

PHYSICAL CHEMISTRY
OF SURFACE PHENOMENA

^{137}Cs Desorption from Lichen Using Acid Solutions*

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Abstract—Desorption of ^{137}Cs from samples of *Cetraria islandica* lichen using HCl (A) and HNO₃ (B) acid solutions with pH values from 2.00 to 3.75 was investigated. After five consecutive desorptions lasting 24 h it was shown that between 52.2% (solution B pH 3.28) and 72.2% (solution A pH 2.00) of ^{137}Cs was desorbed from the lichen and the initial desorptions were the most successful. Lichen desorbed with the stated solutions did not undergo structural changes. The amount of absorbed water from solutions A and B, used for desorption from lichen, in relation to the starting volume (expressed in %) showed that solution concentration did not take place. Lichen act as neutralizing agents because the pH of the lichen thallus is higher than the pH value of the solution used

DOI: 10.1134/S0036024409090234

INTRODUCTION

Lichen can adopt and accumulate polluting substances (radionuclides, heavy metals, pesticides) in tissue or on the thallus surface [1]. After the Chernobyl accident (1986) it was shown that lichen sorption of radionuclides from air was dominant, tolerance to radionuclides was passive, and hyper-accumulation of radionuclides in lichen was the consequence of the properties of the genetically independent organism and that lichen tissue reflected the environment composition [2]. Radionuclides entering the lichen body become sources of internal radiation and also radiation sources for other related organisms. Lichen are natural reservoirs of matter that can be periodically released [3–5]. Thus, the investigation of desorption of accumulated metals such as ^{137}Cs with solutions similar to acid rain with a desorption dynamics of successive solution application is important.

EXPERIMENTAL

200 ml of solutions (A) HCl and (B) HNO₃ was poured over 10 g of dry *C. islandica* lichen, collected from the Sinjajevina Mountain, Montenegro, for commercial purposes in 1994. Solutions A, i.e., B were made by adding concentrated HCl or HNO₃ to 200 ml of water until a desired pH value of 2.00, 2.58, 2.87, 3.28, and 3.75 was reached. Samples were consecutively desorbed with solutions five times and desorption series were repeated twice. Desorptions were performed at room temperature lasting 24 h. After each desorption, following filtration, lichen samples were

dried at room temperature until they became a constant mass. Activity levels of ^{137}Cs were measured in samples before and after each desorption on an ORTEC-AMETEK gamma spectrometer with 8192 channels, resolution of 1.65 keV and efficiency of 34% at 1.33 MeV ^{60}Co with a measurement error below 5%. The specific activities (Bq/kg) were calculated. All desorptions were repeated twice and the mean values are given in the Tables 1, 2. The sorbent absorbed a certain volume of water from the added desorption solution after each of the five desorptions. The remaining desorption solution was strained through filter paper and its volume was measured. Knowing the starting and measured solution volumes obtained after each desorption, the absorption percentage of desorption liquid by the lichen was calculated. The pH of the lichen thallus was determined by destructing 100 g of lichen thallus with liquid nitrogen and mixing it with 4 ml of de-ionized water (pH 5.77) followed by treatment in a centrifuge at 100 g 10 min. The solution pH value was measured on a pH meter Iskra MA 5730 [6, 7].

RESULTS AND DISCUSSION

Activity levels of ^{137}Cs in samples of *C. islandica* lichen before desorption were from 1786 to 2994 Bq/kg. After five consecutive desorptions, each lasting 24 h, at room temperature, the most of 58.1% solution B (pH 2.00) and of 72.2% solution A (pH 2.00) of the starting value of ^{137}Cs was desorbed (Table 1). The first desorption in relation to the total amount of desorbed ^{137}Cs is smaller than 50.0% in all cases, except case pH 2.00 solution A. The pH

*The article is published in the original.

Table 1. Total desorbed ^{137}Cs from lichen *C. islandica* (y , %) and percentage of remaining ^{137}Cs in lichen after each desorption using solutions HCl (A) and HNO_3 (B) (in relation to the starting content in lichen, 100%). Room temperature ($\sim 22^\circ\text{C}$). Desorption time 24 h for each desorption. Mean measurement error, 2.4%

pH	$y(\text{A})$	$y(\text{B})$	Solution A					Solution B				
			I	II	III	IV	V	I	II	III	IV	V
2.00	72.2	58.1	46.4	42.7	39.0	37.3	27.8	60.3	49.9	45.8	44.4	41.9
2.58	64.8	56.6	54.1	43.8	43.6	42.3	35.2	61.7	50.0	47.9	47.2	43.4
2.87	60.6	53.1	56.2	44.8	43.7	41.0	39.4	65.0	57.6	51.5	47.4	46.9
3.28	58.0	52.2	65.6	47.6	46.2	46.1	42.0	61.7	56.3	50.1	49.5	47.8
3.75	56.4	53.7	59.1	52.1	48.4	47.8	43.6	65.3	59.0	51.3	50.0	46.3

value has an influence on ^{137}Cs desorption from lichen.

