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Solid phase extraction of arsenic on modified MWCNT/Fe_3O_4 magnetic hybrid nanoparticles from copper ores samples with ETAAS determination

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ABSTRACT

A simple procedure for the synthesis of magnetic hybrid nanoparticles (MHNP) was developed by combining multi-walled carbon nanotubes modified by microwave energy and magnetic iron oxide nanoparticles. MHNP were introduced as sorbents in a magnetic solid phase extraction methodology for the total Arsenic determination in copper ore samples. Arsenic is penalized contaminant element in copper ores. Arsenic was determined by electrothermal atomic absorption spectrometry with a reduced temperature program. Arsenic adsorption corresponded to 96 - 104%, at ug g^{-1} levels. After a variable screening stage using a Placket-Burman (PBD) experimental design, the developed methodology was optimized using a Box-Behnken experimental design. Based on the optimal working parameters, a detection limit of 30 ng L^{-1} was reached, with a relative standard deviation of 7.1% and a preconcentration factor (PF) of 50. The Certified Geochem Base Metal Reference Material Product Code GBM900-10 was analyzed for the validation stage.

1. Introduction

Arsenic is a metalloid element widely distributed in nature. Its main species in soil and water are arsenite [As (III)] and arsenate [As(V)]. As (III) is more toxic and often more mobile than As (V). However in the environment As (III) is oxidyzed under aerobic conditions [1]. There are hundreds of minerals discovered to date that contain arsenic. The most common being arsenopyrite (FeAsS), enargite (Cu_3AsS_4), tenantite ($Cu_{12}As_4S_{13}$), realgar (As_4S_4), and orpiment (As_2S_3). Enargite is mainly found in copper ores [2]. Although its As contribution is low, it becomes significant when it accumulates in the final Cu concentrate during extraction processes [3]. This affects the market for copper concentrates, since the costs of smelting and refining operations increases [4,5]. Arsenic is harmful to the environment and human health when it is present in concentrations higher than those found naturally. It tends to be highly volatile in thermal processes at risk of being emitted into the atmosphere during smelting [6]. Human exposure to arsenic can damage the lungs, kidneys, bladder and skin [7].

Since the maximum limit of arsenic present in copper cathodes is 0.005% [3], different techniques for arsenic removal are proposed, including oxidation, sedimentation, coagulation, ion exchange, electrodialysis system and reverse osmosis [8–10]. However, the effectiveness, costs and sludge generation of such approaches are not entirely optimal. The determination of arsenic concentration in the copper ores is of great importance, because it establishes the quality of the ore to be extracted, affecting investment decisions related to ore treatments. Among the different methodologies developed for As determination, electrothermal atomic absorption spectrometry (ETAAS) is one of the simplest and least expensive, with good selectivity and sensitivity [11–14].

For the determination of As in copper ore samples, the combination of preconcentration/separation technology is necessary since the matrix is complex and the content of As is below the limit of detection of ETAAS for As. Nowadays, dispersive solid phase extraction (DSPE) technology is considered an effective enrichment method [15–17]. The adsorbent selected in DSPE is a determining factor for preconcentration of trace metals. Nanostructured materials have significantly contributed to this technology, since they have improved advantages compared to conventional powder materials, such as a higher specific surface area, more active sites, easy functionalization and uniform dispersion [18,19].

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Among the different known nanostructured materials, carbon nanotubes (CNTs) have been the most widely used as a sorption substrate in the preconcentration of metals in analytical chemistry due to their adsorbent properties [20–22]. It should be noted that crude CNTs have drawbacks for the adsorption of metals in an aqueous medium because they are insoluble and hardly dispersible due to strong Van Der Waals forces. For this reason, surface treatment like oxidation and hybridization, plays a determining role when implementing them as sorbents in order to improve their dispersibility, metal adsorption and elution [23,24].

Although only milligrams of CNTs are needed for extraction, efficient recovery of these solid nanomaterials from the liquid phase can be challenging. Magnetic materials combined with DSPE, or so called magnetic solid phase extraction (MSPE), has proven to be a fast, simple and effective way of adsorbent recovery [25–27]. This methodology is based on the use of a magnetic or magnetically modified sorbents, which allows its dispersion in large sample volumes and its subsequent recovery with an external magnetic field. In this sense, the use of superparamagnetic magnetite nanoparticles (Fe_3O_4) stands out [28–30]. They have good biocompatibility, strong superparamagnetic properties, catalytic activity, ecology, low toxicity and low cost. Nevertheless, it has been reported that they present aggregation problems between particles, poor cyclic stability, low selectivity and extraction capacity that limits their direct application [31,32].

In recent years, different functionalization strategies have been carried out to modify Fe_3O_4 nanoparticles to improve their adsorption properties. One strategy is the combination with carbon-based nanomaterials, like graphene and CNTs, to synthesized magnetic hybrid materials [32–34]. Previous works investigate the synthesis and application of hybrid materials in SPE systems [23,35–38]. Hybrid materials advantageously combine properties of two types of chemical compounds, organic and inorganic, reaching a synergistic effect of both nanoparticles that cannot be achieved by acting alone. Various lines of synthesis of hybrid materials have been investigated in the last decade, even in the removal of arsenic from wastewater. However, they had not been applied to the development of analytical methods for As determination in copper minerals samples. In the same way, few studies describe As recovery from hybrid nanomaterials and reuse. This fact can be explained considering difficulties during analyte elution and sorbent deterioration [39–42].

In the present work, a novel and simple method was developed to synthesize magnetic hybrid nanoparticles (MHNP) of modified multiwall carbon nanotubes (MCNT) and magnetite (Fe_3O_4) hybridization. For the first time, CNTs were modified by thermal stress under microwave radiation, significantly reducing operating times compared to other methods where a different energy source is applied. The synthesized MHNP were first implemented in the extraction and preconcentration of arsenic in digested samples of copper ores by MSPE, with its subsequent elution and determination by ETAAS, with a reduced temperature program. The concentration of As in the copper ore defines the As removal treatment in mining, prior to the smelting stage.

2. Experimental

2.1. Reagents and chemicals

All chemicals and reagents used in experiments were of analytical grade unless otherwise noted. The MWCNTs were obtained from Sigma-Aldrich (St. Louis, USA). The solutions used in arsenic determination were prepared daily from a 1000 mg L^{-1} stock solution (Sigma Aldrich, ICP MS grade) diluted in ultra-pure water. Thus, for the optimization stage, dilutions of 100 ng L^{-1} were used.

2.2. Apparatus

To determine the concentration of arsenic in the eluate, an atomic absorption spectrometer model AA-7000 from Shimadzu (Tokyo, Japan) was used, equipped with a background correction system that uses a continuous source, a GFA-EX7 electrothermal atomizer and an ASC-7000 autosampler. In all experiments, L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used. Instrumental and operational conditions of ETAAS are listed in Table S1 (Appendix).

