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Metal extraction from *Cetraria islandica* (L.) Ach. lichen using low pH solutions

ANA A. ČUČULOVIĆ[1*#], MIRJANA S. PAVLOVIĆ[2#], DRAGAN S. VESELINOVIĆ[3#] and ŠĆEPAN S. MILJANIĆ[3]

[1]*INEP – Institute for the Application of Nuclear Energy, Banatska 31b, 11080 Zemun,*
[2]*Institute of Nuclear Science "Vinča", Department of Physical Chemistry, P. O. Box 522, 11001 Belgrade and* [3]*University of Belgrade, Faculty of Physical Chemistry, P. O. Box 137, 11001 Belgrade, Serbia*

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Abstract: Extraction of metals (K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn and Sr) from dry *Cetraria islandica* (L.) Ach. lichen was performed using solutions similar to acid rain (solution A – H_2SO_4–HNO_3–$(NH_4)_2SO_4$ and solution B – H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3). The pH values of these solutions were 2.00, 2.58, 2.87, 3.28, and 3.75. Five consecutive extractions were performed with each solution. In all solutions, the extracted metal content, except Cu and Ca, was the highest in the first extract. The highest percentage of the metals desorbed in the first extraction was obtained using solutions with low pH values, 2.00, 2.58, and 2.87. The lowest percentage in the first extraction was obtained using solutions with pH 3.28 and pH 3.75, indicating influence of the H^+ ion on the extraction. According to the results obtained, the investigated metals form two groups. The first group includes K, Al, Ca, Mg, and Fe. They were extracted in each of the five extractions at each of the pH values. The second group includes Ba, Zn, Mn, Cu, and Sr, which were not all extracted at each pH value. The first group yielded three types of extraction curves when the logarithms of extracted metal amounts were plotted as a function of the number of successive extractions. These effects indicate that three different positions (centres) of metal ion accumulation exist in the lichen (due to sorption, complex formation, or other processes present in the tissues).

Keywords: *Cetraria islandica* (L.) Ach. lichen; acid rain; extraction; heavy metals.

INTRODUCTION

Cetraria islandica (L.) Ach. lichen was taken as the model system in the present research. It is one of the 25,000 lichen species in the world and is widely used in the food industry (starch from this lichen can be used for human con-

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[*] Corresponding author. E-mail: anas@inep.co.yu

[#] Serbian Chemical Society member.

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sumption, *e.g.*, for making bread and other starch products), the alcoholic beverage industry, the pharmaceutical industry, the cosmetic industry and in medicine and veterinary science.[1–3] In cold regions, it represents the main flora and is consumed by wild and domestic animals. This indicates that the metals present in the lichen enter the food chains.

Lichens are good bio-indicators of environmental pollution. They can absorb many elements, in concentrations that are many times higher than their physiological demand. The degree of environmental pollution can be deduced from the content of radionuclides and heavy metals in lichens.[4–6] More detail on the origin of the metals and ways of entering the lichen can be found in the cited literature. It has been established that there are two types of polluting substances bound in lichen. Their presence is predominant in ion exchange or complex formation outside the cells and, to a much lesser extent, in the ion distribution inside the cells.

Our research has confirmed that lichens are bio-indicators of environmental pollution by radionuclides, both man-made and natural.[7–9] Earlier research showed that treatment of lichens with distilled water for different durations (from 1 to 24 h, five successive extractions) successfully desorbs part of the amount of ^{137}Cs in plants (49 to 60 %).[10] These results indicate that lichen can be considered as a secondary pollution source of these radionuclides in the environment because acid rain and other types of rainfall extract pollutants from the lichen and transfer them to the surroundings.[11]

Polluting compounds such as SO_2, CO_2, NO_2, NH_4^+ and fluoride have a negative effect on the development and growth of lichens. In highly polluted environments, lichens disappear. A large amount of research has been concerned with the effect of SO_2 and fluoride, showing that the chemical form in which they are introduced into the atmosphere is of biological significance.[12–14] Most lichens are very sensitive to acid rain. A lot of experimental research has dealt with solutions of pH similar to acid rain,[15–17] ranging from pH 1.0 to pH 5.5.

