Arsenic determination in complex mining residues by ICP OES after ultrasonic extraction

Jéssica F.R. Paula [a], Roberta E.S. Froes-Silva [b,c,*], Virgínia S.T. Ciminelli [a,b]

[a] Universidade Federal de Minas Gerais, Escola de Engenharia, Departamento de Engenharia Metalúrgica e de materiais, Brazil
[b] Instituto Nacional de Ciência e Tecnologia, Recursos minerais, Água e Biodiversidade, Brazil
[c] Universidade Federal de Ouro Preto, Instituto de Ciências Exatas e Biológicas, Departamento de Química, Morro do Cruzeiro, Campus Universitário, Ouro Preto/MG, 35.400-000, Brazil

ARTICLE INFO

ABSTRACT

The impact caused by mining residue deposits with high amounts of arsenic is a potential environmental problem and motive for investigations. Arsenic is always associated with gold ores and is present in mining areas, probably due to sulfide oxidation and the high pH range where arsenic is soluble. It has been shown that some samples of residues coming from the studied deposits presented arsenic concentrations above 2500 mg kg^{-1}. The aim of this work is to develop methods for arsenic extraction in mining residues employing ultrasound assistance extraction and analyte determination by hydride generation ICP OES. The analytical method provided analysis precision and a better evaluation of environmental impact of mining residue deposits. Optimal conditions for ultrasound assisted extraction were obtained by evaluation of parameters such as the position of the sample flask inside the ultrasound bath and temperature as a function of the immersion time. These tests identified the ideal position of the sample flask and indicated that the maximum time that the sample could be analyzed without arsenic lost due to increase of the temperature was 180 minutes. With these conditions, an experimental design was developed to obtain the optimal conditions of arsenic extraction, evaluating the type of extraction solution and the sonication time. A 2^2 Central Composite Design (CCD) was employed to evaluate the acid concentration (HCl, HNO$_3$ and H$_3$PO$_4$) and the sonication time (maximum 180 minutes). The quadratic equation of response surface generated by CCD, employing HNO$_3$, indicated that the best condition for arsenic extraction is using an acid concentration of 2.7 mol L^{-1} and sonication for 136 minutes to give an average concentration of 1847 ± 17 mg kg^{-1}. Recovery studies were carried out and the obtained values were close to 100%. Optimal conditions of arsenic extraction were obtained by evaluating the operational parameters of ultrasound bath and the analysis conditions with the experimental design. The method developed contributes significantly to a more precise evaluation of the real environmental impact caused by the mining residues deposit.

© 2012 Elsevier B.V. Open access under the Elsevier OA license.

1. Introduction

Arsenic in mining areas has created an environmental problem. The presence of arsenic in certain mining areas has been highlighted in the scientific literature by various research groups [1–5]. Arsenic is always associated with gold ores and is present in mining areas, probably due to sulfide oxidation and the high pH range where arsenic is soluble [6]. It has been shown that some samples of residues coming from a deposit of mining waste presented arsenic concentrations above 2500 mg kg^{-1} [7].

Some mining wastes are difficult to solubilize and new so extraction procedures are needed to assess the free arsenic. Alternative studies evaluating the potential arsenic extraction are being realized to understand the arsenic readiness in the residue and soils. Sequential chemical extraction procedure was used to evaluate the arsenic concentration in mining waste and soils by [8]. Ruiz-Cancho et al. [9] used a block digester and a microwave digestion to obtain the extract to evaluate the arsenic species present by LC-HG-AFS. The application of ultrasound is very promising in hydrometallurgy, including accelerating the processes of extraction and leaching. The ultrasound procedure can make available a chemical species present in a solid matrix for the extraction or for the dissolution of the species of interest. The energy required for extraction of metals is provided by the field of cavitation, which causes an increase in local temperature in the order of hundreds of degrees and a pressure increase of several hundred atmospheres. In addition, micro turbulent pulsations in thin layers of liquid in contact with the solid particles [10]. This technique promotes the larger interaction between the liquid phase and the solid surface by reduction of particles size and acceleration of chemical dissolution and thus increasing the concentration of inorganic species in the liquid phase [11,12].