The study of the morphology and characterization of the hybrid nanoparticles was carried out using a field emission scanning electron microscope (FEI Quanta 200). The crystal structure of the modified MWCNT/Fe_3O_4 prepared material was investigated in an X-ray diffractometer Shimadzu with a geometry of the Bragg-Brentano type (Θ/2Θ). Cu Kα radiation (λ=1.540600 Å) and graphite secondary monochromator were used, operating at 15 mA and 35 kV in the high voltage source.

Ultrasound-assisted microextraction (US) was carried out using a KQ-200 VDE ultrasonic device with frequency and temperature controller (Kunshan Ultrasonic Instrument Co., Ltd., China). pH was measured with a Sartorius model PT-10 pH meter.

A Whirlpool model JQ280IX (Guangdong, China) domestic microwave oven with a frequency of 2450 MHz and operating at a maximum output power of 1500W was used to modify commercial multiwall carbon nanotubes.

To measure the temperature of carbon nanotubes after microwave heating, a GIS 1000C Professional Bosch thermal detector (-40°C to 1000°C) was used.

The series of experiments for the evaluation of the optimization was carried out with the Design-Expert® software version 7.0.

2.3. Samples

The samples of copper ores were obtained by the Geology Department of the Mining Research Institute, National University of San Juan from the Los Andes Mountain Range area of San Juan province, Argentina.Prior to analysis, ore samples were treated in various stages: crushing, roll mill grinding, quartering, and charter pulverizing. Then, 500 mg were accurately weighed and transferred to a 250 mL beaker, followed by the addition of 2.5 mL HNO_3 and 1 mL H_2SO_4. The containers were then brought to a hot plate (180°C) until sequencing. The beakers were then allowed to cool to room temperature and the residue was dissolved and brought to a final volume of 50 mL with milli-Q water. Samples were stored in PVC containers until analysis. For the validation stage, a certified reference material, GBM900-10, Murchison Pb-Zn-Cu Ore was used, with a certified As concentration value of 332 ±13.1 μg g^{-1}.

2.4. Nanosorbent synthesis

The synthesis of the nanosorbent was carried out in stages, MWCNT modification, synthesis of magnetic iron oxide nanoparticles and formation of hybrid magnetic nanoparticles by wet immersion.

2.4.1. Microwave thermal stress modification of multiwalled carbon nanotube

A modification procedure of MWCNT by microwave thermal stress was performed. Commercial MWCNT were placed in an alumina cup then this was located in the center of the plate of the domestic microwave and was brought to 950 W for 15 s; in this process a temperature of 400 °C was reached, which was measured with the thermal detector. Then it was cooled at room temperature for approximately 5 min. This procedure was repeated 3 times. Then, they were preserved in a glass container until use.

2.4.2. Synthesis of Fe_3O_4 magnetic nanoparticles

For the synthesis of magnetic nanoparticles (MNPT), a modified method was implemented [43]. In a first step, 50 mL of precursor solutions were prepared. Solution 1: $FeCl_3.6H_2O$ 1.87 M; Solution 2:

$FeSO_4.7H_2O$ 1.71 M; Solution 3: NaOH 12.81 M. The collected solutions were sonicated for 15 min. Solutions 1 and 2 were placed in a 250 mL beaker. The mixture was then placed in a thermostatic bath at 50°C under argon atmosphere. Solution 3 was added to the mixture drop by drop, with a 200 μL micropipette, stirring with a glass rod until a reddish-brown color was observed on the vessel walls. At that time the entire content of solution 3 was added under vigorous stirring. Upon adding all the sodium hydroxide solution, stirring continued for 10 min. Washing was carried out with Milli-Q water and a 0.1 M HCl solution (the latter was used to adjust the pH of the solution, until neutral pH was reached).

2.4.3. Synthesis of MHNP by encapsulation of MNPT in MCNT channels

The wet impregnation technique was performed for MHNP synthesis. A mixture of 400 mg of MNPT with 100 mL of tetrahydrofuran (THF) was prepared. It was placed in a 250 mL beaker together with 300 mg of MCNT and mixed. Then it was sonicated for 1 h, at room temperature and covering the container, to avoid solvent losses. At this stage, the MNPT are encapsulated in the MCNT. Then they were left in a fume hood at room temperature for 12 h to vaporize the solvent. The mixture was then placed in an oven at 70°C for 5 h. Finally, the nanoparticles were calcined in a muffle at 250°C, where they were kept for 2 h. For conservation, the MHNP obtained were pulverized in a mortar and stored in a glass bottle until use.

2.5. Preconcentration procedure

For the preconcentration step, 10 mg of MHNP were weighed and placed in a 15 mL metal-free polypropylene tube with a screw cap. Then, 12 mL of the sample digest were added and capped. Ultrasound (US) was carried out for 60 s. Following this, the phases were separated by means of an external magnet, eliminating the supernatant.

For the elution step, 250 μL of 0.05% NaOH solution were added and vortexed for 60 s. The magnet was replaced and the eluate was recovered to be read by ETAAS.

The MHNP were washed with milli-Q water, using the magnet to keep them in the container after each wash. In this way, the nanoparticles were ready for the next test, being able to repeat up to 10 As preconcentration/elution cycles.

3. Results and discussion

3.1. Characterization of MHNP

The effectiveness of thermal stress to oxidize and modify MWCNT has been recently demonstrated [39]. In our proposal, a domestic microwave was used as an energy source, reducing the time of the procedure, modifying carbon nanotubes in a simpler and faster way (less than 30 min). This strategy presents a great advantage compared to conventional methods that use concentrated acids.

The use of THF as a solvent in wet impregnation methods has been highlighted in the synthesis of nanoparticles due to its surface tension. THF allows loading carbon nanotube channels with oxide iron nanoparticles with capillary force [44].

To study the chemical composition of the MHNP, the X-ray diffraction technique (XRD) was applied. In the diffractogram of Fig. S1, two predominant peaks are observed at angles 26, 60° and 43.40° corresponding to crystallographic planes (111) and (100), and a third peak of lesser intensity at angle 56.92° corresponding to plane (211), of the graphite structure (C). Card COD. 96-901-2706. On the other hand, the two peaks located at 35.70° and 63.10° for the (211) and (404) reflection planes respectively, can be attributed to magnetite (Fe3O4). Other less intense peaks for this compound are located at 30.60° (202), 43.50° (400), 54° (422) and 57°45 (511). Card COD. 96-900-2321. These results are consistent with the literature [40,41].

