm × 7 mm i.d.) (Shafa Co., Iran) packed with 0.2 g of Mg–Al–Fe(NO_3^-) LDH is applied for column preparation. The flow rate of solution through the column is controlled with a pressure pump model XX 55 220 50 (Millipore). In order to structural study of the LDH, XRD measurements are performed on a Bruker AXS (D8 Advance) X-ray powder diffractometer (Cu K_α radiation source, $\lambda=0.154056$ nm) between 5° and 70° generated at 40 kV and 35 mA at room temperature. In addition, FT-IR spectra (4000–400 cm^{-1}) are recorded on a Vector 22 (Bruker, Germany) Fourier transform infrared spectrometer using the KBr disk method with a sample/KBr ratio of 1:100 by mass. A field emission scanning electron microscope (FESEM), model S-4160 Hitachi (Japan) is additionally used to examine the morphological characteristics of the sorbent. Elemental analysis of the LDH is carried out by a Varian SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer. Hot plate stirrer model Jenway 1000 (U.K.), Selecta lab centrifuge model Tl 320 and nitrogen gas (99.9995%, Azaroxide Co., Iran) are used in the LDH preparation process. An ultrasonic bath (AXUY-01D, Turkey) operated at 32 kHz is used to investigate the LDH sorption capacity. A Metrohm model 774 pH-meter is used for pH measurements. An electronic analytical balance (AB204-S, Switzerland) is used for weighing the solid materials.

2.2. Standard solutions and reagents

All chemicals used are of analytical-reagent grade and all solutions are prepared with deionized water (Shahid Ghazi Co., Iran). The standard stock solution of 1000 mg L^{-1} As(V) is obtained from Chem-Lab (Belgium). A 1000 mg L^{-1} stock solution of As(III) is prepared by dissolving 0.1732 g of $NaAsO_2$ (Panreac) in 100.0 mL deionized water using a calibrated flask. Working standard solutions for As(III) and As(V) are prepared by serial dilutions with deionized water. All salts used for the interference study, $NaBH_4$, NaOH and LDH precursors, i.e., $Mg(NO_3)_2 \cdot 6H_2O$ (99%), $Al(NO_3)_3 \cdot 9H_2O$ (99%) and $Fe(NO_3)_3 \cdot 9H_2O$ (99%) are purchased from Merck (Germany). Nitric acid is purchased from Scharlau (Spain). A 0.25% (m/v) chemical modifier solution is prepared by diluting palladium nitrate stock solution (1000 mg L^{-1}, Merck). The accuracy of the method is assessed by analyzing of a standard reference material, SRM 1643e (Trace Elements in Water), from National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. All the plastic and glassware are cleaned by soaking in 10% (v/v) HNO_3 and are rinsed with deionized water prior to use.

2.3. Preparation of nano-sorbent

The Mg–Al–Fe(NO_3^-) LDH is prepared using a co-precipitation method. Synthesis is carried out under a nitrogen atmosphere, and all of the solutions are prepared using deionized water. In this work, the Mg^{2+}:($Al^{3+}+Fe^{3+}$) and Al^{3+}:Fe^{3+} molar ratios chosen for the synthesis of the LDH precursors are 4:1 and 0.7:0.3, respectively. For this purpose, 1.295 g $Mg(NO_3)_2 \cdot 6H_2O$, 0.333 g $Al(NO_3)_3 \cdot 9H_2O$ and 0.153 g $Fe(NO_3)_3 \cdot 9H_2O$ are added into 35.0 mL deionized water under vigorous stirring at room temperature. Then, the salt solution is added dropwise to the 50 mL of 0.35 mol L^{-1} NaOH solution under vigorous stirring, and pH of the solution is adjusted to 8.5 by the addition of 10% (v/v) HNO_3 solution. Then, the obtained slurry is subjected to hydrothermal treatment at a constant temperature of 60 °C for about 18 h. Afterward, the resulting precipitate is separated by centrifugation at 4000 rpm for 10 min and washed three times with deionized water, and dried at 60 °C for 15 h.