A multivariate optimization can be applied in the development of new methodologies for arsenic extraction. This technique can promote

* Corresponding author. Tel.: +55 31 3559-1233; fax: +55 31 3559 1228.
E-mail address: robertafroes@iceb.ufop.br (R.E.S. Froes-Silva).

a fast and precise design evaluating multi parameters at the same time [13–15]. The surface response generated by this design can indicate the optimal condition for analysis. The application of multivariate optimization in the arsenic extraction could be an alternative for analysis of the complex mining waste, which can be useful for the evaluation of real impact caused by the complex mining waste deposit.

The aim of this work is the development of a new and alternative methodology for arsenic extraction from complex mining waste with difficult decomposition using ultrasound extraction.

2. Experimental

2.1. Instrumentation

An analytical balance Kern 410 model was used to measure the mass of the samples. An ultrasonic cleaning bath GA1000/TA1800 (Thornton; São Paulo, Brazil) with a frequency of 25 Hz was used for the extraction of arsenic from mining tailings samples.

A closed vessel microwave oven (Ethos 1, Milestone; Sorisole, Italy) was used to decompose the sample in order to compare the efficiency between the open ultrasonic bath using optimized conditions and the experiment performed under microwave conditions. The extracts were analyzed in an inductively coupled plasma optical emission spectrometer (ICP OES) model: DV 7200 (Perkin Elmer instruments, Shelton, USA) with hydride generation. The operational conditions are presented in Table 1.

2.2. Reagent, solution and sample

A standard 1000 mg L^{-1} arsenic solution (ICP Standard, Merck Certipur®, Darmstadt, Germany) was used to prepare the calibration curve and reference solutions. All the solutions were prepared with ultrapure water. For hydride-generating were used hydrochloric acid solution (2 mol L^{-1}) (37% HCl, Merck), sodium borohydride (NaBH$_4$ tablets, Fluka, purum, purity >97%) at 1.5% in 0.2% NaOH (Merck). The HNO$_3$, HCl and H$_3$PO$_4$ (Merck, analytical grade) concentrated acids used were diluted with ultrapure water to prepare the solutions for analysis. The reference material Buffalo River Sediment (National Institute of Standards and Technology, NIST RM 8704), were used as reference for some tests. Real sample of complex mining waste, collected in a deposit of mining, was used in the multivariate optimization and the recovery studies.

2.3. Evaluation of axial position in the flask

In order to assess the influence of the position of the sample inside the ultrasonic bath, the tub was divided into four quadrants, 15 cm by 15 cm. Next, nine locations in the tub were selected, as indicated in the layout of Fig. 1.

The samples are prepared in duplicate using 0.1 g of a reference material Buffalo River Sediment 8704 and mixed in a flask containing 10.0 mL of HNO$_3$ 0.5 mol L^{-1} solution. The flasks were sonicated for 1 hour. Subsequently, the samples were centrifuged and the supernatant was transferred to 15 mL polyethylene tubes for analysis of the arsenic concentration via ICP-OES.

Table 1
Operational conditions of ICP OES.

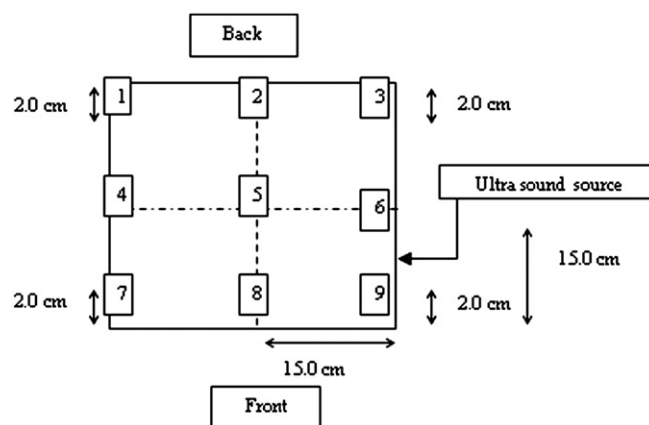| Parameter	
Auxiliary gas flow rate (L min^{-1})	0.2
Plasma gas flow rate (L min^{-1})	15
Injector tube diameter (mm)	2.0
View	Axial
Interface	Shear gas
Applied power (kW)	1.3
Nebulization gas flow rate (L min^{-1})	0.6

Fig. 1. Layout of selected positions in the ultrasound bath.