The MHNP morphology was investigated using SEM images (Fig. S2). It should be noted that the MHNP samples were placed on a carbon tape, but no type of bath or treatment was carried out to avoid altering its morphological characteristics, considering that it is not necessary since the composition of the sample allows a good electronic conductivity. Fig. S2A shows that the modified MWCNT/Fe_3O_4 nanomaterial has a filamentary structure, randomly oriented forming tangles, where the nanotube fibers are connected to each other. It is clearly observed the tubular structure of the microwave functionalized carbon nanotubes, with an average diameter of 13.64 nm (Fig. S2B). From the EDS spectrum in Fig. S2C and D, the presence of C, Fe and O in ratios of 23.28%, 24.18% and 51.86% respectively can be confirmed, which is consistent with an oxidized carbon base typical of functionalized nanotubes and decorated with Fe_3O_4 nanoparticles.

3.2. MSPE study

As a preliminary stage prior to the multivariate optimization, a series of studies were carried out in order to establish a general procedure framed in MSPE. Among the objectives of the work, low reagents consumption and reduction of analysis time were sought. These goals were achieved by synthesizing a magnetic hybrid material.

For the adsorption stage, the use of ultrasonic energy was evaluated compared to mechanical agitation for MHNP dispersion. Results showed an improved performance employing US energy compared to mechanical agitation. US energy presented a 20% increased in As adsorption compared to mechanical agitation. It was observed that a longer mechanical stirring time was required to achieve the results obtained with US energy. US energy favors mixing and dispersion of the sorbent in the sample through cavitation and sound flow; modifying mass transfer coefficients, improving adsorption times [45]. In contrast, for the elution stage, better results were obtained with mechanical agitation. The basic eluent under US energy attacks MHNP, affecting the latter ETAAS determination. Based on these results, the use of US was established in the analyte preconcentration stage and mechanical agitation for the elution stage.

In SPE methods, the elution stage is of great importance, this is reflected in the fact that the selection of a suitable eluent guarantees a total recovery of the analyte of interest and the desorbed sorbent can be perfectly recovered to its initial adsorption performance. There is scarce information in the literature on regeneration tests of carbon adsorbents used for arsenic removal [46,47], so it is speculated that most traditional adsorbents have low As desorption efficiency. In our work, different types of eluents were tested, the best results were obtained for As desorption with diluted NaOH solutions [48]. The MHNP showed a high desorption efficiency of 94% after 100 cycles.

SPE methods applied to ETAAS determinations have a significant advantage, since analytes are extracted from its matrix, the pyrolysis stage can be omitted from the temperature program implemented for atomization [23]. Consequently, a temperature program for ETAAS was studied, eliminating the pyrolysis stage, and no differences were observed in the As signal. In this way, the analysis time was reduced, modifying the temperature program of the graphite furnace, becoming attractive in view of the analytic frequency.

On the other hand, to study the distribution of As on the sorbent nanomaterial and its elemental composition, an EDX mapping analysis of MHNP was performed after As preconcentration. Fig. S3 shows a field image of the nanomaterial where the mapping of the elements of interest was performed. The results show how arsenic is well dispersed on the surface of the adsorbent, whose distribution is mainly similar to that of carbon, and to a lesser extent to that of iron. On the other hand, the distribution of oxygen is comparable to that of As, from which it can be inferred that arsenic is mainly adsorbed as oxoanion on the surface of carbon nanotubes by an electrostatic interaction or surface complexation [42,49].

Copper ores are complex samples with high Cu concentration, so a possible interference of this element and others on As adsorption on

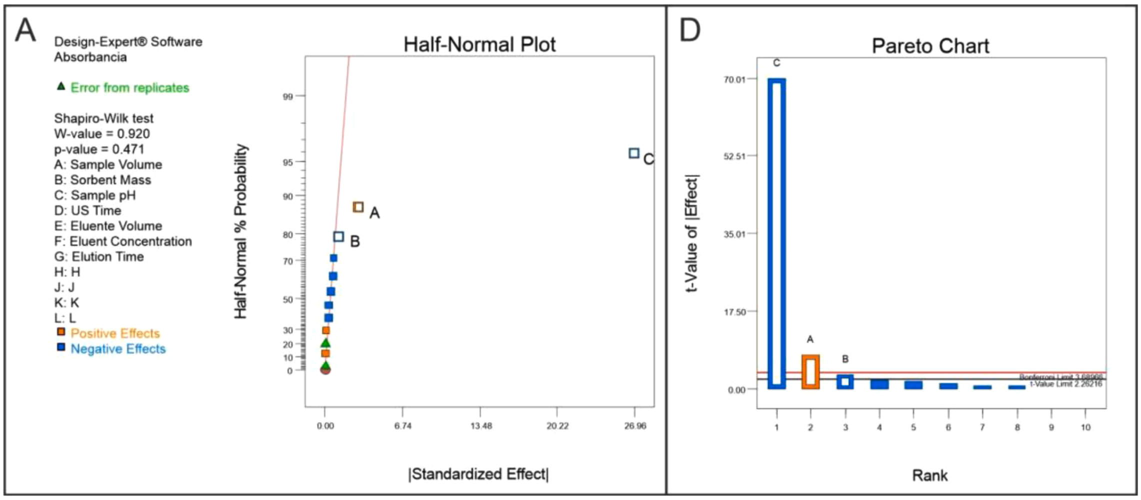

Fig. 1. A) Half-Normal graphs; B) Pareto graphs.