2.4. Characterization of the nano-sorbent

The M^{2+}:M^{3+} molar ratio of the LDH has a significant influence on its analyte uptake. So, the Mg–Al–Fe(NO_3^-) ternary layered double hydroxide with different Mg^{2+}:($Al^{3+}+Fe^{3+}$) molar ratios are synthesized. The powder X-ray diffraction patterns of the synthesized samples with Mg^{2+}:($Al^{3+}+Fe^{3+}$) molar ratios of 2:1, 3:1 and 4:1 are obtained. The XRD patterns exhibit the characteristic reflections of the LDH structure with a series of sharp and intense lines, corresponding to a well crystallized layered structure, which are in agreement with the results from the literature [37–39]. High degree of crystallinity is obtained in the Mg^{2+}:($Al^{3+}+Fe^{3+}$) molar ratio of 4:1 because its XRD pattern shows narrow, symmetric and strong reflections at corresponding 2θ. As a result, the Mg–Al–Fe(NO_3^-) LDH with Mg^{2+}:($Al^{3+}+Fe^{3+}$) molar ratio of 4:1 is applied as a nano-sorbent in SPE experiments.

The FT-IR spectrum of Mg–Al–Fe(NO_3^-) LDH is shown in Fig. 1. The broad band at 3482 cm^{-1} is due to the stretching mode of hydroxyl groups of LDH layers and interlayer water molecules. The presence of water molecules is also responsible for the medium intensity band close to 1638 cm^{-1} (bending mode). A sharp and intense band is observed at 1384 cm^{-1} corresponding to stretching vibration of intercalated NO_3^- ions. The absorption band at 596 cm^{-1} and 833 cm^{-1} are attributed to M–O stretching and M–OH bending vibrations.

A FESEM image of the synthesized Mg–Al–Fe(NO_3^-) LDH shows an aggregate that consists of crystallites that are collected as small pseudo-spherical particles with approximate size range of 20–100 nm and stacking with each other, which makes plate-like morphology (Fig. 2).

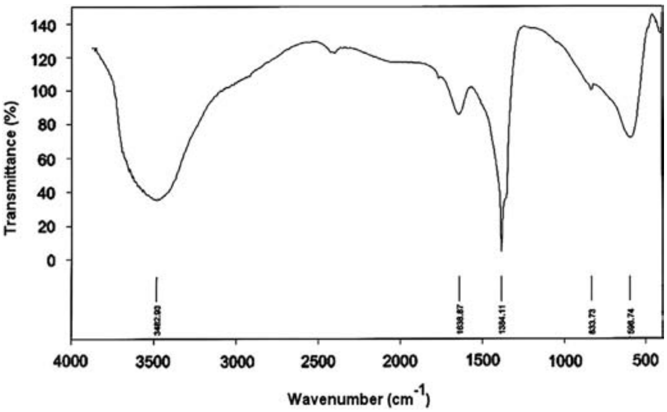

Fig. 1. FT-IR spectrum of the synthesized Mg–Al–Fe(NO_3^-) LDH.

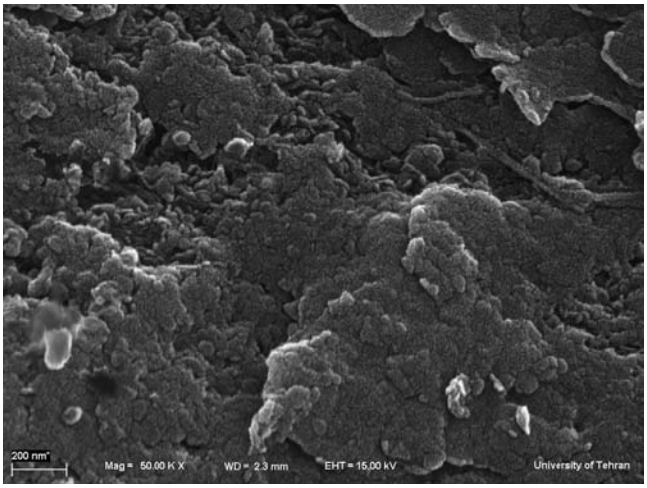

Fig. 2. FESEM image of the synthesized Mg–Al–Fe(NO_3^-) LDH.

2.5. *Column preparation*

In order to prepare the SPE column, 200 mg of nano-sorbent packed into an 2 mL polypropylene cartridge, then plugged with a small portion of cotton at both ends. Before loading a sample, 3 mL of eluent solution and 5 mL deionized water are passed through the column in sequence to clean and condition it prior to each use.