The purpose of this study was to investigate K, Al, Ca, Mg, Fe, Cu, Ba, Mn, and Sr desorption from *Cetraria islandica* lichen, using acid solutions that correspond to acid rain, important in the transfer (possibility of transfer or transfer mechanism) of these elements from the lichen into the environment, *i.e.*, secondary environment pollution. These elements represent essential macroelements (K, Mg, Ca), essential microelements (Cu, Mn, Fe, Sr), and non-essential elements (Ba, Al).[18]

MATERIALS AND METHODS

Apparatus

The K content was determined using a stabilized direct current arc spectrometer built at the Institute of Nuclear Sciences, Vinča.

The other metals were determined by ICP spectrometry, employing a Spectro-flame model, Spectro-Analytical Instruments, Germany.

Furthermore, a Mettler analytical balance (sensitivity 0.1 mg) and a pH meter Iskra MA 5730 were used.

Graduated glass beakers with a volume of 2 l, glass cylinders with a volume of 100 ml (1 ml graduation) and Teflon glasses were used.

Chemicals

H_2SO_4 conc., p.a., and NH_4NO_3, p.a., Merck, HNO_3, conc., p.a., Alkaloid, $(NH_4)_2SO_4$, p.a., Euro Hemija, HF 48 %, p.a., and $HClO_4$ 70 %, p.a., Superlaboratory, pH 4.00 and 7.00 buffer solutions, Carlo Erba, and certified atomic spectral standards, J. T. Baker Analyzed, were used. The solutions were prepared in distilled water. Standard filter paper was used for filtration.

Sample

Bushy lichen *Cetraria islandica* (L.) Ach. samples were collected from the Sinjajevina Mountain, Montenegro, in 1994 for commercial purposes. The lichen samples were prepared for extraction using the procedure described previously.[12]

Extraction solutions

Two types of extraction solutions were used, with compositions similar to acid rain:

1) solution A of composition H_2SO_4–HNO_3–$(NH_4)_2SO_4$ and

2) solution B of composition H_2SO_4–HNO_3–$(NH_4)_2SO_4$–NH_4NO_3.

Both solutions had five variants, *i.e.*, five different pH values: A_1 and B_1 pH 2.00; A_2 and B_2 pH 2.58; A_3 and B_3 pH 2.87; A_4 and B_4 pH 3.28; A_5 and B_5 pH 3.75. Extraction solutions were prepared in the following way: concentrated H_2SO_4 was added to 100 ml of distilled water until the desired pH values of 2.00 (a_1), 2.58 (b_1), 2.87 (c_1), 3.28 (d_1), or 3.75 (e_1) were attained. In the same manner, concentrated HNO_3 was added to 100 ml of distilled water until solutions a_2, b_2, c_2, d_2 or e_2 attained the above pH values. Mixing of solutions a_1 with a_2, b_1 with b_2, c_1 with c_2, d_1 with d_2 and e_1 with e_2 in 1:1 volume ratios yielded solutions a, b, c, d and e with the above pH values. Solutions A_1, A_2, A_3, A_4 and A_5 were obtained by adding 1.00 g of $(NH_4)_2SO_4$ into 100 ml of each of the solutions a, b, c, d and e and subsequently adjusting the pH to the corresponding value using concentrated H_2SO_4. Solutions B_1, B_2, B_3, B_4 and B_5 were obtained by adding 0.500 g of $(NH_4)_2SO_4$ and 0.500 g of NH_4NO_3 into 100 ml of each of the solutions a, b, c, d and e, and subsequently adjusting the pH as in the case of solutions A.

Extraction procedure

Extractions were performed at room temperature (22 °C) with intermittent mixing, so that 200 ml of extraction solution was poured over 10.0 g of dry lichen mass. After the first extraction, the lichen samples were dried at room temperature until constant mass and extracted again with the corresponding solutions. Each sample was extracted five times consequently, using 24 h as the equilibrium time for each extraction. Five successive extractions were performed for each of the A_1–A_5 and B_1–B_5 solutions. All extraction series were repeated twice.