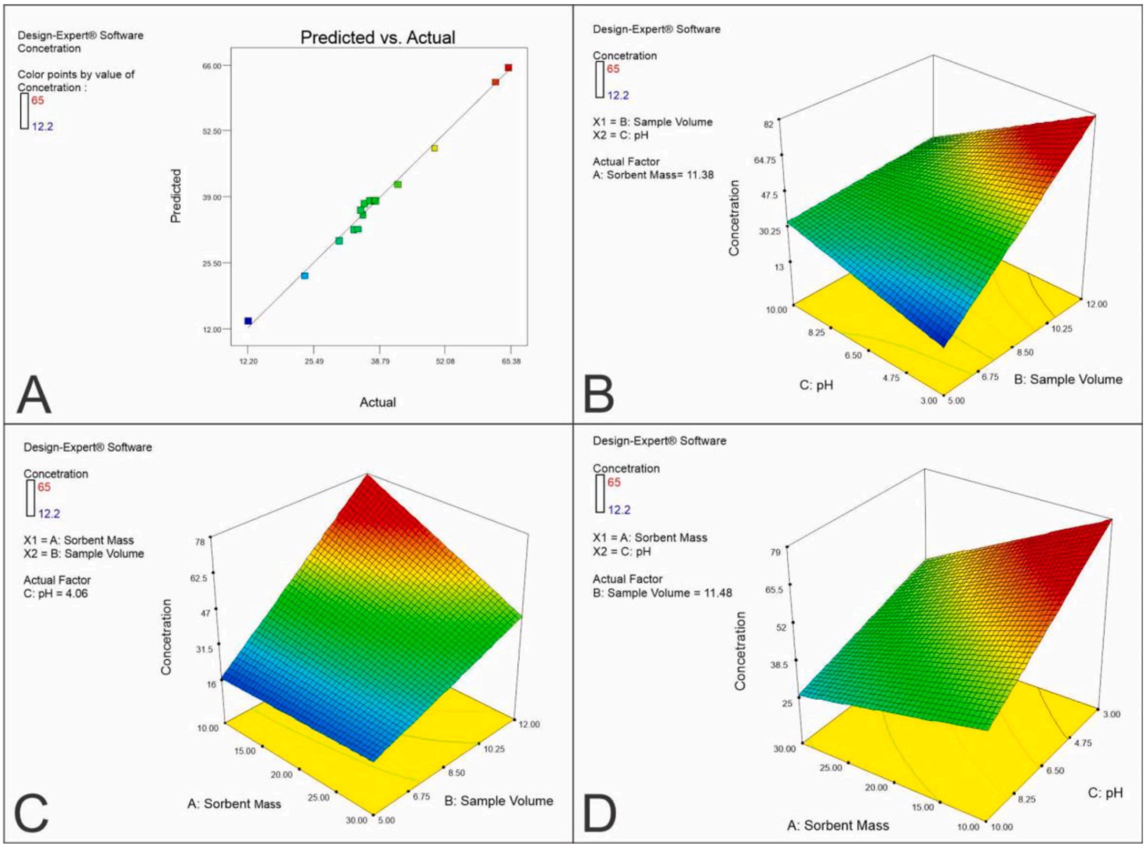

Fig. 2. A) Graph of predicted values versus experimental values; B, C, and D) Response surface graphs 3D for As concentration (ng L^{-1}) versus pH and sample volume, sorbent mass and sample volume, and sorbent mass and pH, respectively.

HNPs was evaluated. To this end a multielement solution of As, Bi, B, Ca, Fe, K, Mg, Na, Zn, Ni, P, Pb, Sn, Sr, Ti, Tl, V, Al, Ba, Cd, Co, Cr, Ga, In, Li, Mn and Mo of 5 μg L^{-1} was prepared. In addition a Cu solution of 5 % (w v^{-1}) was also evaluated considering Cu concentration after microwave assisted digestion. Once treated by the proposed MSPE method, the eluate was analyzed by ETAAS for As determination. It was found that As recoveries were quantitative at the interferences concentration levels studied.

3.3. *Multivariate optimization*

In the proposed procedure, there are a series of factors influencing the performance of As preconcentration. In order to identify which of these factors are significant, a screening stage was first carried out, implementing a multivariate experimental design Placket-Burman (PBD). After that, a Box-Behnken design (BBD) was used to evaluate the importance of the significant variables and to investigate the interactions between them [23].

Table 1
Comparison of methodologies for As analysis.

Volume of sample digest solution	Extraction	Sorbent	Sample conditioning	Analysis time	PF	LOD	RSD (%)	Method	Reference
15 mL	SPE	CNT	Ammonium iodide / APDC	< 35 min	75	30 ng L^{-1}	3.1	ETAAS	[53]
200 mL	MSPE	$Fe_3O_4@SiO_2/GO-NH_2$	$HNO_3/NH_3{\cdot}H_2O$	< 35 min	392	1.02 ng L^{-1}	7.9	ETAAS	[32]
50 mL	MSPE	SMNPs-APTES	$HNO_3/NH_3{\cdot}H_2O$	< 60 min	25	10.5 ng L^{-1}	2.5	ICP-MS	[25]
1 mL	MSPE	α-amilasa-Fe_3O_4/ MWCNTs	Buffer solution	< 15 min	-	14,3 μg kg^{-1}	7.5	ICP-MS	[54]
12 mL	MSPE	NPHM	It does not require	< 15 min	50	30 ng L^{-1}	7.1	ETAAS	This work

APDC: ammonium pyrrolidinedithiocarbamate
$Fe_3O_4@SiO_2/GO-NH_2$: magnetic graphene oxide (GO) chemically modified by cysteamine hydrochloride
SMNPs-MPTMS and SMNPs-APTES: Mercapto- and amino-functionalized magnetic nanoparticles, $Fe_3O_4@SiO_2@MPTMS$ and $Fe_3O_4@SiO_2@APTES$

3.3.1. *Selection of significant factors using Plackett-Burman design*

The studied variables were: sample volume, sorbent mass, sample pH, ultrasound time, eluent volume, eluent concentration and elution time. The response was As concentration (Table S2, Appendix). In this design, 15 experiments with 3 central points were carried out and the level of significance of each factor was statistically evaluated from the Half-Normal and Pareto graphs (Fig. 1 A and B, respectively). This indicated that the following variables significantly affect the system: sample volume, sorbent mass, and sample pH. Regarding the factors that were less significant, for the optimization stage, their minimum values were set considering reduced time of analysis and reagents volume.

3.3.2. *Optimization of significant variables*

In order to obtain the maximum information from a minimum number of experiments, an experimental Box-Behnken Design (BBD) was implemented. The experiments to be carried out were 15, with 3 central points of three factors at three levels, A: sample volume (5, 8.5, 12 mL), B: sorbent mass (10, 20 and 30 mg) and C: sample pH (3, 6.5 and 10). The factors that remained fixed were maintained at the following values: ultrasound time, 60 s; eluent volume, 0.250 mL; eluent concentration, 0.05% NaOH; elution time, 1 min.

The data obtained was fitted to a 2FI vs Linear model with regression analysis. From the analysis of variance (ANOVA) in Table S3 (Appendix), it can be corroborated from the F-value of 179.97 that the model is significant; with an R-squared and an adjusted R-squared of 0.992% and 0.987%, respectively. In this way, the response surface (Fig. 2) shows that the optimal working conditions were found for a sample volume of 12 mL, sorbent mass of 10 mg and a sample pH of 3.

The effects of the interactions of the variables with each other in the proposed working conditions can be visualized in response surfaces graphs. Fig. 2 B shows the response surface of the sorbent mass and sample volume in the As concentration, with a fixed pH at an optimal value. At higher sample volumes, the adsorbed As increases. In our work, the volume was limited to a maximum of 12 mL, since it allows low reagents consumption during the sample treatment, and it is compatible with the As concentration levels in the sample. Regarding the mass of sorbent, it could be interpreted that with a lower amount of sorbent, it is possible to obtain a better dispersion in the aqueous medium, avoiding MHNP agglomeration, increasing the contact surface [50].