2.6. *Sample preparation*

Water samples; i.e. tap water, well water, spring water and rain water are sampled from a local source (Tabriz, Iran). After collection of the water samples in pre-washed (with detergent, deionized water, dilute HNO_3 and deionized water, respectively) polyethylene bottles, they are filtered through a 0.45 μm pore size cellulose membrane filter and then aliquots of 150.0 mL are analyzed within 24 h of collection without previous treatment by the procedure described in Section 2.7. In the case of certified reference material, SRM 1643e, a suitable aliquot is diluted with deionized water prior to sample loading.

2.7. *General procedure*

For pre-concentration of As, a 150.0 mL portion of aqueous standard or sample solution containing As in the range of 0.015–0.650 ng mL^{-1} is passed through the nano-sorbent in a column at a flow rate of 4.0 mL min^{-1}. Afterwards, the retained analyte on the micro-column is stripped by 0.5 mL of 3.0 mol L^{-1} NaOH solution at an elution rate of 1.0 mL min^{-1}. Then, 20 μL of the resulting solution and 10 μL of $Pd(NO_3)_2$ (0.25% (m/v)) as a chemical modifier are directly injected into the graphite tube and submitted to the heating program as shown in Table 1. A blank is prepared following the same procedure as described above, and then it is measured parallel to the samples and calibration solutions.

3. Results and discussion

3.1. *Optimization of the ETAAS conditions*

The ETAAS is an efficient technique for the determination of As, because the matrix can be eliminated at least in part during the gradual increase in temperature prior to the atomization of the analyte. As is one of the relatively volatile elements, so a certain loss of As may occur during pyrolysis stage. To reduce matrix interferences and to increase accuracy, the use of a chemical modifier has become indispensable for the stabilization of volatile

Table 1
Instrumental parameters and temperature program for arsenic determination.

Spectrometer parameter	
Wavelength (nm)	193.7
Lamp current (mA)	6
Spectral bandpass (nm)	0.4
Integration time (s)	3
Sample volume (μL)	20
Measurement mode	Peak area

Graphite furnace heating program

Step	Temperature (°C)	Time (s)		Argon gas flow (mL min^{-1})
		Ramp	Hold	
Drying	110	10	15	450
Pyrolysis	900	10	20	450
Atomization	2300	0	3	0
Cleaning	2400	1	3	450

elements during the pretreatment step [7]. Palladium nitrate is highly recommended and widely used as a modifier in As determination using ETAAS [5–7]. For this reason, it is chosen as a chemical modifier, and its amount is also investigated. Based on the obtained results, addition of 0.25% (m/v) palladium nitrate solution is sufficient to get a good sensitivity without increasing the pyrolysis temperature. Since for portions more than 10 μL the signals are not further improved, the palladium modifier injection volume is chosen as 10 μL.

The pyrolysis and atomization temperature should be optimized to obtain the maximum analytical signals. For this purpose, the pyrolysis temperature and atomization temperature is investigated in the range of 400–1100 °C and 1600–2500 °C, respectively, and their curves are shown in Fig. 3. As it can be seen, in the presence of the chemical modifier, the maximum absorbance is achieved when the pyrolysis temperature is close to 900 °C. Thus, a pyrolysis temperature of 900 °C is selected as optimum and the effect of the atomization temperature in the range of 1600–2500 °C on analytical signal of As is also studied. Based on the experimental results, shown in Fig. 3, the maximum signal is obtained at about 2300 °C. So, the atomization temperature of 2300 °C is selected for the further experiments.

3.2. *Optimization of SPE conditions*

To obtain the most suitable data from the presented preconcentration system, the effect of different parameters such as amount of LDH, pH of sample solution, sample loading flow rate, type and concentration of eluent, and sample volume on the retention efficiency is investigated by varying a parameter while the others are kept constant. A 0.2 ng mL^{-1} As solution is used for all the measurements, and in the optimization procedure, the limits marked on the figures are obtained from three independent experiments that repeated under the same conditions.

3.2.1. *Effect of pH*

The influence of pH on the retention of As(III) and As(V) on nano-sorbent in SPE column is investigated in the pH range of 4.0–12.0. The pH adjustment is performed with minimum volume of 0.01 mol L^{-1} HNO_3 and/or NaOH. It is obvious that at pH values lower than 4 the uptake capacity of the LDH is low owing to dissolution of the layered materials in strong acidic media. The results show that the retentions of both As(III) and As(V) on the LDH nano-particles are not affected by pH and recovery value is almost constant in the wide pH range. Accordingly, there is no need to adjust the pH in the studied real samples i.e., natural water samples because the initial pH values of the analyzed samples are between 5.8 and 6.5. On the other hand, speciation of As(III) and As(V) by pH variation using the presented SPE procedure is not practically possible.