Determining the metal content in samples

The contents of K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn, and Sr were determined in untreated samples and in the solutions after each of the five successive extractions of the same sample. In order to determine the contents of the elements in a sample of lichen before extraction, 0.500 g of the sample was disintegrated by pouring liquid nitrogen over it. It was then completely homogenized and dissolved in a 20 ml mixture of concentrated acids HNO_3/ /$HClO_4$/HF (10:1:1) in Teflon vessels.[6] The solutions were cooled, filled up to the mark in a 100.0 ml volumetric flask and the content of each metal determined.

Procedures for determining the metal concentrations in the solutions have been published in literature.[6,19-21] The elements Ca, Al, Fe, Mg, Zn, Ba, Mn, Sr, and Cu were determined by ICP spectroscopy and K using a U-shaped DC arc plasma spectrometer. The limits of detection, in (ng dm^{-3}) were: 0.3 for K, 0.13 for Ca, 15 for Al, 3.1 for Fe, 0.1 for Mg, 1.2 for Zn, 0.9 for Ba, 0.93 for Mn, 0.28 for Sr and 6.0 for Cu. Individual deviations ranged from 10 % to 30 %, depending on the total metal concentration in the sample and on the percentage of the metal extracted. The determination error was thus taken as the standard deviation of 20 individual measurements at the same pH with same extracting agent. This was used in the construction of the curves.

RESULTS AND DISCUSSION

The results for extracting agents A and B are given in Tables I and II, respectively, as the mean values from two series of measurements. The tables contain: a) the total metal contents in the lichen samples and b) the total metal content, in %, extracted by each extraction, as well as the total amount extracted by all five partial extractions.

High amounts of Ca and K were found in the lichen, while the amounts of Cu, Sr, and Mn were low (Table I). The highest percentages of the extracted metals in the first extraction, as compared to the second extraction, were obtained for K, Mg, Zn, and Mn. These differences between these two extractions were not as high for the other metals, except for Cu. This element was not extracted in the first extraction, or in any of the extractions at pH 3.28 or 3.75. This indicates its strong bonding to the tissue components, most probably inside the cell.

The contents of the investigated metals in the lichen before desorption are given in Tables I and II. The highest concentrations in the lichen were those of Ca and K. The lowest were those of Cu, Mn, and Sr.

The change of the sorbed amount of substance, C_x, in the sorbent with the extraction number, n_x, for successive extractions with the same volume of extraction agent is given by the following equation:[10]

$$\ln C_x = \ln C_0 - a n_x \tag{1}$$

where C_0 is the content of the sorbed substance before extraction and a is a constant.

It follows from Eq. (1) that the logarithm of the amount of the sorbed substance in the solid phase is a linear function of the number of successive volumes used for extraction. In a real system, it is valid only if one type of sorption exists or if one of the types is dominant, so that the other ones can be neglected. If this is not so, a deviation from the straight line occurs, indicating that the sorbent can bind the sorbed substance through different types of sorption, *i.e.*, at different sorbent positions.

Three types of curves were obtained using Eq. (1). The first type was a straight line, with the value of $\ln C_0$ being obtained by extrapolation and corresponding to 100 % metal content in the sorbent (lichen) before extraction, Fig. 1.

This indicated the existence of only one dominant type of sorption from which most of the metal was extracted.

TABLE I. Initial contents of metals in the lichen before desorption and percentages of desorbed metals after each successive desorption by solutions A and B