2.4. Evaluation of the temperature as a function of time in the ultrasound bath

The effect of sonication in the sample system cannot be considered only as a mechanical wave effect. The temperature increasing in the bath due the energy liberated [16] should also be considered. The monitoring of the temperature was made in a range of 180 minutes, by measuring the temperature at intervals of 25 minutes.

To evaluate the influence of temperature on the extraction of arsenic, the reference material "Buffalo River Sediment 8704" was weighed in duplicate samples with a nominal mass of 0.2 g and then placed in 50 mL polyethylene tubes. To the tubes containing the samples 20.0 mL of HNO$_3$ 2.0 mol L^{-1} was added before washing them in the ultrasonic bath. One sample was placed in the bath at room temperature, 25 °C, and the other to the initial temperature of 40 °C. Both were sonicated for 1 hour. Subsequently the samples were centrifuged for 10 minutes and the supernatant was stored in 50 mL polypropylene tubes until analysis via ICP-OES.

2.5. Multivariate optimization

For the extraction of arsenic by ultrasound sonication it was used a mass ratio of solid / solution volume of extractant 0.01 g mL^{-1}. This mass ratio is based in the work where the same ratio was used to evaluate arsenic extraction to speciation in soil using a probe ultrasonic [17].

Ten samples were weighed in duplicate, 0.1 g of solid waste (with arsenic concentration estimated in 2000 mg kg^{-1}) in polyethylene bottles (15 mL). To each bottle 10.00 mL of extractant solution was added, minutes before the samples were subjected to ultrasonic bath. The flasks were shaken manually to allow contact between the entire solid with the acid solution.

A Central Composite Design 2^2 (CCD) was used in order to assess the concentration of acid (HCl, HNO$_3$ and H$_3$PO$_4$) and sonication time (maximum 180 minutes). To avoid the mixing of the acids, the same study design was employed individually for HCl, HNO$_3$ and H$_3$PO$_4$. The implementation of the design was done in Statistica ® 7.0 software. The design data are shown in Table 2.

The bottles were placed in the ultrasound bath tub in the region determined to have higher-intensity ultrasonic waves (see layout) at room temperature initially, and subjected to ultrasonic energy at a frequency of 25 kHz.

After soaking in a bath of ultrasound during the specific time for each sample, the resulting mixture was filtered and the supernatant was stored in polyethylene bottle and cooled to 5 °C and subsequently analyzed by ICP-OES.

Table 2
Parameters of time and acid concentration determined by the CCD design.

Sample	Time (min)	Acid concentration (mol L^{-1})
2	50	3.0
7	195	2.0
6	25	2.0
9	110	3.5
10 (C)	110	2.0
1	50	1.0
5 (C)	110	2.0
8	110	0.6
3	170	1.0
4	170	3.0

Fig. 2. Temperature in function of the time.

2.6. Extraction of arsenic in the microwave

A 0.1 g of the milling waste were weighed in duplicate, in watch glasses and transferred to Teflon tubes. To the Teflon tube was added 9.0 ml of HNO$_3$ and 3.0 ml of HF in order to remove the rest of the solid adhered to the watch glass. We prepared two blank samples containing the same volume of acid added to the samples. The samples were taken to the microwave oven for 30 minutes, 15 minutes warming up to the temperature of 200 °C and dwelled at same temperature for 15 minutes. After a complete cooling system, 0.8 g of H$_3$BO$_3$ was added to neutralize residual hydrofluoric acid and the heating program was repeated. The samples, after cooling, were diluted with ultrapure water to a final volume of 50.0 ml and stored in a refrigerator at 5 °C and analyzed by ICP-OES.