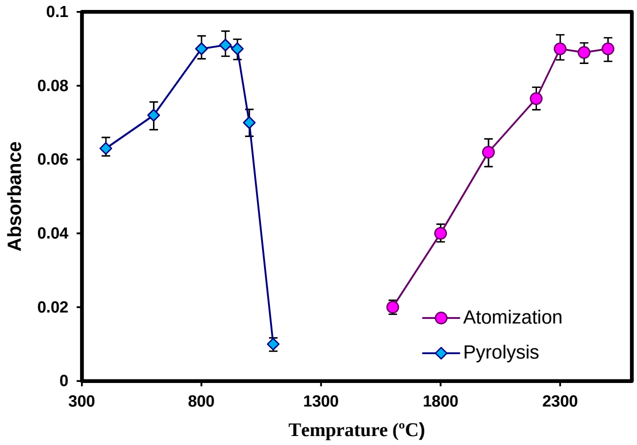

Fig. 3. Pyrolysis curve (left) and atomization curve (right) for the solid phase extraction of 0.2 ng mL^{-1} As.

3.2.2. *Effect of flow rate of sample loading*

The influence of As retention on nanometer-sized sorbent is investigated by passing sample solution through the micro-column at flow rate between 0.5 and 6.0 mL min^{-1}. No obvious difference in the retention of the analyte is observed when the sample flow rate varied up to 4.0 mL min^{-1}. However, at flow rates higher than 4.0 mL min^{-1}, the recovery of As is reduced (Fig. 4). In order to achieve high frequency of analysis, a flow rate of 4.0 mL min^{-1} is consequently chosen for all subsequent experiments.

3.2.3. *Optimization of elution conditions*

The nature and volume of the solution to be used for the elution stage are important to achieve the highest pre-concentration factor. For this reason, stripping of the retained As from the sorbent packed cartridge is studied using different eluents such as NaOH, $NaBH_4$, NaCl and Na_2CO_3. The results demonstrate that the stripping ability of NaOH is the best, therefore, it is selected for As elution. For investigation of eluent concentration, the elution of retained analyte from the column is also studied in the range of 0.5–4.0 mol L^{-1} of NaOH. As it can be seen in Fig. 5, the retained As could be completely

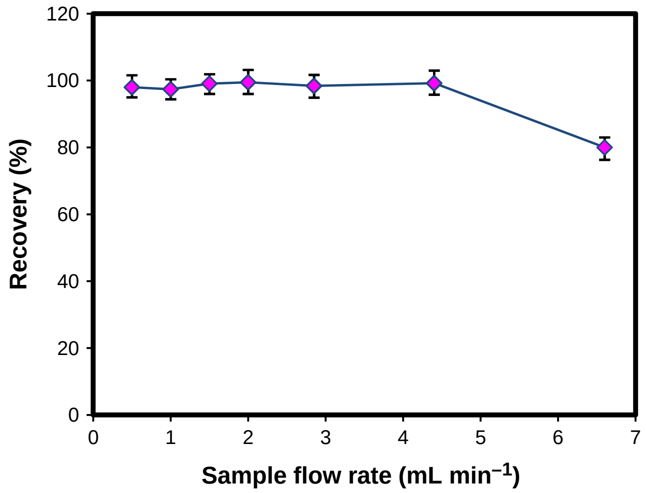

Fig. 4. Effect of sample loading flow rate upon the retention of As on the Mg–Al–Fe (NO_3^-) LDH nano-particles.