Fig. 2 C and D shows the calculated response surface based on the interaction between the sample pH compared to sample volume and sorbent mass respectively. These graphs show the importance of pH in As recovery. As pH decreases, arsenic recovery significantly increases. The optimal pH is lower than 5. Considering that once the ore sample has been treated and digested, As is found in solution in its oxidized form. At this pH range, the predominant As (V) species in solution is H_2AsO^{4-}, while H_3AsO_4 can be present at strongly acidic pH values. These results are in agreement with others reported in the literature, where it was stated that at low pH values As adsorption increases [51]. It has been reported that the adsorption mechanism of As with carbon- and iron- based sorbents at acidic pH is carried out by electrostatic interactions and surface complexation [32,52].

3.4. *Analytical characteristics of the proposed system*

The decrease in the use of chemical reagents is a global trend in analytical chemistry motivating the development of methodologies based on solid-phase extraction and preconcentration processes involving high-performance selective sorbents. The main advantages of the proposed methodology are reduced time of analysis (less than 15 min per sample), non-use of reagents to condition the sample after digestion, lower sample consumption, quantitative adsorption of As on MHNP in samples with high concentration of Cu (> 0.4%), that consequently impacts in a lower use of reagents for sample digestion. The MHNP could be reused for a minimum of 10 analysis cycles without loss of adsorption efficiency; this is directly linked to the low concentration of the eluent used (NaOH 0.05% v v^{-1}), which prevents nanoparticle deterioration.

Regarding the time of analysis, considering each stage from the arrival of the sample, it consisted in 30 min for sample preparation, 120 min for sample treatment and 12.5 min to apply the proposed MSPE procedure. It should be clarified that the time of analysis for the MSPE procedure was calculated considering the following stages: addition of NPHM and the sample (1 min), US time (1 min), separation of the sorbent by magnetization (2 min), addition of eluant and agitation by vortex (3 min), phase separation by magnetization and collection of the eluate to introduce and determine by ETAAS (5 min), washing and conditioning (0.5 min). Which gives an approximate time of 12.5 min. After the use of the external magnet in the preconcentration, elution and washing steps, the magnetic hybrid nanoparticles dispersed instantly. This is due to the intrinsic property of nanoparticles of superparamagnetism, which makes them an ideal sorbent for this type of procedure [31].

Once the optimal working conditions were established, the analytical parameters of the proposed methodology were studied. Framed in the IUPAC definition for the limits of detection (LOD) and quantification (LOQ) [15], it was determined that the LOD and LOQ correspond to 30 ng L^{-1} and 99 ng L^{-1}, respectively. For the calibration curve, standard solutions were processed whose linear concentration range was from 170 to 800 ng L^{-1} with an R^2 of 0.998±0.07 for total As. Precision was determined by analyzing several samples of a concentration equal to 200 ng L^{-1} and expressing it as the relative standard deviation (RSD%) corresponding to 7.1% ($n = 10$).

On the other hand, the preconcentration factor (PF) was calculated in the optimal working conditions, calculated as the ratio of the final concentration of arsenic in the eluent and in the sample corresponding to 50.

Table 1 shows a comparison of the developed method in this work with others reported in the literature for the analysis of As by MSPE. As it can be seen, the method has comparable analytical characteristics with more sophisticated techniques such as ICP-MS, with relatively low LOD,

Table 2
As analysis in copper ore samples[b].

Sample	Aliquot	Base Value (µg g^{-1})	Added Value (µg g^{-1})	Found Value (µg g^{-1})	Recovery %
Sample 1	1	0,33±0.07	-	-	-
	2	0,33±0.07	0,50	0,84±0.08	102,00[a]
	3	0,33±0.07	1,00	1,32±0.08	99[a]
Sample 2	1	0.28±0.07	-	-	-
	2	0.28±0.07	0,50	0,80±0.08	104[a]
	3	0.28±0.07	1,00	1,28±0.08	100[a]
Sample 3	1	0.34±0.07	-	-	-
	2	0.34±0.07	0,50	0,82±0.08	96[a]
	3	0.34±0.07	1,00	1,32±0.08	98[a]
Sample 4	1	0.6±0.07	-	-	-
	2	0.6±0.07	0,50	1,12±0.08	104[a]
	3	0.6±0.07	1,00	1,61±0.08	101[a]
Sample 5	1	0.45±0.07	-	-	-
	2	0.45±0.07	0,50	0,94±0.08	98[a]
	3	0.45±0.07	1,00	1,44±0.08	101[a]

[a] As 100 × (found-base)/(added).

[b] Confidence intervals: t(0.05,df)S/(n)0.5. Informed values as average amounts of three replicate determinations (n=3).

great simplicity as it does not use reagents to condition the sample and low sample consumption.

3.5. Validation and application

The validation stage involved the use of a certified reference material, GBM900-10, with a certified As concentration value of 336 µg g^{-1}. This material was digested following the same procedure of the sample. Dilutions according to the concentration range of the calibration curve of the method were made. The average As concentration value obtained for the reference material was 332±13.1 µg g^{-1}, with no significant difference with certified As concentration value.

A standard addition method was also performed for validation. To this end five copper ore samples were added with 0.5 and 1.0 µg g^{-1} As solution. Samples were digested and analyzed by the proposed method. Table 2 shows a summary of the results obtained. The data obtained showed quantitative As recoveries in a range of 96 to 104%.

Copper concentrates with a copper concentration of 0.4% (w w^{-1}) showed As concentrations in a range of 0.03 to 0.06% (w w^{-1}), which are below the penalized limits (0.2 % w w^{-1}) [3]. These results allow us to infer that the developed methodology was used successfully in the determination of As in copper ores samples.

4. Conclusion

In this work, microwave energy was implemented for the first time for the thermal stress stage to obtain modified carbon nanotubes, avoiding the use of reagents and considerably reducing operation times. By means of the wet immersion method with THF, it was possible to synthesize MHNP of modified CNT and NPM. MHNP showed a high arsenic sorption capacity with a quantitative extraction of the analyte. A good dispersibility in aqueous media and excellent superparamagnetic properties, allowed a short time for phase separation with magnetization. The use of an external magnet favored the operability of the proposed methodology by avoiding the use of a centrifuge or filtration. No extra conditioning of the sample is necessary, since the optimal pH for As adsorption on MHNP is equal to the pH value after acid digestion. The developed SPE methodology reached a low detection limit for As becoming suitable for the analysis of copper ores.

CRediT authorship contribution statement

Gastón Villafañe: Conceptualization, Data curation, Formal analysis, Investigation, Validation, Writing – original draft. **Vanesa Bazán:** Conceptualization, Data curation, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing. **Elena Brandaleze:** Data curation, Formal analysis, Investigation, Project administration, Resources, Validation. **Ayelén López:** Formal analysis, Investigation, Validation, Visualization. **Pablo Pacheco:** Conceptualization, Data curation, Formal analysis, Methodology, Resources, Supervision, Visualization, Writing – original draft, Writing – review & editing. **Ariel Maratta:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

There are no conflicts to declare.