3. Results and discussion

3.1. Evaluation of axial position in the flask

Nine positions were evaluated in this test as shown in the figure below (Fig. 1). The arsenic concentrations in the extracts for each position are listed in Table 3.

Higher concentrations of arsenic were obtained in the square region of 5–6–8–9 position. This region is close to the ultrasound source suffering more impact by the waves. The radial position was constant in all experiments.

3.2. Evaluation of the temperature as a function of time in the ultrasound bath

The control of the temperature was made by measuring the temperature value every 25 minutes for 180 minutes. The data obtained are presented in Fig. 2.

It is noteworthy that there occurs a non-linear increase in temperature with averages of 2.3 °C every 25 minutes. To evaluate the influence of the temperature in the arsenic extraction duplicate samples with 2.0 g of reference material and 20.0 mL of HNO$_3$ solution 2.0 mol L^{-1} were prepared. The duplicates were put inside the bath in the same position (square 5–6–8–9). In the first tests, the sample
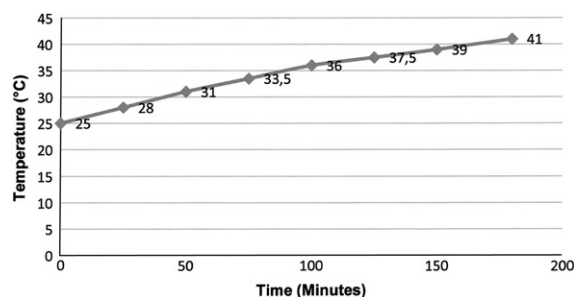
was put in the ultrasound bath at an initial temperature of 25 °C and in the second test at an initial temperature of 40 °C. The total time of sonication was 180 minutes. The results are shown in Table 4.

The results indicate that there is no significant influence of the temperature on the arsenic extraction when using ultrasound bath in the studied range. From here on, a maximum time of 180 minutes will be used given that at temperatures higher than 40 °C the arsenic concentration can be compromised.

The operating conditions for the appropriate use of the ultrasound bath was evaluated when developing an experimental design to determine the optimal conditions for extraction of arsenic in complex mining residues. This design allows the evaluation of multiple factors, and time, type of extractant solution and the concentration factors in this study.

3.3. Multivariate optimization

A 2^2 Central Composite Design (CCD) was employed to evaluate the acid concentration (HCl, HNO$_3$ and H$_3$PO$_4$) and the sonication time (maximum, 180 minutes). The design execution was made in the Statistica® 7.0 software. The design data are show in Table 5.

The mining waste samples were used in the design. The results for each acid are shown below.

3.3.1. Arsenic extraction in complex mining residues employing H$_3$PO$_4$

The results using H$_3$PO$_4$ arsenic extraction in ultrasound bath are shown in Table 6.

The model generated explains 81% of total variance and the response surface (Fig. 3), generated by quadratic Eq. (1) and indicates that with a time of 104 minutes and H$_3$PO$_4$ concentration of 2.4 mg L^{-1} the maximum arsenic extraction will be achieved from the sample.

$$z = 70256 + 00264 * x00001 * x^2 + 27741 * y - 05799 \\ * y^2 - 00043 * x * y \tag{1}$$

3.3.2. Extraction of arsenic in complex mining residues using HCl complex

The data were evaluated in the experimental design but the model generated was not suitable for the removal of arsenic, due to inappropriate operating conditions and therefore optimal conditions could not be established by the model. For this acid, another experimental

Table 3
Arsenic concentration in function of the flask position.