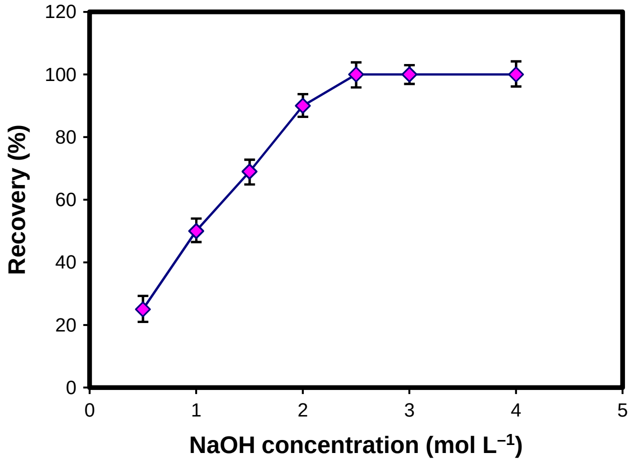

Fig. 5. Effect of NaOH concentration on the elution of retained As from the Mg–Al–Fe(NO_3^-) LDH nano-sorbent.

eluted by NaOH solution in concentration higher than 2.5 mol L^{-1} at an elution rate of 1.0 mL min^{-1}. Thus, the concentration of 3.0 mol L^{-1} NaOH solution is selected as the optimum. By using 3.0 mol L^{-1} NaOH as eluent, the effect of eluent volume on the recovery of As is studied with eluent volume varying from 0.5 to 2.0 mL. It is found that 0.5 mL of 3.0 mol L^{-1} NaOH is sufficient for complete elution of As from the column. Therefore, 0.5 mL of 3.0 mol L^{-1} NaOH is used as eluent in the following experiments.

3.2.4. Amount of sorbent, breakthrough volume and sorption capacity

The effect of amount of nano-sorbent packed in the micro-column is evaluated by changing the packing amounts from 100 to 400 mg. It is found that the extraction rate of the analyte increases by increasing the nano-sorbent amount up to 200 mg and remains constant at higher amounts. Therefore, in the presented procedure, 200 mg of nano-sorbent is recommended.

In order to explore the possibility of enriching low concentrations of As from large volumes and to get higher enrichment factor, the effect of sample volume on the recovery of As is investigated. For this purpose, 10.0, 25.0, 50.0, 100.0, 150.0 and 200.0 mL of sample solutions containing 0.03 μg As are passed through the column, packed with 200 mg nano-sorbent, at a flow rate of 4.0 mL min^{-1}. The recovery of As is found to be quantitative when sample volume is chosen between 10.0 and 150.0 mL. Above 150.0 mL, the recovery decreases for the analyte. Consequently, by analyzing 0.5 mL of the final solution after the pre-concentration of 150.0 mL of sample solution, an enrichment factor is found as 300.

To determine the sorption capacity, 200 mg of the nano-sorbent is added to 50 mL of solution containing 50.0 mg L^{-1} of the analyte and sonicated for 30 min and then the mixture is centrifuged. Loaded As in the LDH nano-particles is stripped with 5 mL of 3.0 mol L^{-1} NaOH and concentration of the analyte is then determined by ETAAS after appropriate dilution. As a result, capacity of the nano-sorbent for As is found to be 8.7 mg g^{-1}.

3.2.5. Retention/desorption mechanism and regeneration of the sorbent

LDHs consist of positively charged hydrotalcite-like layer of metal hydroxide and the interlayer region typically occupied by anionic species and water molecules. The interlayer bonding is relatively weak and, consequently, various anions could be introduced from aqueous solution into the hydroxide interlayer via three mechanisms: (i) adsorption on external surface, (ii) intercalation by anion exchange, and (iii) intercalation by reconstruction of calcined products [40]. In this work, comparisons of XRD patterns of the LDH materials' before and after analyte uptake reveal that both surface physical adsorption and ion-exchange with the interlayer nitrate ions may take place during the analyte uptake. Because, the intensity of the 0 0 3 diffraction peak is decreased on and shifted to the lower 2θ due to interlayer nitrate ions exchange with the analyte. The presence of the 1 1 0 diffraction peak at the same position before and after analyte uptake indicates that there is no change in basic LDH structure due to analyte exchange. Various alkaline solutions and salt solutions or the mixture of these solutions have been successfully used to desorb and regenerate oxyanion-loaded LDHs [40]. Based on the obtained results (Section 3.2.3), the retained As could be completely eluted by NaOH solution.

The stability and regeneration potential of the micro-column packed with nano-sorbent are investigated. The column can be reused after regeneration with 3 mL of 3.0 mol L^{-1} NaOH solution and 5 mL deionized water, respectively. It is found that column is stable in operation process, and enables more than 200 loading and elution cycles to be performed without the loss of analytical performance.