Data availability

No data was used for the research described in the article.

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Supplementary materials

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Reference

[1] Y. Chaolei, L. Qi, S. Zhaoyang, Z. Wenjun, C. Jiangrong, C. Zheng, N. Shuo, S. Hongwen, Chemical oxidation of arsenic in the environment and applications: a mini review, Pedosphere (2022), 1, https://doi.org/10.1016/j.pedsph.2022.06.033.

[2] Y. Zhao, H. Zhao, T Abashina, M.J.M. Vainshtein, Review on arsenic removal from sulfide minerals: an emphasis on enargite and arsenopyrite, Miner. Eng. 172 (107133) (2021), https://doi.org/10.1016/j.mineng.2021.107133.

[3] D.J. Lane, N.J. Cook, S.R. Grano, K.J.M.E. Ehrig, Selective leaching of penalty elements from copper concentrates: a review, Miner. Eng. 98 (2016) 110–121, https://doi.org/10.1016/j.mineng.2016.08.006.

[4] W. Bruckard, K. Davey, F. Jorgensen, S. Wright, D. Brew, N. Haque, E.J.M.E. Vance, Development and evaluation of an early removal process for the beneficiation of arsenic-bearing copper ores, Miner. Eng. 23 (15) (2010) 1167–1173, https://doi.org/10.1016/j.mineng.2010.03.015.

[5] M. Velásquez, J. Álvarez, C. Sandoval, E. Ramírez, M. Bravo, R. Fuentes, A. K. Myakalwar, R. Castillo, D. Luarte, D.J.S.A.P.B.A.S. Sbarbaro, Improved elemental quantification in copper ores by laser-induced breakdown spectroscopy with judicious data processing, Spectrochim. Acta Part B: At. Spectrosc. 188 (2022), 106343, https://doi.org/10.1016/j.sab.2021.106343.

[6] W. Yang, L. Qian, B. Jin, Q. Feng, L. Li, K. He, J.J.J.o.E.C.E. Yang, Leaching behaviors of copper and arsenic from high-arsenic copper sulfide concentrates by oxygen-rich sulfuric acid leaching at atmospheric pressure, J. Environ. Chem. Eng. 10 (2) (2022), 107358, https://doi.org/10.1016/j.jece.2022.107358.

[7] M. Spaur, M.A. Lombard, J.D. Ayotte, D.E. Harvey, B.C. Bostick, S.N. Chillrud, A. Navas-Acien, A.E.J.S.o.T.T.E. Nigra, Associations between private well water and community water supply arsenic concentrations in the conterminous United States, Sci. Total Environ. 787 (2021), 147555, https://doi.org/10.1016/j.scitotenv.2021.147555.

[8] Y. Liu, L. Dai, X. Ke, J. Ding, X. Wu, R. Chen, R. Ding, B.J.J.o.C.P. Van der Bruggen, Arsenic and cation metal removal from copper slag using a bipolar membrane electrodialysis system, J. Clean. Prod. 338 (2022), 130662, https://doi.org/10.1016/j.jclepro.2022.130662.

[9] F. Verbruggen, P. Ostermeyer, L. Bonin, A. Prévoteau, K. Marcoen, T. Hauffman, T. Hennebel, K. Rabaey, M.S.J.M.E. Moats, Electrochemical codeposition of arsenic from acidic copper sulfate baths: the implications for sustainable copper electrometallurgy, Miner. Eng. 176 (2022), 107312, https://doi.org/10.1016/j.mineng.2021.107312.

[10] W. Zhang, J. Che, L. Xia, P. Wen, J. Chen, B. Ma, C.J.J.o.H.M. Wang, Efficient removal and recovery of arsenic from copper smelting flue dust by a roasting method: process optimization, phase transformation and mechanism investigation, J. Hazard. Mater. 412 (2021), 125232, https://doi.org/10.1016/j.jhazmat.2021.125232.

[11] M. Finšgar, T. Govejšek, K.J.S.T.T.L.S.I. Gradišek, Trace arsenic determination in a TiO2 pigment matrix using electrothermal atomic absorption spectrometry, SLAS Technol. 25 (2) (2020) 123–131, https://doi.org/10.1177/2472630319877378.

[12] T.J.S.A.P.B.A.S. Stafilov, Determination of trace elements in minerals by electrothermal atomic absorption spectrometry, Spectrochim. Acta Part B: At. Spectrosc. 55 (7) (2000) 893–906, https://doi.org/10.1016/S0584-8547(00)00227-5.

[13] S.N. Bruno, R.C. Campos, A.J.J.J.o.A.A.S. Curtius, Determination of lead and arsenic in wines by electrothermal atomic absorption spectrometry, J. Anal. At. Spectrom. 9 (3) (1994) 341–344, https://doi.org/10.1039/JA9940900341.

[14] I.N. Pasias, N.S. Thomaidis, E.A.J.M.J. Piperaki, Determination of total arsenic, total inorganic arsenic and inorganic arsenic species in rice and rice flour by electrothermal atomic absorption spectrometry, Microchem. J. 108 (2013) 1–6, https://doi.org/10.1016/j.microc.2012.11.008.

[15] A. Maratta, G. Villafañe, E. Brandaleze, P. Pacheco, V.J.S.A.P.B.A.S. Bazán, Photocatalytic preconcentration of Bi on TiO2 nanoparticles, Spectrochim. Acta Part B: At. Spectrosc. 171 (2020), 105945, https://doi.org/10.1016/j.sab.2020.105945.

[16] S. Chen, C. Wang, J. Yan, D.J.M.J. Lu, Use of fibrous TiO2@ graphitic carbon nitride nanocomposites in dispersive micro-solid phase extraction for arsenic species before inductively coupled plasma mass spectrometry determination, Microchem. J. 158 (2020), 105211, https://doi.org/10.1016/j.microc.2020.105211.

[17] R. Sanmartín, V. Romero, I. Lavilla, C.J.S.A.P.B.A.S. Bendicho, Ultrasound-assisted dispersive micro-solid phase extraction of Pb (II) in water samples with *in situ* synthesis of magnetic Fe3O4-PbS nanocomposites followed by electrothermal atomic absorption spectrometry determination, Spectrochim. Acta Part B: At. Spectrosc. 188 (2022), 106349, https://doi.org/10.1016/j.sab.2021.106349.

[18] M. Ghorbani, M. Aghamohammadhassan, H. Ghorbani, A.J.M.J. Zabihi, Trends in sorbent development for dispersive micro-solid phase extraction, Microchem. J. 158 (2020), 105250, https://doi.org/10.1016/j.microc.2020.105250.

