

Environmental Hazard Assessment of Jarosite Waste Using Batch Leaching Tests*



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doi: 10.15255/CABEQ.2017.1120

Original scientific paper

Received: March 14, 2017

Accepted: November 5, 2017

Jarosite waste samples from Trepča Zinc Industry in Kosovo were subjected to two batch leaching tests as an attempt to characterize the leaching behavior and mobility of minor and major elements of jarosite waste. To achieve this, deionized water and synthetic acidic rain leaching tests were employed. A two-step acidic treatment in microwave digestion system were used to dissolve jarosite waste samples, followed by determination of Al, Ag, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, S, Si, Sr, and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES). The validation of the procedure was performed by the analysis of two geochemical reference materials, S JR-3 and S Jsy-1. Two toxicity leaching tests revealed a high metal releasing of Cd, Cu, Ni, Mn, Pb, Zn, and As, and the metal release risk for these elements is still very high due the low pH and acid rain. The statistical analysis showed useful data information on the relationship between elements in jarosite samples in two different extraction conditions (deionized water and synthetic acid rain).

Key words:

leaching test, jarosite waste, deionized water, synthetic acid rain

Introduction

Industrial processes inevitably impact the environment on varying scales. There are different ways to measure pollutants when evaluating the environmental threat from a solid material of different industrial processes. Detailed characterization and leaching tests are required to assess the environmental stability of waste before any treatment possibility. Standard leaching tests are used to estimate the potential mobility of trace and major elements from the deposited waste. These tests are also used to assess the remediation options of contaminated sites, their range of efficiency and source of environmental risk characterization¹. In general, leaching is a method that is used to remove soluble components from a solid matrix. In order to protect human health and groundwater quality from contamination by metals, over 100 leaching methods have been developed over the last few decades to

determine metal release and mobility in soils from waste materials^{2,3,4,5}. These methods vary in mass of the samples, type and volume of leachant solution, method delivery, and time². Leaching tests used in the laboratory are usually conducted using European Standard EN 12457-2:2005 (or German standard DIN 38414-S4) in deionized water⁴. Further, the Synthetic Precipitation Leaching Procedure (SPLP)⁶ test is currently used by several researchers to evaluate leaching of constituents from waste using dilute sulfuric/nitric acid solution^{2,6,8,9}. Leaching of trace and major elements from jarosite waste is strongly affected by pH, while the concentration of trace and major elements in the solution is the factor that classifies the jarosite as hazardous or non-hazardous waste. Researchers have suggested that waste material should be tested under conditions similar to their actual applications in re-use scenarios in order to achieve reliable results¹⁰. The framework of this study includes the comparison of two batch leaching methods using leachants of deionized¹¹ and synthetic acidic rain⁶. More specifically, the leaching tests for environmental hazard assessment of jarosite tailing waste of Trepča Zinc Industry, Kosovo were examined.

*Presented at the “4th International Symposium on Environmental Management – Towards Circular Economy (SEM2016), December 7 – 9, Zagreb, Croatia”

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Materials and methods

The jarosite waste used for testing was obtained from the jarosite tailing dumps located in Mitrovica City, Kosovo. This waste is produced from the jarosite process that was used in Trepça Zinc Industry. In order to assess the leaching test, three jarosite samples in a depth of 0.20 m, 1 m, and 2 m were taken. After sampling, the samples were air-dried, sieved to a fraction less than 2 mm, and stored in polypropylene containers until analyzed.

Batch leaching tests

The leaching potential of the elements present in the jarosite waste samples was determined using the batch leaching test in deionized water according to HRN EN 12457-2¹¹, as well as the leaching test in synthetic acid rain according to the modification of Synthetic Precipitation Leaching Procedure (SPLP) Method 1312:1994⁶.

Chemical analysis methodology

Total metal content of trace and major metals was determined using microwave digestion method (MARSX XP1500 Microwave Digestion System, CEM, SAD). Microwave digestion of jarosite waste samples was carried out in two stages with the use of reagents HCl, HNO₃, HF and H₃BO₃^{12,13}. Certified reference materials, S JR-3 and S Jsy-1 (MBH Analytical LTD), were analyzed in order to test the accuracy of the applied method for determination of total metal concentrations in the investigated jarosite samples. The concentrations of constituents (Al, Ag, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, S, Si, Sr, and Zn) in the leachates were determined by Thermo Inductive Coupled Plasma Optical Emission Spectrometer (ICP-OES, IRIS Interpid II XSP). The concentration of constituents in leachates was compared with the leaching limit values of the decision 2003/33/EC¹⁴. The electrical conductivity and pH were measured using conductivity meter (MA 5964 Iskra, Croatia) and pH meter (FE20, Mettler Toledo, Switzerland). Both these pieces of equipment were calibrated using standard solution before measurements. The measurements for all parameters were conducted simultaneously or different times of 1 day, 7 days, 14 days, and 21 days. Quality assurance of the leaching process was achieved with the application of US EPA QA/QS protocol⁷ and the use of blank method for every batch of samples.

Statistical analysis

The influence of the variables, such as concentration, depth, and time of the extraction, were investigated using the mathematical and statistical

analysis method of Response Surface Methodology (RSM). The statistical analyses were performed using Statistica (data analysis software system), version 10 and software Excel 2010. Statistical significance of the variables was determined at the 5 % probability level ($p < 0.05$). Statistical significance was determined by Student's *t*-test and polynomial equations describing the responses of variations. The three-dimensional surface was plotted for the results of leaching tests in deionized water and synthetic acid rain. The interaction and the effects during the leaching process between concentration, depth, and leaching time were analyzed using Pareto charts. Moreover, the mathematical models for description of responsive variables of the depth and time in the concentration of each leachant ratio were established.

Results and discussions

Total metal content

The results of total metal content determined in accordance with the described microwave digestion method are presented in Table 1 for the samples of depth 0.20 m (Sample 1), 1 m (Sample 2), and 2 m (Sample 3). In samples 1, 2, and 3, respectively, Fe in the form of Fe₂O₃ had the highest content (44.94 wt.%, 45.14 wt.% and 44.37 wt.%) among all other elements. SiO₂ is also an important component with 6.31 wt.%, 5.92 wt.% and 4.20 wt.%. Zn had the highest content among all heavy metals (10.91 wt.%, 5.24 wt.%, 1.33 wt.%), followed by Pb (7.51 wt.%, 5.17 wt.%, 6.93 wt.%), where Pb in sample 1 had the highest concentration, and Cu (0.97 wt.%, 0.679 wt.%, 0.40 wt.%). The concentration of other metals ranged as follows: Ag (133.82–151.87), Ba (370.62–578.90), Co (9.79–30.3), Cd (418.25–2308.69), Cr (79.30–416.59), Mn (1905.07–6391.71), Ni (6.13–93.50), Sr (156.20–200.36), and As (200.36–5075.53) mg kg⁻¹ jarosite waste. The concentration of heavy metals varied from 0.20 m to 2 m sample depths. In all cases, the difference was higher than 40 % from 2 m up to 0.20 m depth, indicating a high degree of concentration of available heavy metals in the surface of jarosite tailing dump.