3.3. Study of interferences

The interference of other coexisting ions on the pre-concentration and determination of As are examined under the optimal conditions described above. An ion is considered to interfere when its presence produced a variation of more than ±5% in the analytical signal of the sample. In these experiments, different amounts of some interfering ions are added to the test solutions containing 0.2 ng mL^{-1} of As and then, followed according to general procedure. The results (see Table 2) reveal that the developed method is fairly free from the interference resulting from the coexisting ions commonly found in natural water samples. From the experiment results obtained, it could be concluded that the sorbent has a good selectivity towards the target analyte.

3.4. Analytical figures of merit

In the optimized conditions given in Table 3, the analytical performance of the method for As determination is evaluated. The calibration function is $A=0.294C+0.032$, where A and C correspond the integrated absorbance and concentration of As in ng mL^{-1}, respectively.

3.5. Validity of the method and application to real samples

The nano-sorbent ability for retention of both forms of inorganic As is studied. For this purpose, synthetic solutions containing different amounts of As(III) and/or As(V) are prepared and then followed according to general procedure. The results are given in

Table 2
Tolerance limits of coexisting ions in the determination of 0.2 ng mL^{-1} of As.

Coexisting ions	Interferent to analyte ratio
Na^+, K^+, Ca^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Pb(II), Sn(II), Bi(III), I^-	1000:1
F^-, Cl^-, Br^-, NO_3^-	500:1
BrO_3^-, $H_2PO_4^-$, CH_3COO^-, CO_3^{2-}, HPO_4^{2-}, SO_4^{2-}, Te(IV)	250:1
Se(IV)	100:1

Table 3
Optimum extraction conditions and analytical performance of the presented method for As determination.

Experimental conditions	
pH	4–12
Amount of sorbent (mg)	200
Eluent concentration (mol L^{-1} NaOH)	3
Eluent volume (mL)	0.5
Sample flow rate (mL min^{-1})	4
Maximum sample volume (mL)	150
Analytical parameters	
Linear range (ng mL^{-1})	0.015–0.650
Intercept	0.032
Slope	0.294
Detection limit (ng mL^{-1})[a]	0.0046
Correlation coefficient	0.9979
Relative standard deviation (RSD%) ($n=6$)[b]	3.9 (0.2)
Enrichment factor[c]	300

[a] Calculated as three times the standard deviation of the blank signal divided by the calibration curve slope.

[b] Value in parentheses is the As concentration (ng mL^{-1}) for which the RSD was obtained.

[c] Enrichment factor calculated as the ratio between the volume of the initial aqueous solution and the final elution volume.

Table 4
Determination of total As in different synthetic solutions containing As(III) and/or As(V).

Added (ng mL^{-1})		Found[a] (ng mL^{-1})	Recovery (%)
As (III)	As (V)	Total As	Total As
0	0.60	0.59 ± 0.03	98.3
0.20	0.40	0.62 ± 0.05	103.3
0.30	0.30	0.60 ± 0.05	100.0
0.40	0.20	0.58 ± 0.04	96.6
0.60	0	0.60 ± 0.03	100.0

[a] Mean of three experiments ± standard deviation.

Table 5
Determination of total arsenic in water samples (results of recoveries of spiked samples and certified reference material analysis).

Sample	Added arsenic (ng mL^{-1})	Found arsenic (ng mL^{-1})[a]	Recovery (%)[b]
Tap water[c]	–	0.18 ± 0.02	–
	0.3	0.49 ± 0.03	103.3
	0.5	0.67 ± 0.05	98.0
Rain water[d]	–	0.26 ± 0.04	–
	0.3	0.55 ± 0.05	96.6
	0.5	0.76 ± 0.08	100.0
Well water[e]	–	2.4 ± 0.21	–
	3.0	5.4 ± 0.23	100.0
	5.0	7.3 ± 0.45	98.0
Spring water[f]	–	1.8 ± 0.11	–
	3.0	4.9 ± 0.24	103.3
	5.0	6.8 ± 0.36	100.0
NIST SRM 1643e	Certified value (ng mL^{-1})	Assayed values[a] (ng mL^{-1})	Relative error (%)
	58.98 ± 0.70	60.18 ± 0.82	+2.03

[a] Mean of three experiments ± standard deviation.
[b] Recovery (%)=[(found-base)/added] × 100.
[c] From drinking water system of Tabriz, Iran.
[d] Collected at Tabriz city, Iran (April 6, 2012).
[e] Obtained from local source, Tabriz, Iran.
[f] From spring water of Ligvan village, Iran.