Amount of the desorbed element in successive desorption solutions relative to the initial content, %											
No. of desorption	pH	Initial content, μg g^{-1}									
		K		Ca		Al		Fe		Mg	
		1475±75		6880±345		450±45		265±26		260±26	
		Solutions									
		A	B	A	B	A	B	A	B	A	B
I	2.00	60	88	19	25	6.8	11	8.5	14.0	43	55
	2.58	61	89	11	16	6.0	8.1	4.8	7.0	45	57
	2.87	60	86	9.1	14	8.7	8.7	2.6	3.9	43	58
	3.28	52	89	7.7	11	4.8	8.7	1.6	2.9	35	55
	3.75	52	85	7.5	10	6.3	6.0	1.5	2.3	36	54
II	2.00	2.1	4.9	12	21	1.2	1.5	2.9	6.3	2.2	4.9
	2.58	2.5	4.9	7.8	11	1.6	1.4	3.3	5.0	3.1	4.8
	2.87	2.8	4.7	6.7	10	2.0	2.9	3.5	4.2	3.0	6.0
	3.28	2.3	3.9	4.4	6.9	1.5	2.5	1.2	2.0	3.0	6.0
	3.75	2.9	4.0	4.7	6.6	1.9	2.7	1.2	1.4	3.3	5.8
III	2.00	0.31	0.5	16	21	0.7	1.9	2.3	5.0	1.7	3.9
	2.58	0.16	0.6	8.0	12	*	1.7	2.3	3.9	1.9	3.1
	2.87	0.18	0.49	6.8	11	1.0	1.8	2.6	3.9	1.6	3.3
	3.28	0.10	0.6	5.0	6.5	0.6	0.8	1.2	2.3	1.4	3.7
	3.75	0.19	0.45	4.3	5.5	1.9	1.1	0.8	2.1	1.8	3.1
IV	2.00	0.08	0.6	16	20	0.6	1.2	1.7	4.2	1.5	3.5
	2.58	0.05	0.34	9.0	11	0.22	4.6	1.9	2.6	1.4	3.7
	2.87	0.07	0.35	6.3	10	0.6	1.6	1.9	3.6	1.3	3.5
	3.28	0.07	0.5	5.6	6.6	0.5	0.7	1.4	2.1	1.8	4.0
	3.75	0.08	0.31	5.3	5.4	0.8	1.3	0.8	1.5	2.5	3.0
V	2.00	0.19	0.5	24	18	0.8	1.1	2.1	3.0	3.1	3.9
	2.58	0.14	0.24	13	10	0.31	*	1.9	2.2	2.9	3.2
	2.87	0.12	0.42	10	9.1	1.0	0.4	2.2	2.6	4.1	4.0
	3.28	0.08	0.27	8.5	6.2	0.6	0.22	2.1	1.6	2.5	2.5
	3.75	0.12	0.24	7.0	4.7	1.0	0.53	0.8	1.1	3.9	2.1
		Total amount of the desorbed elements from lichen, %									
–	2.00	63	94	87	105	10	17	18	32	52	71
	2.58	63	95	49	60	8	16	14	21	55	72
	2.87	63	92	39	54	13	15	13	18	53	75
	3.28	55	94	31	37	8	13	8	11	44	73
	3.75	55	90	29	32	11	12	5	8	48	68

*Concentration in the extract was below the detection limit

The second type was also a straight line (Fig. 2) but with the ln C_0 value below 100 %, *i.e.*, less than the amount of the metal in the sorbent. This indicated the existence of at least two types of sorption. In one type, the metal was very strongly bound in the lichen, causing the amount of the extracted metal to be lower than in the other type of sorption.

TABLE II. Initial contents of metals in the lichen before desorption and percentages of the desorbed metals after each successive desorption by solutions 1, 2 and 3