Position	[As] (µg L^{-1})	Position	[As] (µg L^{-1})
1A	184.5	1B	192.9
2A	193.6	2B	177.8
3A	189.2	3B	191.2
4A	182.4	4B	201.8
5A	197.9	5B	198.9
6A	203.6	6B	180.2
7A	204.2	7B	198.5
8A	216.7	8B	210.2
9A	216.3	9B	213.8

Table 4
Influence of the temperature of the ultrasound bath in the arsenic extraction.

Initial temperature (°C)	Sample average (n = 2)	[As] µg L^{-1}
25	1[a]	174.2
25	1B	169.1
40	2[a]	171.5
40	2B	172.7

Table 5
2^2 CCD design data.

| Sample	Time (min)	Concentration of extractants (mol L^{-1})
2	50	3.0
7	195	2.0
6	25	2.0
9	110	3.41
10(C)	110	2.0
1	50	1.0
5(C)	110	2.0
8	110	0.6
3	170	1.0
4	170	3.0

Table 6
Extraction of arsenic in H$_3$PO$_4$, HCl and HNO$_3$ with ultrasound bath.

Sample	Time (min)	Concentration of extractants (mol L^{-1})	Concentration As (mg kg^{-1})		
			H$_3$PO$_4$	HCl	HNO$_3$
2	50	3.0	27.9	32.6	1209.5
7	195	2.0	32.7	36.5	1683.5
6	25	2.0	29.2	33.8	677.7
9	110	3.5	31.8	34.8	1903.7
10(C)	110	2.0	36.0	39.0	1710.7
1	50	1.0	32.3	40.1	178.5
5(C)	110	2.0	27.4	35.0	1684.5
8	110	0.6	34.4	43.9	591.7
3	70	1.0	29.5	40.9	1200.2
4	170	3.0	22.1	31.6	1641.7

design needs be tested in order to obtain the best operational conditions. The data from the arsenic extraction with HCl are shown in Table 6 and were obtained using the operational condition employed in the evaluation the axial position in the flask (2.3).

3.3.3. Extraction of arsenic in complex mining residues using complex HNO$_3$

Table 6 displays the results of the extraction of arsenic in the bath HNO$_3$ using ultrasound. Equation and response surface are also displayed below (Fig. 3).
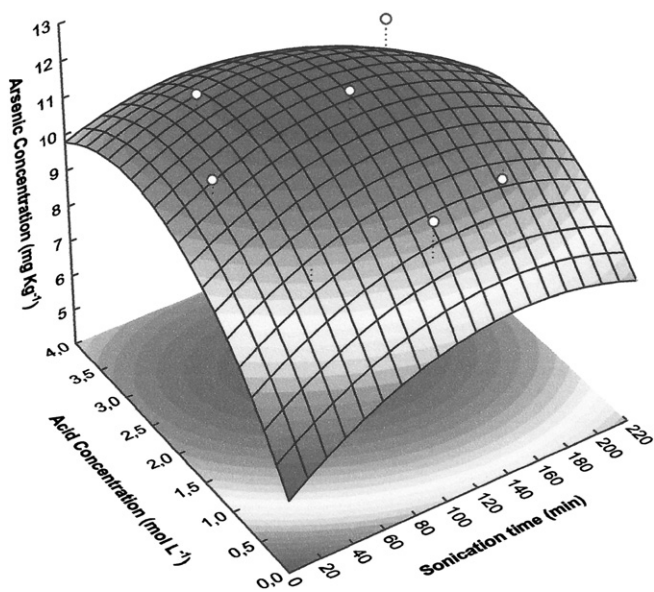
Fig. 3. Surface response corresponding to the influence of concentration and time of sonication for the extraction of arsenic from mining waste sample with H$_3$PO$_4$.
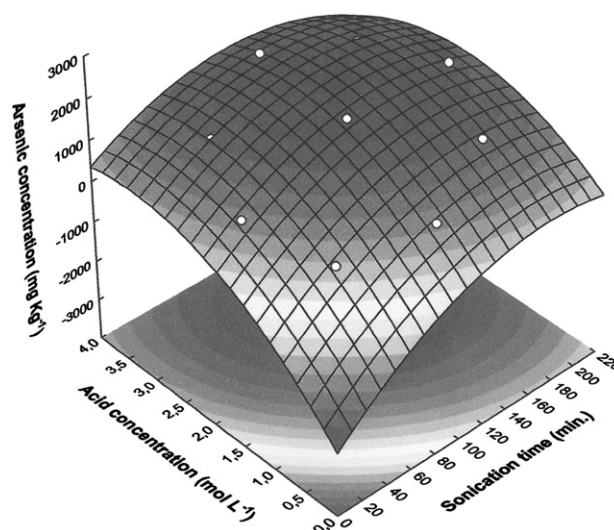
Fig. 4. Surface response corresponding to the influence of concentration and time sonication on the extraction of arsenic from mining waste sample with HNO$_3$.