pH values and electrical conductivity (EC) of leachates

Fig. 1 shows the changes in pH values during contact time of jarosite waste with deionized water and synthetic acid rain leaching tests. The initial pH value in deionized water was 5.53, while the pH values in the period of 1 day, 7 days, 14 days, and 21 days ranged from 3.96 to 3.66 for sample 1, 3.68

Table 1 – Total metal content in jarosite waste samples (n = 3)

Element	Sample 1 (0.2 m depth) mean ± σ	Sample 2 (1 m depth) mean ± σ	Sample 3 (2 m depth) mean ± σ
Al ₂ O ₃ , wt. %	1.42 ± 0.02	1.09 ± 0.01	0.62 ± 0.001
Fe ₂ O ₃ , wt. %	44.94 ± 0.05	45.14 ± 0.54	44.37 ± 0.48
SiO ₂ , wt. %	6.31 ± 0.7	5.92 ± 0.6	4.20 ± 0.2
Zn, wt. %	10.91 ± 0.02	5.24 ± 0.2	1.33 ± 0.01
Pb, wt. %	7.51 ± 0.13	5.17 ± 0.04	6.93 ± 0.04
Cu, wt. %	0.97 ± 0.01	0.679 ± 0.01	0.40 ± 0.00
Ag, mg kg ⁻¹	133.82 ± 11.82	139.77 ± 6.29	151.87 ± 1.38
Ba, mg kg ⁻¹	578.90 ± 194.73	428.12 ± 121.03	370.62 ± 64.49
Co, mg kg ⁻¹	30.38 ± 0.27	27.55 ± 0.48	9.79 ± 0.65
Cd, mg kg ⁻¹	2308.69 ± 24.47	1359.03 ± 9.48	418.25 ± 2.59
Cr, mg kg ⁻¹	416.59 ± 14.35	96.71 ± 0.80	79.30 ± 1.29
Mn, mg kg ⁻¹	6391.71 ± 84.06	3741.27 ± 58.43	1905.07 ± 20.19
Ni, mg kg ⁻¹	93.50 ± 1.10	53.00 ± 0.45	6.13 ± 2.89
Sr, mg kg ⁻¹	156.20 ± 2.01	177.84 ± 0.04	200.36 ± 0.57
As, mg kg ⁻¹	5075.53 ± 5.52	3014.85 ± 0.00	2534.93 ± 0.64

to 3.59 for sample 2, and 3.57 to 3.52 for sample 3. The pH value of leachates ranged stably from 3.96 to 3.52, which indicated that the jarosite waste had high acidic buffering capacity. The pH value in the acid rain condition during the leaching process changed negligibly. This complies with the conclusion of Min *et al.*¹⁴, that, under these conditions, the leaching of heavy metals from waste was a long-term process that accumulated in the environment. Fig. 2 shows the changes in electrical conductivity (EC) during time in contact of jarosite waste. According to the obtained results, the electrical conductivity (EC) increases very fast in a short period from the initial value for both leaching tests (in deionized water and synthetic acid rain). Higher values of the electrical conductivity were obtained for the leaching with the synthetic acid rain.

Leaching tests of jarosite samples with deionized water and synthetic acid rain

The results of the leaching jarosite samples in deionized water and synthetic acid rain are presented in Tables 2 and 3. As may be seen, constituents such as Zn, S, and Mn presented high mobility. As many studies have shown, the release potential of constituents from jarosite waste materials may vary depending on various physicochemical factors, such as pH, L/S (liquid/solid) ratio, the matrix of solid waste and the leaching type¹⁶. According to the results shown in Table 2, the highest values of Al, Cd,

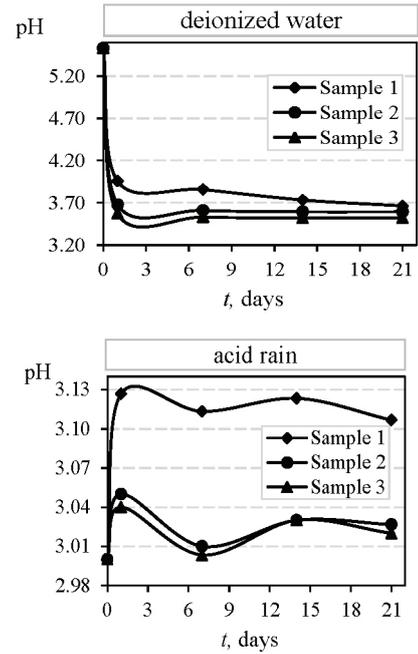


Fig. 1 – pH values of leachates in deionized water and synthetic acid rain in deionized water as leachant

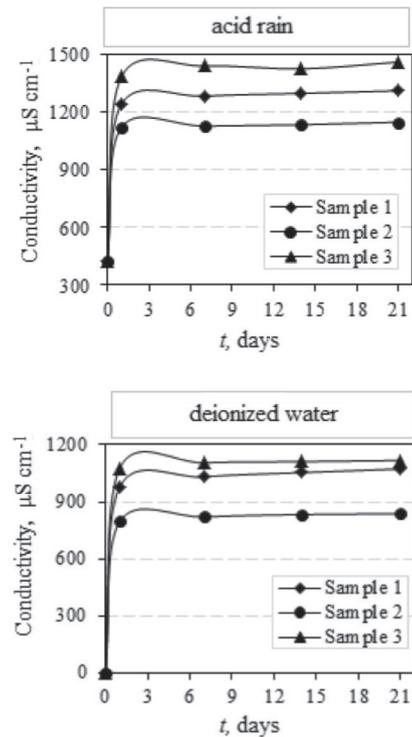


Fig. 2 – Electrical conductivity (EC) of leachates in deionized water and synthetic acid rain

Cu, Fe, Pb, and Si were 212.11 mg kg⁻¹, 69.95 mg kg⁻¹, 139.30 mg kg⁻¹, 39.16 mg kg⁻¹, 168.21 mg kg⁻¹, and 194.09 mg kg⁻¹, respectively. These elements showed the highest value on the 21-day leaching time, except Mn, which showed the highest value of leaching after 1 day.