Amount of the desorbed element in successive desorption solutions relative to the initial content, %											
		Initial content, μg g^{-1}									
No. of desorption	pH	Zn		Ba		Mn		Sr		Cu	
		30±3		13±1		10±1		10±1		6.0±0.6	
		Solutions									
		A	B	A	B	A	B	A	B	A	B
I	2.00	40	40	4.6	4.6	48	58	16	28	*	*
	2.58	42	40	4.6	3.1	52	50	14	24	*	*
	2.87	27	39	6.1	4.6	50	50	16	20	*	*
	3.28	13	20	1.5	6.1	24	46	8.0	20	*	*
	3.75	27	17	4.6	7.7	34	*	10	20	*	*
II	2.00	*	*	*	*	*	*	2.0	*	*	33
	2.58	*	*	*	*	*	*	2.0	*	*	*
	2.87	*	*	*	*	4.0	6.0	2.0	8.0	*	3.3
	3.28	*	*	*	*	*	6.0	*	*	*	*
	3.75	*	*	*	4.6	*	*	*	*	*	*
III	2.00	*	*	*	*	*	*	2.0	*	*	*
	2.58	*	*	*	*	*	*	2.0	*	*	17
	2.87	*	*	*	*	*	4.0	*	6.0	*	17
	3.28	*	*	*	*	*	*	*	*	*	*
	3.75	*	*	*	*	*	*	*	*	*	*
IV	2.00	*	*	*	*	*	*	2.0	*	*	*
	2.58	*	*	*	*	*	*	*	*	*	*
	2.87	*	*	*	*	*	4.0	6.0	6.0	*	20
	3.28	*	*	*	*	*	*	*	*	*	*
	3.75	*	*	*	*	*	*	*	*	*	*
V	2.00	13	*	*	*	*	*	6.0	*	67	*
	2.58	*	*	*	*	*	*	5.0	*	17	*
	2.87	*	*	*	*	*	*	*	8.0	17	10
	3.28	*	*	*	*	*	*	*	*	*	*
	3.75	*	*	*	*	4.0	*	4.0	4.0	*	*
		Total amount of the desorbed elements from lichen, %									
–	2.00	53	40	5	5	48	58	28	28	67	33
	2.58	42	40	5	3	52	50	23	24	17	17
	2.87	27	39	6	5	54	64	24	48	17	50
	3.28	13	20	2	6	24	52	8	20	*	*
	3.75	27	17	5	13	38	*	14	24	*	*

*Concentration in the extract was below the detection limit

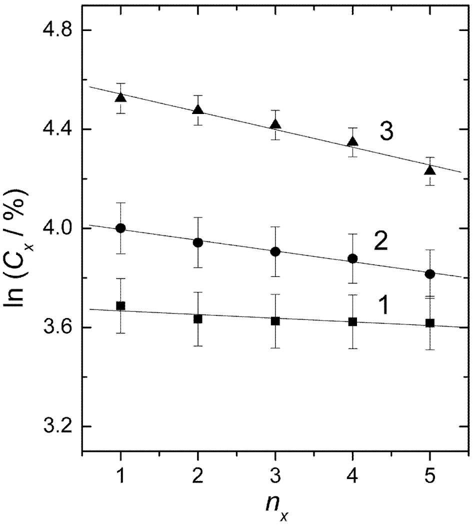

Fig. 1. Logarithm of the amount of sorbed metal *vs*. desorption number. 1) K, solution A, pH 2.00; 2) Mg, solution A, pH 2.58; 3) Ca, solution A, pH 3.28.

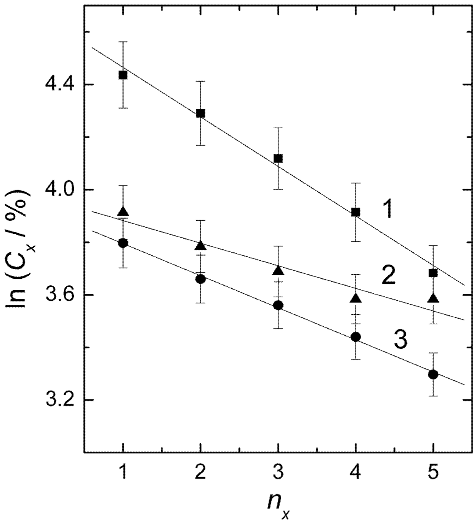

Fig. 2. Logarithm of the sorbed amount of metal *vs*. desorption number. 1) Ca, solution B, pH 2.58; 2) Mg, solution B, pH 3.28; 3) Mn, solution B, pH 2.87.

The third type of curve was not a straight line. This indicated two or more types of sorption processes, without a dominant type.

The C_0 values obtained from the straight lines according to Eq. (1) are given in Table III. In 38.0 % of the cases, a single sorption process was present, whereas two or more processes were present in 62.0 % of the cases.