Eq. (2) was generated to explain the model and the surface area of the response using HNO$_3$ extraction of arsenic (Fig. 4).

$$z = 2390,9853 + 29,0969 * x0,0827 * x^2 + 1742,7075 * y - 264,1269 * y^2 - 2,4565 * x * y \tag{2}$$

The generated model explains 97% of the total variance and the surface generated by Eq. (2) indicates that the maximum extraction of arsenic is hit when employing a sonication time of 136 minutes and a HNO$_3$ concentration of 2.7 mol L^{-1}.

Comparing the efficiency of arsenic extraction by the different acids tested, it was concluded that maximum concentration of arsenic was 1903.7 ± 50.0 mg kg^{-1} for the extraction performed with HNO$_3$ and was much higher than those achieved by H$_3$PO$_4$ and HCl, whose concentration maximum were 36.3 ± 2.0 mg kg^{-1} and 43.9 ± 1.3 mg kg^{-1}, respectively. The high oxidizing power of HNO$_3$ explains the superior performance over H$_3$PO$_4$. A more appropriate experimental design is needed for the employment of HCl given that design used in this study was unable to derive the proper operating condition for this acid. Thus, recovery studies employing the optimum conditions of time and concentration determined for HNO$_3$ (time equal to 136 minutes and the concentration of 2.7 mol L^{-1}) were performed and the values obtained were close to 100% as shown in Table 7.

3.4. Results for the extraction of arsenic in the microwave

Employing the conditions specified for the extraction of arsenic in the microwave closed vessels resulted in an average arsenic concentration of 1385.0 ± 41.0 mg kg^{-1} (Table 8). This concentration was lower than that for the optimized method, whose average was 1847.0 ± 17.0 mg kg^{-1}. The decrease of arsenic concentration in the

Table 7
Study of arsenic recovery for optimized conditions for HNO$_3$.

Sample	Concentration As (mg kg^{-1})
A	1872
B	1748
C	1842
D	1760
F	1885
G	1975

Table 8
Arsenic concentrations determined after microwave assisted.

Sample	Concentration As (mg L^{-1})	Concentration As (mg kg^{-1})
A	3.08	1529
B	2.52	1240

microwave extraction probably is due the some loss by volatilization caused by the high temperatures in the digester vessel.

4. Conclusions

The results for the extraction of arsenic in complex mining waste by employing a CCD design for the use of an ultrasonic bath for energy proved to be quite satisfactory. Optimum conditions for extraction of arsenic were obtained by evaluating operational parameters of the ultrasonic bath and conditions of analysis with the experimental design.

In assessing the influence of temperature on the extraction of arsenic in ultrasound, it was noted that there is no significant influence up to 40 °C. However, it was noted that the position of the sample in the ultrasonic bath tub is significant in that a greater proximity between the samples and the source of ultrasonic waves allows the intensification of the phenomenon of cavitation in the vicinity of the sample and thus, extraction of arsenic.

The concentration of arsenic obtained using the method optimized for ultrasound (HNO$_3$, 2.7 mol L^{-1} and 136 minutes of sonication) was superior to that obtained by the standard method performed in the microwave, which indicates that the method developed contributes significantly to the establishment of a more accurate assessment of the real environmental impact caused by mining waste deposits.