Table 2 – Average concentration of major and minor elements in samples leached with deionized water

Element	Sample	<i>t</i> , days			
		1	7	14	21
		mg kg ⁻¹ mean ± σ			
Ag	1	0.11 ± 0.07	0.09 ± 0.03	0.03 ± 0.05	0.13 ± 0.01
	2	0.36 ± 0.22	0.29 ± 0.10	0.11 ± 0.04	0.63 ± 0.39
	3	0.07 ± 0.04	0.06 ± 0.02	0.10 ± 0.04	0.32 ± 0.09
Al	1	82.24 ± 5.00	77.68 ± 1.29	78.82 ± 0.97	97.82 ± 3.67
	2	197.60 ± 6.02	191.32 ± 7.26	184.24 ± 1.29	212.11 ± 5.32
	3	181.95 ± 7.82	170.08 ± 1.02	167.65 ± 0.71	194.27 ± 1.07
Ba	1	0.13 ± 0.11	0.03 ± 0.06	0.06 ± 0.03	0.28 ± 0.06
	2	0.77 ± 0.11	0.62 ± 0.05	0.64 ± 0.04	0.76 ± 0.15
	3	0.55 ± 0.05	0.36 ± 0.03	0.46 ± 0.03	0.70 ± 0.09
Cd	1	51.67 ± 3.89	51.06 ± 1.09	50.67 ± 0.26	56.98 ± 0.31
	2	62.68 ± 1.17	63.21 ± 1.71	62.82 ± 0.81	69.95 ± 0.69
	3	58.60 ± 2.15	59.51 ± 0.61	59.17 ± 0.49	66.06 ± 1.06
Co	1	0.67 ± 0.02	0.71 ± 0.02	0.69 ± 0.02	0.92 ± 0.04
	2	1.26 ± 0.03	1.21 ± 0.07	1.22 ± 0.03	1.54 ± 0.02
	3	1.28 ± 0.09	1.30 ± 0.03	1.26 ± 0.02	1.59 ± 0.06
Cr	1	0.03 ± 0.04	–	–	–
	2	0.13 ± 0.02	–	–	0.08 ± 0.05
	3	0.30 ± 0.07	0.06 ± 0.03	0.07 ± 0.07	0.18 ± 0.05
Cu	1	59.37 ± 3.51	62.52 ± 1.66	61.58 ± 1.06	71.42 ± 1.47
	2	116.89 ± 6.60	115.23 ± 3.56	109.06 ± 1.64	124.77 ± 3.30
	3	122.63 ± 6.00	32.38 ± 9.77	121.24 ± 0.54	139.30 ± 1.50
Fe	1	27.04 ± 9.97	22.55 ± 4.53	14.71 ± 10.68	10.14 ± 2.23
	2	12.71 ± 5.87	3.69 ± 3.26	6.12 ± 1.25	27.53 ± 14.69
	3	27.87 ± 3.22	39.16 ± 2.10	32.51 ± 2.90	42.37 ± 8.93
Mn	1	373.70 ± 31.58	363.89 ± 7.97	14.71 ± 10.68	10.14 ± 2.23
	2	902.87 ± 18.02	888.39 ± 21.88	6.12 ± 1.25	27.53 ± 14.69
	3	711.29 ± 25.79	32.38 ± 9.77	32.51 ± 2.90	42.37 ± 8.93
Ni	1	2.71 ± 0.77	2.36 ± 0.05	2.66 ± 0.28	3.97 ± 0.52
	2	3.32 ± 0.24	2.61 ± 0.14	2.72 ± 0.12	3.31 ± 0.11
	3	2.96 ± 0.75	2.42 ± 0.06	2.38 ± 0.06	2.81 ± 0.07
P	1	1.13 ± 0.36	1.33 ± 0.72	0.66 ± 0.70	0.28 ± 0.38
	2	1.60 ± 0.43	1.65 ± 0.07	1.00 ± 0.19	0.77 ± 0.55
	3	0.98 ± 0.24	1.13 ± 0.14	0.85 ± 0.68	0.47 ± 0.36
Pb	1	141.54 ± 5.79	158.52 ± 2.50	163.26 ± 2.53	168.21 ± 8.35
	2	99.20 ± 6.47	119.15 ± 2.72	110.59 ± 4.14	146.33 ± 22.32
	3	111.64 ± 10.5	132.69 ± 8.88	126.69 ± 7.92	139.30 ± 7.41
S	1	9667.37 ± 434	10159.97 ± 209	9968.83 ± 219	11956.19 ± 68.6
	2	7317.88 ± 83	7761.42 ± 346	7575.21 ± 186	9199.62 ± 41.52
	3	10179.06 ± 291	10466.74 ± 247	7454.01 ± 5567	12332.77 ± 174
Si	1	31.82 ± 0.67	118.76 ± 1.57	153.95 ± 4.20	194.09 ± 2.65
	2	21.35 ± 0.52	78.91 ± 2.82	100.56 ± 3.76	128.39 ± 2.87
	3	22.20 ± 1.25	77.96 ± 0.98	407.40 ± 526.15	129.51 ± 6.64
Sr	1	10.61 ± 0.28	11.70 ± 0.13	12.53 ± 0.19	14.49 ± 0.38
	2	20.33 ± 0.85	24.88 ± 0.68	25.03 ± 0.69	29.49 ± 0.21
	3	17.78 ± 0.74	19.68 ± 0.05	20.52 ± 0.47	24.11 ± 0.44
Zn	1	5601.21 ± 49	5617.90 ± 38	4109.97 ± 2684	3331.20 ± 25.76
	2	4886.89 ± 87	4893.50 ± 26	4883.12 ± 61.08	2897.89 ± 4.61
	3	4694.21 ± 148	4807.21 ± 78	4684.80 ± 38.98	2787.88 ± 47.86
As	1	0.33 ± 0.07	0.67 ± 0.00	2.04 ± 0.00	2.84 ± 0.19
	2	0.53 ± 0.00	0.10 ± 0.00	0.23 ± 0.00	0.54 ± 0.23
	3	0.10 ± 0.00	0.08 ± 0.00	0.19 ± 0.00	0.28 ± 0.08

Table 3 – Average concentration of major and minor elements in samples leached with synthetic acid rain leaching tests