[19] T. Khezeli, A.J.T.T.i.A.C. Daneshfar, Development of dispersive micro-solid phase extraction based on micro and nano sorbents, TrAC Trends Anal. Chem. 89 (2017) 99–118, https://doi.org/10.1016/j.trac.2017.01.004.

[20] A. Maratta, M. Acosta, L.D. Martinez, P.H. Pacheco, R.A.J.J.o.A.A.S. Gil, Ultratrace arsenic determination through hydride trapping on oxidized multiwall carbon nanotubes coupled to electrothermal atomic absorption spectrometry, J. Anal. At. Spectrom. 28 (6) (2013) 916–922, https://doi.org/10.1039/C3JA30385C.

[21] A. Maratta, L.D. Martinez, P.J.M.J. Pacheco, Development of an on line miniaturized non-chromatographic arsenic speciation system, Microchem. J. 127 (2016) 199–205, https://doi.org/10.1016/j.microc.2016.03.010.

[22] A.M. Martínez, S. Vázquez, R. Lara, L.D. Martínez, P.J.S.A.P.B.A.S. Pacheco, Selenium analysis by an integrated microwave digestion-needle trap device with hydride sorption on carbon nanotubes and electrothermal atomic absorption spectrometry determination, Spectrochim. Acta Part B: At. Spectrosc. 140 (2018) 22–28, https://doi.org/10.1016/j.sab.2017.12.001.

[23] A. Maratta, B. Carrizo, V.L. Bazán, G. Villafañe, L.D. Martínez, P.J.J.o.A.A. S. Pacheco, Antimony speciation analysis by hydride trapping on hybrid nanoparticles packed in a needle trap device with electro-thermal atomic absorption spectrometry determination, J. Anal. At. Spectrom. 33 (12) (2018) 2195–2202, https://doi.org/10.1039/C8JA00311D.

[24] A. Jakubus, K. Godlewska, M. Gromelski, K. Jagiello, T. Puzyn, P. Stepnowski, M.J. M.J. Paszkiewicz, The possibility to use multi-walled carbon nanotubes as a sorbent for dispersive solid phase extraction of selected pharmaceuticals and their metabolites: effect of extraction condition, Microchem. J. 146 (2019) 1113–1125, https://doi.org/10.1016/j.microc.2019.02.051.

[25] F. Faiz, J.-q. Qiao, H.-z. Lian, L. Mao, X.-b.J.T. Cui, A combination approach using two functionalized magnetic nanoparticles for speciation analysis of inorganic arsenic, Talanta 237 (2022), 122939, https://doi.org/10.1016/j.talanta.2021.122939.

[26] H. Yu, C. Li, Y. Tian, X.J.M.J. Jiang, Recent developments in determination and speciation of arsenic in environmental and biological samples by atomic spectrometry, Microchem. J. 152 (2020), 104312, https://doi.org/10.1016/j.microc.2019.104312.

[27] A. Conde-Díaz, R. Rodríguez-Ramos, B. Socas-Rodríguez, P.Á. Salazar-Carballo, M.Á.J.J.o.C.A. Rodríguez-Delgado, Application of polyaniline-based magnetic-dispersive-solid-phase microextraction combined with liquid chromatography tandem mass spectrometry for the evaluation of plastic migrants in food matrices, J. Chromatogr. A. 1670 (2022), 462988, https://doi.org/10.1016/j.chroma.2022.462988.

[28] M. Mehrabian, E. Noroozian, S.J.M.J. Maghsoudi, Preparation and application of Fe3O4@ SiO2@ poly (o-phenylenediamine) nanoparticles as a novel magnetic sorbent for the solid-phase extraction of tellurium in water samples and its determination by ET-AAS, Microchem. J. 165 (2021), 106104, https://doi.org/10.1016/j.microc.2021.106104.

[29] M.G. Santos, D.T. de Carvalho, L.B. Caminitti, B.B.A. de Lima, M.H. da Silva Cavalcanti, D.F.R. Dos Santos, L.S. Virtuoso, D.B. Hirata, E.C.J.F.C. Figueiredo, Use of magnetic Fe3O4 nanoparticles coated with bovine serum albumin for the separation of lysozyme from chicken egg white, Food Chem. 353 (2021), 129442, https://doi.org/10.1016/j.foodchem.2021.129442.

[30] Y.P. Yew, K. Shameli, M. Miyake, N.B.B.A. Khairudin, S.E.B. Mohamad, T. Naiki, K. X.J.A.J.o.C. Lee, Green biosynthesis of superparamagnetic magnetite Fe3O4 nanoparticles and biomedical applications in targeted anticancer drug delivery system: a review, Arab. J. Chem. 13 (1) (2020) 2287–2308, https://doi.org/10.1016/j.arabjc.2018.04.013.

[31] S. Yan, T.-T. Qi, D.-W. Chen, Z. Li, X.-J. Li, S.-Y.J.J.o.C.A. Pan, Magnetic solid phase extraction based on magnetite/reduced graphene oxide nanoparticles for determination of trace isocarbophos residues in different matrices, J. Chromatogr. A. 1347 (2014) 30–38, https://doi.org/10.1016/j.chroma.2014.04.073.

[32] Y. Yang, M. He, B. Chen, B.J.T. Hu, The amino-functionalized magnetic graphene oxide combined with graphite furnace atomic absorption spectrometry for determination of trace inorganic arsenic species in water samples, Talanta 232 (2021), 122425, https://doi.org/10.1016/j.talanta.2021.122425.

[33] H. Alinezhad, M. Zabihi, D.J.J.o.p. Kahfroushan, c.o. solids, Design and fabrication the novel polymeric magnetic boehmite nanocomposite (boehmite@ Fe3O4@ PLA@ SiO2) for the remarkable competitive adsorption of methylene blue and mercury ions, J. Phys. Chem. Solids 144 (2020), 109515, https://doi.org/10.1016/j.jpcs.2020.109515.

[34] J.W. Lee, H.M. Jeong, G.H. Lee, Y.W. Jung, S.G. Jo, J.K.J.J.o.E.C.E. Kang, Agglomeration-Free Fe3O4 anchored via nitrogen mediation of carbon nanotubes for high-performance arsenic adsorption, J. Environ. Chem. Eng. 9 (3) (2021), 104772, https://doi.org/10.1016/j.jece.2020.104772.

[35] H.K. Kaya, N. Haghmoradi, B.Y. Kaplan, F.J.J.o.E.C. Kuralay, Platinum nanoparticles loaded carbon black: reduced graphene oxide hybrid platforms for label-free electrochemical DNA and oxidative DNA damage sensing, J. Electroanal. Chem. 910 (2022), 116180, https://doi.org/10.1016/j.jelechem.2022.116180.