Acknowledgment

References

[1] B.G. Rawlins, T.M. Williams, N. Breward, L. Ferpozzi, B.F. Figueiredo, R.P. Borba, Preliminary Investigation of Mining-Related Arsenic Contamination in the Provinces of Mendoza and San Juan (Argentina) and Minas Gerais State (Brazil), British Geological Survey, London, 1997 25 pp.
[2] E. Deschamps, V.S.T. Ciminelli, F.T. Lange, J. Matschullat, B. Raue, H. Schmidt, Soil and sediment geochemistry of the Iron Quadrangle, Brazil—the case of arsenic, J. Soils Sediments 2 (4) (2002) 216–222.
[3] H.S.S. Pimentel, J.C. Lena, J.R. Nalini, Studies of water quality in the Ouro Preto region, Minas Gerais, Brazil: the release of arsenic to the hydrological system, Environ. Geol. 43 (2003) 725–730.
[4] R.P. Borba, B.R. Figueiredo, J. Matshullat, Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil, Environ. Geol. 4 (2003) 39–52.
[5] R.P. Borba, B.R. Figueiredo, B.G. Rawllins, J. Matchullat, Arsenic in water and sediment in the Iron Quadrangle, Minas Gerais state, Brazil, Rev. Bras. Geociênc. 30 (3) (2000) 554–557.
[6] L.X.L. Capanema, V.S.T. Ciminelli, An investigation of Acid Rock Drainage (ARD) occurrence in a gold mine located in a southeastern Brazil region, Rev. Esc. Minas 56 (3) (2003) 201–206 (Ouro Preto).
[7] R. Bayard, V. Chatain, C. Gachet, A. Troadec, R. Gourdon, Mobilisation of arsenic from a mining soil in batch slurry experiments under bio-oxidative conditions, Water Res. 40 (6) (2006) 1240–1248.
[8] P.J. Kavanagh, M.E. Farago, I. Thornton, R.S. Braman, Bioavailability of arsenic in soil and mine wastes of the Tamar Valley, SW England, Chem. Speciation Bioavailability 9 (3) (1997) 77–81.
[9] M.J. Ruiz-Chancho, F. López-Sánchez, R. Rubio, Analytical speciation as a tool to assess arsenic behaviour in soils polluted by mining, Anal. Bioanal. Chem. 387 (2007) 627–635.
[10] P.I. Polyukhin, The Use of Ultrasonics in Extractive Metallurgy, Technicopy, Stonehouse, UK, 1978 (translated from Russian).
[11] P.M. Kanthale, R. Parag, A. Gogate, B. Aniruddha, A. Pandit, A.M. Wilhelm, Mapping of an ultrasonic horn: link primary and secondary effects of ultrasound, Ultrason. Sonochem. 10 (2003) 331–335.
[12] P.R. Gogate, A. Prashant, M.K. Parag, B.P. Aniruddha, Mapping of sonochemical reactors: review, analysis, and experimental verification, AICHE J. 4 (8) (2002) 7.
[13] K.R. Beeb, R.J. Pell, M.B. Seasholtz, Chemometrics: A Practical Guide, Wiley, ed., New York; 1998, 360 pp.
[14] D.L. Massart, B.G.M. Vandeginste, L.M.C. Buydens, S. De Jong, P.J. Lewin, J. Smeyers-Verbeke, Handbook of Chemometrics and Qualimetrics: Part B, Elsevier, Amsterdam, 1998 732 pp.
[15] V. Calado, D. Montgomery, Planejamento de Experimentos usando o Statistica, 85-87922-83-1, 2003.
[16] T. Lepoint, F. Mullie, What exactly is cavitation chemistry? Ultrason. Sonochem. 1 (1994) 13–22.
[17] E. Sanz, Muñoz-OlivasR. , C. Cámara, Evaluation of a focused sonication probe for arsenic speciation in environmental and biological samples, J. Cromatograph. A 1097 (2005) 1–2.