Element	Sample	<i>t</i> , days			
		1	7	14	21
		mg kg ⁻¹ mean ± σ			
Ag	1	0.52 ± 0.42	0.19 ± 0.06	0.23 ± 0.11	0.95 ± 0.69
	2	0.38 ± 0.09	0.56 ± 0.16	0.43 ± 0.07	1.00 ± 1.13
	3	0.34 ± 0.07	0.47 ± 0.12	0.46 ± 0.21	0.59 ± 0.03
Al	1	129.17 ± 4.70	128.92 ± 5.09	130.52 ± 9.25	103.65 ± 86.26
	2	217.85 ± 11.18	209.49 ± 4.54	208.07 ± 15.99	167.50 ± 142.18
	3	198.17 ± 10.29	192.03 ± 6.74	190.04 ± 4.00	217.57 ± 4.30
Ba	1	0.10 ± 0.03	0.02 ± 0.01	0.07 ± 0.02	0.13 ± 0.13
	2	0.60 ± 0.04	0.46 ± 0.03	0.59 ± 0.06	0.49 ± 0.43
	3	0.57 ± 0.08	0.34 ± 0.02	0.49 ± 0.01	0.75 ± 0.30
Cd	1	51.54 ± 1.13	51.51 ± 1.60	52.44 ± 3.38	39.04 ± 32.93
	2	63.79 ± 2.82	62.11 ± 0.21	61.35 ± 3.18	47.82 ± 40.74
	3	61.00 ± 1.53	60.50 ± 1.35	59.19 ± 1.01	66.43 ± 0.88
Co	1	0.72 ± 0.03	0.72 ± 0.04	0.71 ± 0.06	0.63 ± 0.51
	2	1.25 ± 0.08	1.21 ± 0.03	1.19 ± 0.08	1.01 ± 0.85
	3	1.33 ± 0.06	1.31 ± 0.03	1.29 ± 0.04	1.56 ± 0.03
Cr	1	0.25 ± 0.04	0.24 ± 0.03	0.26 ± 0.03	0.28 ± 0.20
	2	0.36 ± 0.03	0.29 ± 0.02	0.30 ± 0.04	0.31 ± 0.24
	3	0.47 ± 0.06	0.41 ± 0.03	0.35 ± 0.04	0.45 ± 0.04
Cu	1	78.93 ± 3.77	84.59 ± 4.01	86.35 ± 6.26	68.98 ± 56.44
	2	133.67 ± 8.03	126.70 ± 1.69	126.48 ± 9.83	99.33 ± 83.37
	3	154.62 ± 11.28	149.47 ± 3.81	146.35 ± 3.84	165.99 ± 3.74
Fe	1	55.30 ± 13.28	49.31 ± 6.62	31.65 ± 2.05	36.86 ± 28.40
	2	40.06 ± 3.77	37.82 ± 13.77	52.04 ± 20.31	34.04 ± 29.43
	3	93.74 ± 5.33	71.25 ± 3.04	85.54 ± 10.16	86.64 ± 11.96
Mn	1	352.31 ± 9.26	354.76 ± 11.62	357.13 ± 22.85	267.14 ± 218.72
	2	812.10 ± 31.92	844.50 ± 4.39	832.91 ± 47.79	639.67 ± 544.45
	3	711.74 ± 23.53	703.48 ± 18.83	690.40 ± 14.53	758.61 ± 10.38
Ni	1	3.00 ± 0.58	2.38 ± 0.03	2.52 ± 0.19	1.95 ± 1.66
	2	3.02 ± 0.39	2.59 ± 0.13	2.42 ± 0.11	2.41 ± 2.15
	3	3.19 ± 0.55	2.75 ± 0.24	2.38 ± 0.03	2.96 ± 0.10
P	1	1.16 ± 0.09	0.61 ± 0.51	0.68 ± 0.57	0.88 ± 0.17
	2	1.34 ± 0.75	0.95 ± 0.52	1.04 ± 0.26	0.98 ± 1.01
	3	1.08 ± 0.75	1.16 ± 0.32	0.72 ± 0.80	1.68 ± 0.35
Pb	1	160.00 ± 4.55	159.52 ± 11.35	162.07 ± 1.92	135.38 ± 113.54
	2	120.86 ± 0.90	127.72 ± 5.65	134.31 ± 16.13	101.34 ± 84.66
	3	125.24 ± 6.48	137.24 ± 1.44	137.97 ± 4.33	154.60 ± 7.79
S	1	11249.93 ± 322.45	11112.74 ± 422.86	11189.72 ± 736.41	12937.33 ± 121.76
	2	8695.83 ± 380.91	8351.59 ± 128.96	8253.54 ± 467.33	9951.62 ± 331.73
	3	11651.58 ± 545.22	11611.46 ± 158.24	11083.29 ± 328.05	13274.34 ± 199.02
Si	1	18.99 ± 0.65	69.46 ± 3.88	96.52 ± 7.08	123.16 ± 1.37
	2	17.79 ± 1.25	55.74 ± 0.84	78.18 ± 5.01	107.03 ± 13.45
	3	17.77 ± 1.14	61.08 ± 1.63	81.11 ± 1.71	101.75 ± 1.84
Sr	1	8.91 ± 0.32	10.50 ± 0.12	11.65 ± 0.37	9.38 ± 7.97
	2	15.15 ± 0.36	17.12 ± 0.16	17.46 ± 0.82	72.35 ± 44.38
	3	12.69 ± 0.54	15.03 ± 0.21	15.64 ± 0.17	71.30 ± 46.20
Zn	1	5494.14 ± 16.14	5490.92 ± 92.84	5619.06 ± 223.09	3422.29 ± 48.60
	2	4901.83 ± 110.16	4756.44 ± 26.53	4679.24 ± 144.79	2933.39 ± 133.04
	3	4746.49 ± 78.19	4747.84 ± 95.63	4642.41 ± 65.81	2834.81 ± 26.92
As	1	0.45 ± 0.00	0.86 ± 0.00	1.57 ± 0.34	2.79 ± 2.43
	2	0.12 ± 0.00	0.14 ± 0.00	0.30 ± 0.00	0.38 ± 0.44
	3	0.35 ± 0.00	0.21 ± 0.00	0.06 ± 0.00	0.43 ± 0.12