Table 4. As it can be seen, the recovery values between 96.6% and 103.3% are obtained concerning the total determination of As in these solutions. As a result, Mg–Al–Fe(NO_3^-) LDH nano-particles could simultaneously retain the As(III) and As(V) oxyanions, and presented SPE-ETAAS method could be applied for determination of total As in aqueous solutions.

To demonstrate the performance of the presented procedure, the method is applied to determine ultra-trace amounts of As in several water samples and the analytical results along with the recoveries for the spiked samples are given in Table 5. To establish the validity of the presented procedure, the method is also applied to the determination of As in a standard reference material. The results show that the presented procedure is reliable for the determination of total As in water samples.

3.6. *Comparison of the presented method with other SPE procedures*

Analytical performance of the presented method is compared with those of previous methods (see Table 6). As it can be seen, the limit of detection and sorption capacity of the presented method are comparable or better than other procedures, and the enrichment factor is significantly higher than others. This method has some advantages such as; lower detection limit, higher pre-concentration factor, simplicity and low cost. Thus, the presented method is versatile for ultra-trace As analysis.

4. Conclusions

A novel nano-sorbent [Mg–Al–Fe(NO_3^-) LDH] is synthesized, characterized and applied to the separation and pre-concentration of As. This newly prepared sorbent is chemically stable with good uptake capacity, low cost and environment-friendly. The combination of this SPE system with a sensitive analytical technique such as ETAAS results in a high sensitive and reliable procedure for the determination of ultra-trace amount of As. Utilizing the presented method, As can be determined in aqueous samples such as tap water, rain water, spring water and well water. The proposed method possesses some advantages such as; simplicity, high kinetic sorption on the target analyte, good precision and excellent accuracy. The presented method has a comparable limit of detection

Table 6
Comparison of the analytical performance of the present method with other SPE methods for As determination.

Sorbent	Detection method	PF	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Sorption Capacity (mg g^{-1})	Sample throughput (h^{-1})[a]	Reference
Cigarette fiber	HGAFS	25.6	0.0074	0.05–2.0	–	11.6	10
Carbon nanofiber	ICP–MS	33.3	0.24	–	2.0	–	11
Modified alkyl silica	ICP–OES	26.7	0.15	0.5–1000	1.7	24	12
Modified Sepabeads SP 70 resin	HGAAS	36	0.013	1–25	7.3	–	21
C_{18} and anion exchange resin	HGAFS	8.2	0.03	0.1–1.5	–	12	22
Modified mesoporous TiO_2	ICP–OES	50	0.1	–	1.9	10	23
Immobilized nanometer TiO_2	GFAAS	50	0.024	Up to 200	4.2	–	24
PTFE turnings	HGAAS	10	0.02	0.04–5	–	25	25
Modified mesoporous silica	ICP–OES	100	0.05	0.3–30	10.3	–	26
Modified activated carbon	ETAAS	50	0.05	–	7.3	–	27
SWCNTs	HGAFS	25.4	0.0043	0.01–2	–	–	28
CNTs	ETAAS	250	0.02	0.03–0.6	–	–	29
MWCNTs	HGAFS	62.5	0.002	0–2	–	–	30
$Y(OH)_3$ coated cellulose fiber	HGAFS	16.4	0.017	0.05–2.0	–	–	32
PHEMA	GFAAS	86	0.010	–	4.1	–	41
Mg–Al–Fe(NO_3 -) LDH	ETAAS	300	0.0046	0.015–0.650	8.7	–	This work

PF: preconcentration factor; SWCNTs: single-walled carbon nanotubes; MWCNTs: multi-walled carbon nanotubes; PHEMA: poly (hydroxyethylmethacrylate); HGAFS: hydride generation atomic fluorescence spectrometry; ICP–MS: inductively coupled plasma-mass spectrometry; ICP–OES: inductively coupled plasma–optical emission spectrometry; GFAAS: graphite furnace atomic absorption spectrometry; HGAAS: hydride generation atomic absorption spectrometry; ETAAS: electrothermal atomic absorption spectrometry.

[a] Only for on-line systems.

and higher enrichment factor with those reported in the literature, and it could be further investigated for the determination of ultra-trace amount of As in various samples with complicated matrix such as biological samples in the future.

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