[36] Y.M.A. Mohamed, M.F. Mady, Silicon-Based Hybrid Nanoparticles, Elsevier, 2022, pp. 353–361, https://doi.org/10.1016/B978-0-12-824007-6.00014-9.

[37] M. Mehmandoust, F. Karimi, N.J.C. Erk, A zinc oxide nanorods/molybdenum disulfide nanosheets hybrid as a sensitive and reusable electrochemical sensor for determination of anti-retroviral agent indinavir, Chemosphere 300 (2022), 134430, https://doi.org/10.1016/j.chemosphere.2022.134430.

[38] X. Sun, Z. Fu, T. Jiang, F. Ning, Y. Cheng, T. Fu, M. Zhu, H. Zhang, M. Zhang, P.J.J. o.C.A. Hu, Application of β-Cyclodextrin metal-organic framework/titanium dioxide hybrid nanocomposite as dispersive solid-phase extraction adsorbent to organochlorine pesticide residues in honey samples, J. Chromatogr. A 1663 (2022), 462750, https://doi.org/10.1016/j.chroma.2021.462750.

[39] F.J.D. Boran, R. materials, encapsulation of CuO nanoparticles inside the channels of the multi-walled carbon nanotubes functionalized with thermal stress, Diam. Relat. Mater. 114 (2021), 108306, https://doi.org/10.1016/j.diamond.2021.108306.

[40] A. Pistone, D. Iannazzo, M. Fazio, C. Celegato, G. Barrera, P. Tiberto, A. Giordano, B. Azzerboni, S.J.P.B.C.M. Galvagno, Synthesis and magnetic properties of multiwalled carbon nanotubes decorated with magnetite nanoparticles, Phys. B. Condens. Matter 435 (2014) 88–91, https://doi.org/10.1016/j.physb.2013.11.015.

[41] M. Krajewski, P.-Y. Liao, M. Michalska, M. Tokarczyk, J.-Y.J.J.o.E.S. Lin, Hybrid electrode composed of multiwall carbon nanotubes decorated with magnetite nanoparticles for aqueous supercapacitors, J. Energy Storage 26 (2019), 101020, https://doi.org/10.1016/j.est.2019.101020.

[42] B. Chen, Z. Zhu, J. Ma, M. Yang, J. Hong, X. Hu, Y. Qiu, J.J.J.o.c. Chen, i. science, One-pot, solid-phase synthesis of magnetic multiwalled carbon nanotube/iron oxide composites and their application in arsenic removal, J. Colloid Interface Sci. 434 (2014) 9–17, https://doi.org/10.1016/j.jcis.2014.07.046.

[43] A.J. Szalai, N. Manivannan, G.J.C. Kaptay, S.A. Physicochemical, E. Aspects, Super-paramagnetic magnetite nanoparticles obtained by different synthesis and separation methods stabilized by biocompatible coatings, Colloids Surf. A Physicochem. Eng. Asp. 568 (2019) 113–122, https://doi.org/10.1016/j.colsurfa.2019.02.006.

[44] C. Wang, S. Guo, X. Pan, W. Chen, X.J.J.o.M.C. Bao, Tailored cutting of carbon nanotubes and controlled dispersion of metal nanoparticles inside their channels, J. Mater. Chem. 18 (47) (2008) 5782–5786, https://doi.org/10.1039/B811560E.

[45] M. Singla, N.J.U.S. Sit, Application of ultrasound in combination with other technologies in food processing: a review, Ultrason. Sonochem. 73 (2021), 105506, https://doi.org/10.1016/j.ultsonch.2021.105506.

[46] M. Deng, X. Wu, A. Zhu, Q. Zhang, Q.J.J.o.e.m. Liu, Well-dispersed TiO2 nanoparticles anchored on Fe3O4 magnetic nanosheets for efficient arsenic removal, J. Environ. Manage. 237 (2019) 63–74, https://doi.org/10.1016/j.jenvman.2019.02.037.

[47] G. Ungureanu, S. Santos, R. Boaventura, C.J.J.o.e.m. Botelho, Arsenic and antimony in water and wastewater: overview of removal techniques with special reference to latest advances in adsorption, J. Environ. Manage. 151 (2015) 326–342, https://doi.org/10.1016/j.jenvman.2014.12.051.

[48] Z. Zou, S. Wang, J. Jia, F. Xu, Z. Long, X.J.M.J. Hou, Ultrasensitive determination of inorganic arsenic by hydride generation-atomic fluorescence spectrometry using Fe3O4@ ZIF-8 nanoparticles for preconcentration, Microchem. J. 124 (2016) 578–583, https://doi.org/10.1016/j.microc.2015.10.005.

[49] R. Sitko, B. Zawisza, E.J.T.T.i.A.C. Malicka, Modification of carbon nanotubes for preconcentration, separation and determination of trace-metal ions, TrAC Trends Anal. Chem. 37 (2012) 22–31, https://doi.org/10.1016/j.trac.2012.03.016.

[50] S.-z. Pan, C.-z. Jin, X.-a. Yang, W.-b.J.T. Zhang, Ultrasound enhanced solid-phase extraction of ultra-trace arsenic on Fe3O4@ AuNPs magnetic particles, Talanta 209 (2020), 120553, https://doi.org/10.1016/j.talanta.2019.120553.

[51] A. Özcan, E.M. Öncü, A.S.J.C. Özcan, s.A. Physicochemical, e. aspects, Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous

solutions onto natural sepiolite, Colloids Surf. A Physicochem. Eng. Asp. 277 (1-3) (2006) 90–97, https://doi.org/10.1016/j.colsurfa.2005.11.017.

[52] E. Darezereshki, A. khodadadi Darban, M. Abdollahy, A.J.E.N. Jamshidi-Zanjani, Monitoring, management, influence of heavy metals on the adsorption of arsenate by magnetite nanoparticles: kinetics and thermodynamic, Environ. Nanotechnol. Monit. Manag. 10 (2018) 51–62, https://doi.org/10.1016/j.enmm.2018.04.002.

[53] R.E. Rivas, I. López-García, M.J.S.A.P.B.A.S. Hernández-Córdoba, Speciation of very low amounts of arsenic and antimony in waters using dispersive liquid–liquid microextraction and electrothermal atomic absorption spectrometry, Spectrochim. Acta Part B: At. Spectrosc. 64 (4) (2009) 329–333, https://doi.org/10.1016/j.sab.2009.03.007.

[54] E. Yilmaz, Z. Erbas, M.J.A.C.A. Soylak, Hydrolytic enzyme modified magnetic nanoparticles: an innovative and green microextraction system for inorganic species in food samples, Anal. Chim. Acta 1178 (2021), 338808, https://doi.org/10.1016/j.aca.2021.338808.