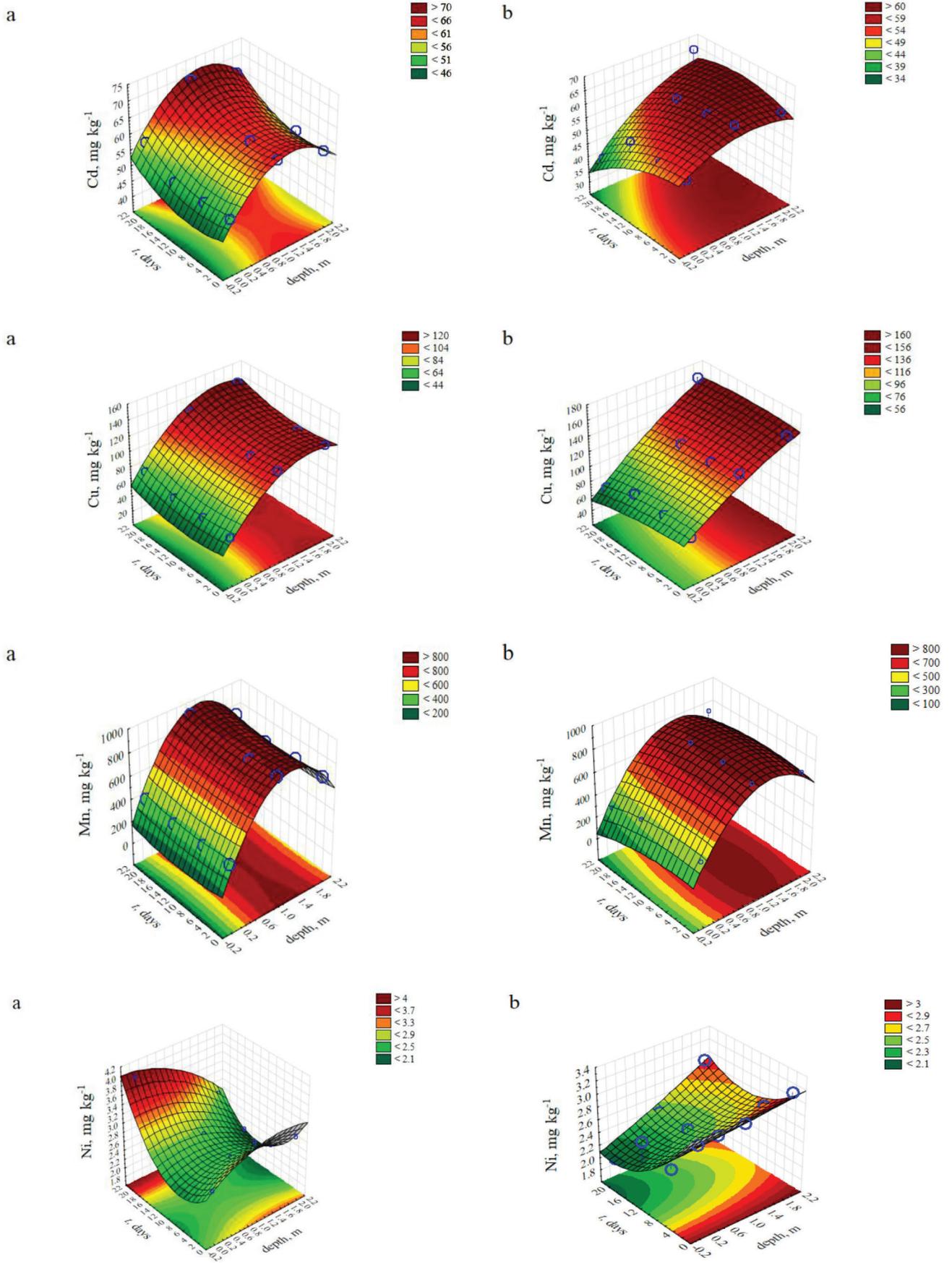


Fig. 3 – Continued on next page...

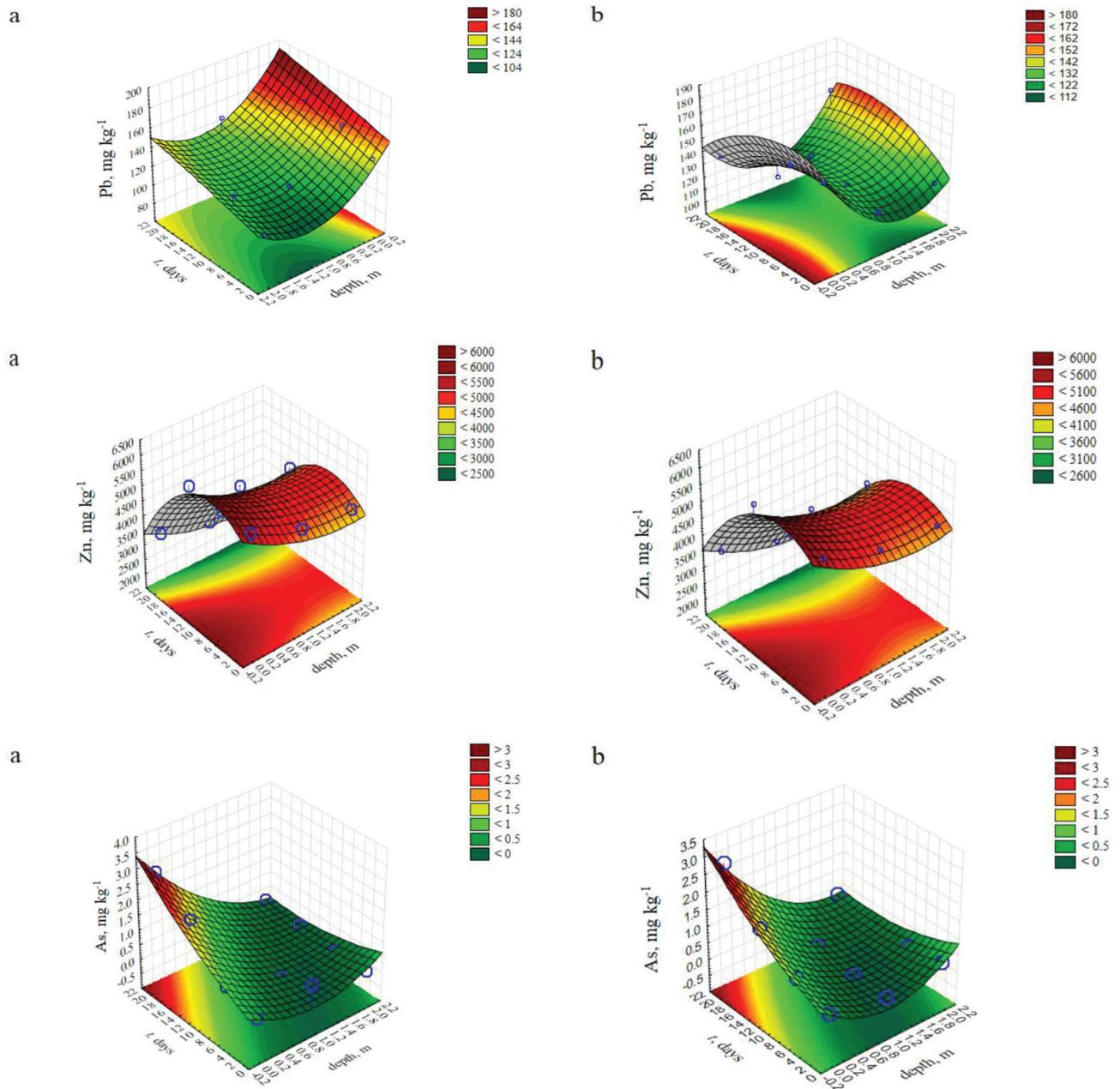


Fig. 3 – Changes in Cd, Cu, Mn, Ni, Pb, Zn, and As concentrations with time and depth during: (a) leaching test in deionized water; and (b) leaching test in acid rain

Furthermore, small concentrations were recorded for the following elements in both procedures: Ag, Ba, Co, Ni, P, Sr, As, and Cr. With regard to quality control, the metal content for the blank method were not detected above detection limits. By comparing the two leaching tests, the results showed a slight difference in the concentrations of the analyzed elements.