TABLE III. C_0 values determined from the plots according to Eq. (1) (relative to the initial content, %)

Metal	pH	Solution A	Solution B
K	2.00	39.7	*
	2.58	38.9	*
	2.87	*	*
	3.28	*	*
	3.75	*	*
Ca	2.00	*	*
	2.58	106.7	104.6
	2.87	102.0	103.0
	3.28	101.5	98.5
	3.75	99.9	96.5
Al	2.00	93.7	90.9
	2.58	93.7	94.6
	2.87	91.8	92.3
	3.28	95.6	91.8
	3.75	94.6	94.6

TABLE III. Continued

Metal	pH	Solution A	Solution B
Fe	2.00	93.7	90.5
	2.58	97.0	95.6
	2.87	99.5	99.5
	3.28	100.5	99.0
	3.75	99.0	99.3
Mg	2.00	59.1	49.9
	2.58	56.8	47.0
	2.87	60.0	47.5
	3.28	66.4	50.2
	3.75	66.7	49.7
Sr	2.87	87.8	88.2
Mn	2.87	–	52.5

*Non-linear function

A total of 308 samples were analysed and the contents of metals determined using both types of extracting agent. The results obtained with solutions A and B are presented in Tables I and II, for five different pH values and five successive extractions. Summarising, 81.4 % of the total metal content was extracted from the lichen at the lower pH values (2.00, 2.58, and 2.87), only 3.6 % at higher pH values (3.28 and 3.75) and 15 % of the metals were equally extracted at any of the employed pH values. These results indicate an effect of H^+ ions on the extraction of metals from the lichen. This is also confirmed by the total amount of metals extracted from the lichen (Tables I and II). The highest percentages of the metals were extracted by the more acidic solutions (pH 2.00–2.87).

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ИЗВОД

ЕКСТРАКЦИЈА МЕТАЛА ИЗ ЛИШАЈА *Cetraria islandica* (L.) Ach. РАСТВОРИМА НИСКИХ pH ВРЕДНОСТИ

АНА А. ЧУЧУЛОВИЋ[1], МИРЈАНА С. ПАВЛОВИЋ[2], ДРАГАН С. ВЕСЕЛИНОВИЋ[3] И ШЋЕПАН С. МИЉАНИЋ[3]

[1]ИНЕП – Институт за примену нуклеарне енергије, Банатска 31б, Земун, [2]Институт за нуклеарне науке 'Винча', Лабораторија за физичку хемију, п. пр. 522, 11001 Београд и [3]Универзитет у Београду, Факултет за физичку хемију, п.пр. 137, 11001 Београд

Испитивана је екстракција метала K, Al, Ca, Mg, Fe, Cu, Ba, Zn, Mn и Sr сорбованих у узорцима лишаја *Cetraria islandica* (L.) Ach. киселим растворима (раствор А – H_2SO_4–HNO_3––$(NH_4)_2SO_4$ и раствор Б – H_2SO_4—HNO_3–$(NH_4)_2SO_4$–NH_4NO_3) сличним киселим кишама. pH вредности раствора су износиле 2,00; 2,58; 2,87; 3,28 и 3,75. Урађено је пет сукцесивних екстракција са сваким раствором. Најуспешније су прве екстракције наведеним растворима, осим код Cu и Ca. Највећи проценат десорпције метала је првим екстракцијама када се користе раствори ниских pH вредности 2,00; 2,58 и 2.87. Нижи проценти код првих екстракција су добијени коришћењем раствора pH 3,28 и 3,75 што указује на утицај H^+ јона на екстракцију. Испитивања су показала да се десорбовани метали могу поделити у две групе. Првој групи припадају K, Al, Ca, Mg и Fe, који се десорбују свим екстракцијама растворима свих pH вредности. Другој групи припадају Ba, Zn, Mn, Cu и Sr који нису десорбовани свим екстракцијама и при свим pH вредностима. Логаритамска зависност садржаја метала у функцији од броја десорпције указује на постојање три типа кривих, тј. на три начина везивања и три јачине везе метала у лишају.

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