The major difference was observed in the amount of Fe, Si, and S, whereas Ba, P, and As vary slightly. Fe and S are more leachable in the synthetic acid rain leaching tests, while Si is more leachable with deionized water. The concentration of Cr

for days 7 and 14 was below the detection limits of analysis, which means that Cr was not leachable after the first day. Therefore, the use of acid rain promoted the release of minor and major elements due to acidification. The concentrations of Zn, Cd, Cu, and Pb were high in the beginning, but declined with prolonged leaching. The results of long-term leaching of heavy metals showed that contamination caused by the above elements was serious in the first days, and the trend slowed down with prolonged leaching. Total concentrations of As and heavy metals in jarosite waste were much higher than those evaluated by leaching tests. These results

were consistent with those reported by Lim *et al.*¹⁷ and Yang *et al.*¹⁸ Overall, according to the results, the jarosite waste contained certain pollutants which are a heavy burden on the environment. The obtained values for Zn, Cd, Mn, Cu, Pb, and As exceed the European regulatory limit for heavy metals in soil¹⁴. The metal release risk for these metals is still very high due to the low pH and acid rain. Researchers have predicted that the increase in concentration in the leachate would affect the efficiency of subsequent leachate treatment^{12,19}. Heavy metals in jarosite waste will be leached out due to weathering and acid rain, and this cumulative effect of leaching will provide favorable conditions for heavy metals to be leached out.

Statistical analysis

The quantities of Cd, Cu, Mn, Ni, Pb, Zn, and As leached out in both tests are considerably higher than in any previous tests²⁰. Three-dimensional surfaces were plotted for the results of the deionized water leaching test (Fig. 3a), and the synthetic acid rain leaching test (Fig. 3b) for the elements with highest impact on the environment.

When comparing the plot of the results of the deionized water leaching test with that obtained for the results of the synthetic acid rain leaching test, it is possible to visualize that the region where the leachates are maximized is not exactly the same in both graphs for each analyzed element. The surfaces presented in Figs. 3, 4, and 5 describe the variations of the leachate amounts as a function of the variations of leaching times and sample depths. In order to visualize a function of two variables (the amount of element leached in deionized water and synthetic acid rain from three-dimensional data presented in Fig. 3, a contour plot for both (a) and (b) graphs was created (Fig. 4). This contour plot shows the level curves of a function of major and minor elements variables from two of the three-dimensional graphs as a function of time and depth. To establish such plot, first the matrix that holds the values of the function was created, and then the contour plot of that matrix. The plotting of a function of two variables such as copper, zinc, lead, manganese, nickel, cadmium, and arsenate are shown in Fig. 4. The overlaying plot attained shows an area where the imposed criteria are satisfied. A point was assigned in this area as the optimization point, which corresponds to the leachant concentration in deionized water and synthetic acid rain leaching conditions. The optimum leaching conditions were performed and the results obtained for metal concentration and the deionized and synthetic acid rain activity of the leachant revealed close agreement with the result predicted by statistical analysis. However, it is worthy emphasizing that,

although the two leaching conditions are the most commonly used as leaching solvents, the toxic characteristics of the metals in acid rain conditions raises serious issues when the purpose of the elements leached by these solvents is the application of the material in industrial processes.

In order to verify the effects of each operational variable in the responses, Pareto charts were plotted as well (Fig. 5). In Fig. 5, bars extending to the vertical line corresponded to the effects of 95 % confidence level. As may be seen from Fig. 5, the variable of depth almost exerted a significance level of $p < 0.05$ in all the evaluated responses with element concentration in both deionized water and synthetic acid rain. Depth showed to be the most important variable affecting the leaching of major and minor elements under water leaching conditions (Fig. 5a), as well as leaching under acidic conditions (Fig. 5b). All investigated samples (from all depths) are mostly composed of approximately the same phases, yet the concentration can differ based on the Treppca working capacity (Table 1). Time was also an important variable contributing to the leaching of elements such as Zn and Ni under synthetic acidic rain conditions. The variable of time exerted a significance level of $p < 0.05$ in the evaluated responses with all element concentration in deionized water and for Zn and As in synthetic acid rain conditions. In general, the Pareto charts allowed observation of both the magnitude and the importance of an effect. These charts displayed the absolute value of the effects, and drew a reference line on the chart. Any effect that extends past this reference line is potentially important. Analysis of the individual factors on the Pareto chart showed that leaching time and depth were statistically significant since they overshoot the critical value line (reference line) for almost all analyzed elements, except Cd and Cu (Fig. 5b). There was no significant interaction (L1×L2) among the factors, because all the interactions fell short of the critical value line. The interactions for the majority of elements, except As and Ni, do not differ much from both chart distributions. The Pareto charts for major elements Cd, Cu, Ni, Mn, Pb, Zn, and As are presented in Fig. 5.

Mathematical models describing the response variations (t , days, and depths) as a function of variances in the major and minor element concentration in deionized water and synthetic acid rain were established (Table 4). All models were established with statistically significant terms of $p < 0.05$. All mathematical models describing the response variations presented linear (L) and quadratic (Q) terms, as shown in Fig. 4, where both variables of time and depth presented a statistical significance at $p < 0.05$. The quadratic term for most of the element concentrations presented the negative signal. This

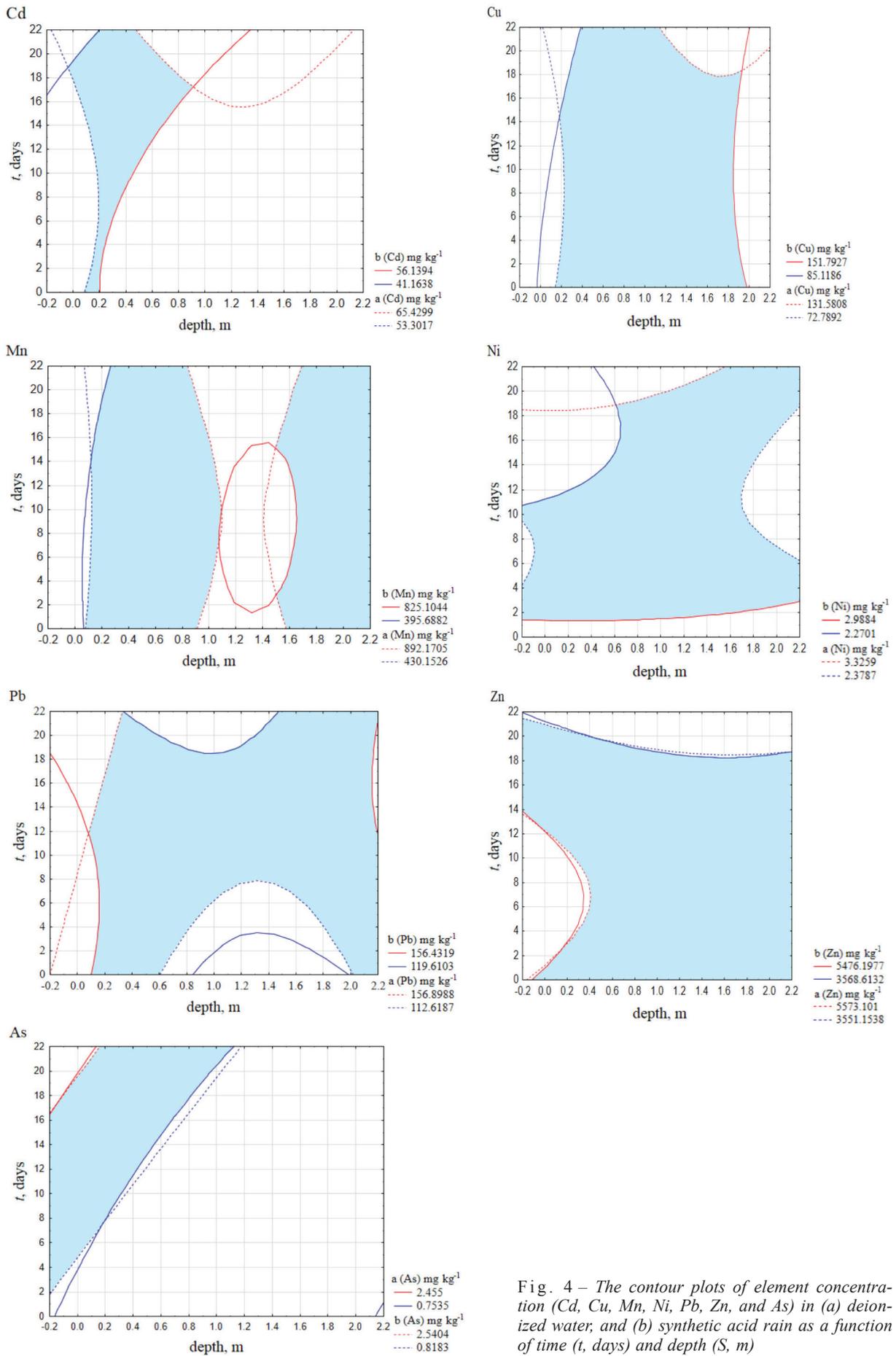


Fig. 4 – The contour plots of element concentration (Cd, Cu, Mn, Ni, Pb, Zn, and As) in (a) deionized water, and (b) synthetic acid rain as a function of time (t , days) and depth (S , m)

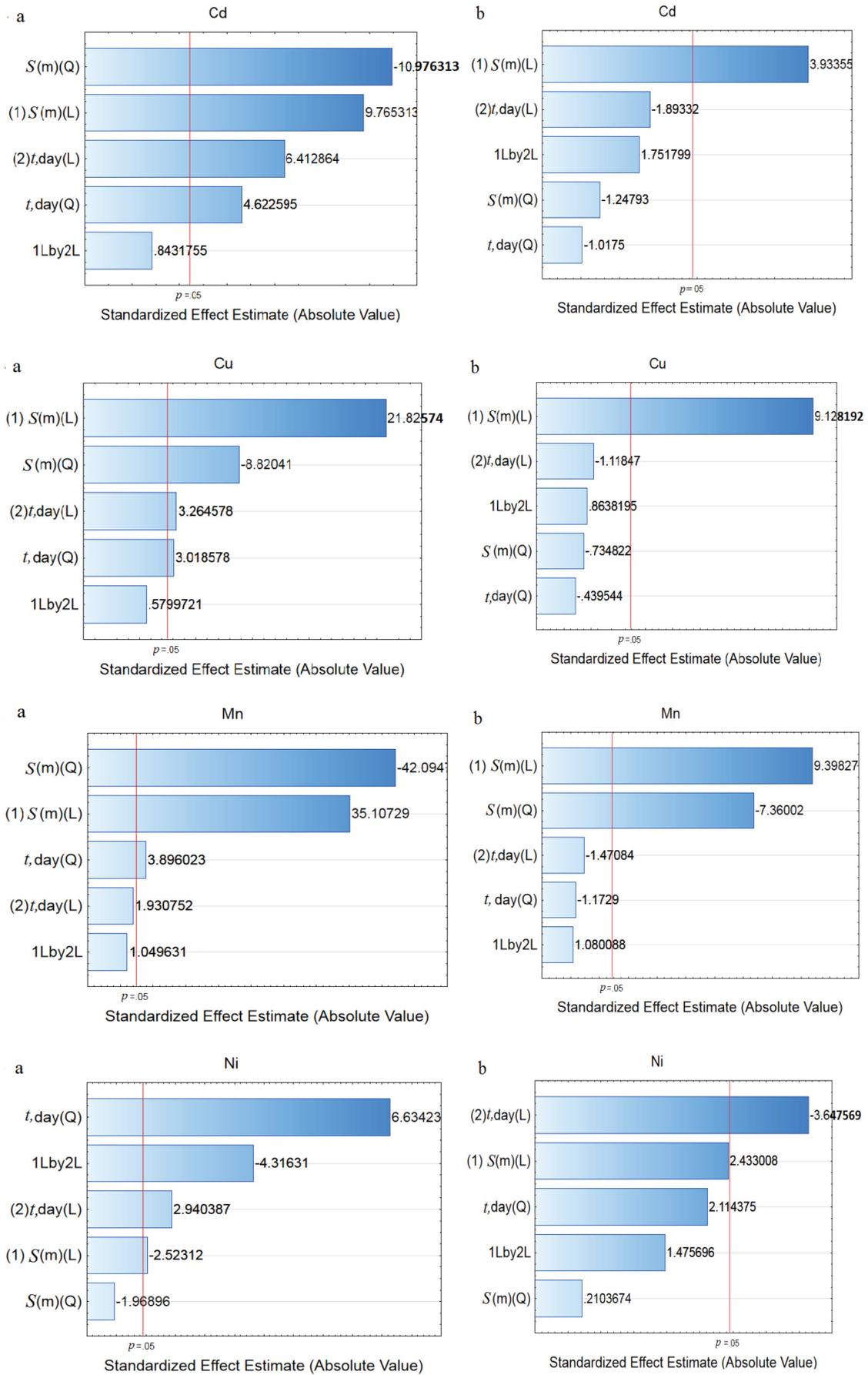


Fig. 5 – Continued on next page

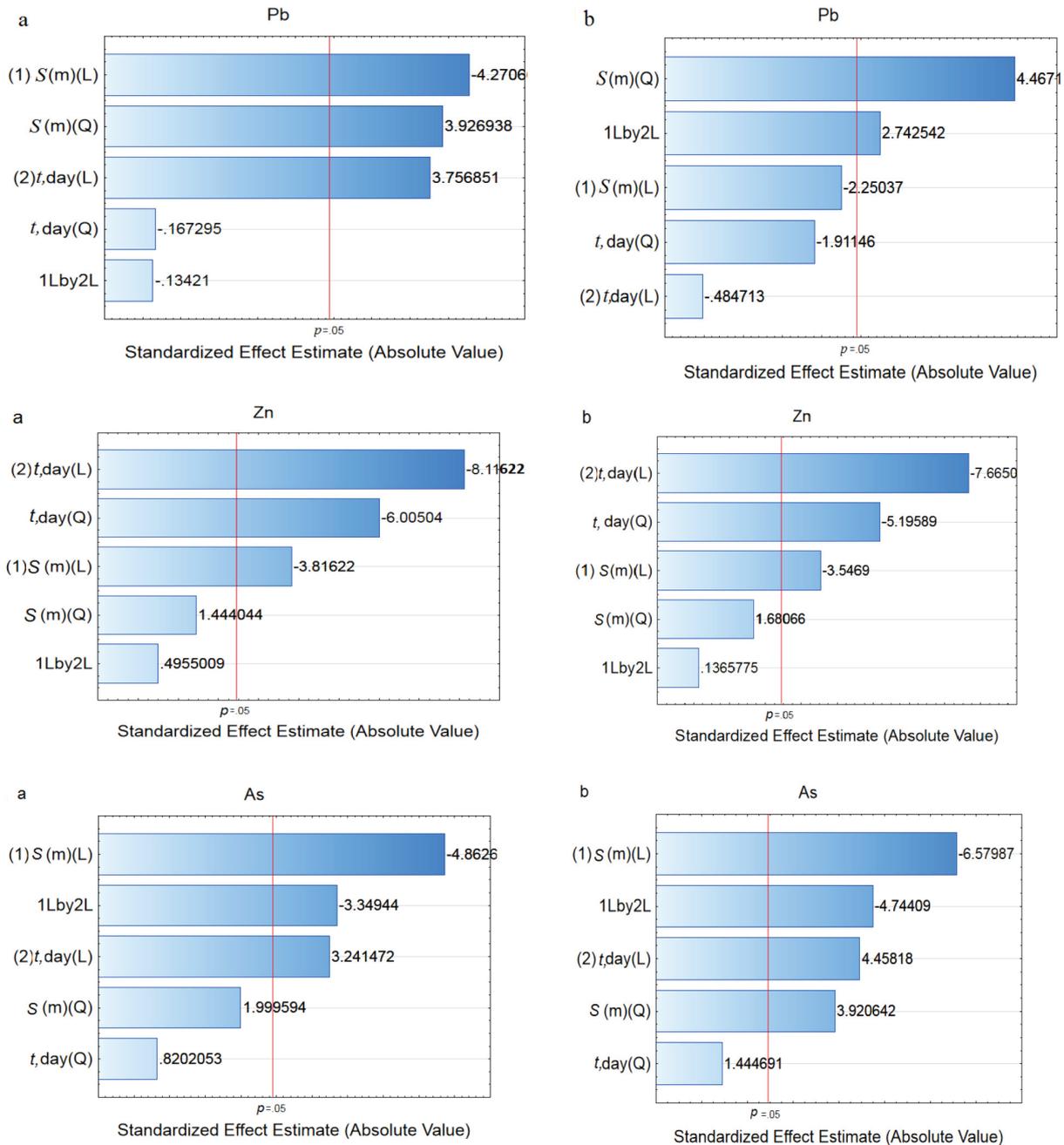


Fig. 5 – Pareto charts for the effects of the element concentration in different leaching time (*t*, days) and different depths (*S*, *m*), (a) Cd, Cu, Mn, Ni, Pb, Zn, and As leaching in deionized water, and (b) Cd, Cu, Mn, Ni, Pb, Zn, and As leaching in synthetic acid rain

means that the leaching results had not linearly increased when the depth and time had changed, but there was an optimal point after which the use of deionized water and synthetic acid rain did not improve the leaching results. Thus, behaviour was well visualized through the three-dimensional plots presented in Figs. 3a and 3b. However, according to Pareto charts, the linear and quadratic term of time and depth showed to be the most significant for the leaching amount of major and minor elements in jarosite waste. For example, the quadratic term was significant for Cd, Ni, and Pb, which means that the

leaching results had not linearly increased when the different time and depth was analyzed, while the linear term showed to be significantly important for the rest of the analyzed elements.

Conclusions

Toxicity leaching test revealed high risk from the jarosite waste tailing dumps in Mitrovica, Kosovo. The heavy metal concentration in the leachates of jarosite samples was high, particularly that of Zn.

Table 4 – Polynomial equations fitted to the results of major elements concentration leached in deionized water and synthetic acid rain as leachant

Response	Model equation ²
Leachant: deionized water	
Ni	$Z = 2.8094 + 0.6527x - 0.1071y - 0.2085x^2 - 0.0347xy + 0.0073y^2$
Pb	$Z = 142.7983 - 65.2128x + 1.7616y + 24.8891x^2 - 0.0645xy - 0.01$
Zn	$Z = 5396.2202 - 1038.8739x + 159.2697y + 271.9854x^2 + 7.0783xy - 11.8033y^2$
As	$Z = 0.4536 - 0.988x + 0.0655y + 0.4901x^2 - 0.0623xy + 0.0021y^2$
Cu	$Z = 62.383 + 76.4699x - 1.3803y - 22.6077x^2 + 0.1127xy + 0.0807y^2$
Cr	$Z = -0.6714 + 10.5696x + 16.3784y - 12.3923x^2 - 2.2132xy - 0.5778y^2$
Mn	$Z = 360.6329 + 922.6969x - 7.5679y - 371.5122x^2 + 0.7026xy + 0.3588y^2$
Leachant: synthetic acid rain	
Ni	$Z = 2.8094 + 0.6527x - 0.1071y - 0.2085x^2 - 0.0347xy + 0.0073y^2$
Pb	$Z = 163.7002 - 74.532x + 1.1687y + 26.3478x^2 + 1.2269xy - 0.1177y^2$
Zn	$Z = 5350.1932 - 1063.7322x + 137.1588y + 322.5079x^2 + 1.9877xy - 10.405y^2$
As	$Z = 0.5296 - 1.2421x + 0.049y + 0.6289x^2 - 0.0577xy + 0.0024y^2$
Cu	$Z = 86.6615 + 43.5113x - 0.2468y - 5.3633x^2 + 0.4782xy - 0.0335y^2$
Cr	$Z = 0.2807 + 0.0522x - 0.01y + 0.0226x^2 - 0.0015xy + 0.0005y^2$
Mn	$Z = 349.8015 + 708.0983x + 3.5212y - 268.8345x^2 + 2.9922xy - 0.4471y^2$

The experimental results proved that the amount of leached Zn, as well as other heavy metals, such as Cd and As, confirms the hazardousness of jarosite waste. This study revealed that the pH values of these solutions are low. However, the applied leaching tests showed that some of the elements in the jarosite waste were easily released, such as Zn, Mn, S and Cd. The low pH values and high EC values favored the mobility of metal species. According to the statistical analysis, heavy metal release is influenced strongly by depth and time. The Pareto charts showed that depth is the most important variable affecting the leaching of major and minor elements under deionized water and acid leaching conditions. Time was also an important variable contributing to the leaching of elements such as Zn and Ni under synthetic acidic rain conditions. Mathematical models that were established with statistically significant terms of $p < 0.05$ for describing the variations between major elements concentration, leaching time, and depth showed that the quadratic term of time and depth was the most significant model for the leaching amount of major elements in jarosite waste. The RSM described the variations of the response as a function of the variations of the variables in the studied range of values. These variations and relationship were well visualized using the three-dimensional surface plotted for the results of element concentration in regard to time and depth.

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