Application of the Origin 7.0 software [8] gave curves showing an exponential dependence of the remaining amount of ^{137}Cs , on the number of successive desorptions, regardless of the solution pH. This is shown in Fig. 1.

The change of the sorbed substance amount, c_x , in the sorbent with the desorption number, n_x , for successive desorptions with the same volume of desorption agent is given by the equation formulated for desorption of ^{137}Cs with water [5]:

$$\ln c_x = \ln c_0 - an_x \quad (1)$$

where c_0 is the content of the sorbed substance (^{137}Cs) before desorption and a is a constant. Application of Eq. (1) on the values given in Table 1 resulted in two types of curves. From Eq. (1), it follows that the dependence of the logarithm of the amount of sorbed substance in the solid state is a linear function of the number of successive volumes employed during extraction. For real systems, this is valid when only one type of sorption exists, or if one type is dominant,

Table 2. Values of the starting activity of ^{137}Cs (c'_0), determined by extrapolation of the curves in Fig. 2, given as a percentage in relation to the experimentally determined values of c_0 (100%)

Desorption solution	pH	c'_0 , %
A	3.75	61.6
B	2.87	68.4
B	3.28	63.4
B	3.75	69.8

Note. Solution compositions are given in the Experimental.

so that the others can be disregarded. In other cases, deviations from a straight line occur, indicating that the sorbent can bind the sorbed substance by different types of sorption, i.e. different sorbent points. A linear dependence was obtained using solutions A for pH 3.75 and B for pH 2.87, 3.28, and 3.75. This indicated that one sorption type is dominant in these cases. Extrapolation of the obtained linear dependences (Fig. 2) gave values denoted as c'_0 in Table 2. They are lower than the corresponding starting values (100%) indicating the existence of a type of ^{137}Cs sorption that greatly differs in bonding intensity i.e. bonding energy. In all the other cases, curves given in Fig. 3 for selected examples were obtained. They indicate the existence of at least two types of sorption, but when corresponding desorbants are used, desorption of ^{137}Cs is not separated enough to be dominant. Also, a type of ^{137}Cs sorption with high bonding energy cannot be excluded. Desorptions performed with solution A pH 2.00, 2.58, 2.87, and 3.28, B pH 2.00 and 2.58 give this curve type.

Table 3. Changes in pH of lichen thallus after treatment with desorption HCl (A) and HNO_3 (B) solutions

pH	A	B
2.00	2.54	2.66
2.57	3.17	3.28
2.87	3.59	3.75
3.28	4.18	4.26
3.75	4.74	4.72

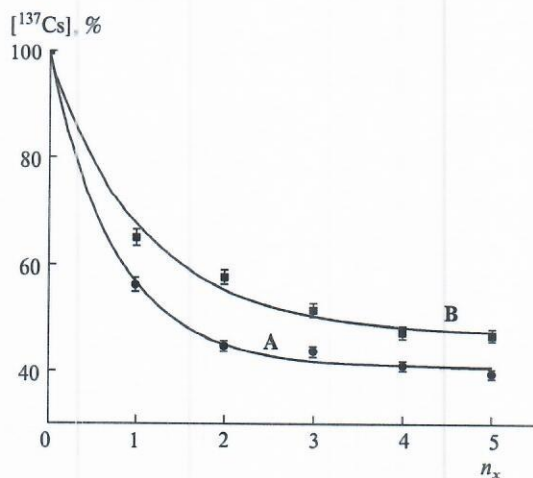


Fig. 1. ^{137}Cs content in lichen (%) in relation to the starting content (100%), in dependence on the successive desorption number (n_x) using solutions A and B pH 2.87, for an equilibrium time of 24 h.

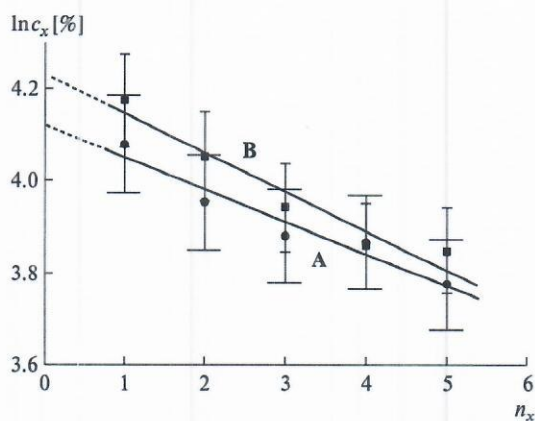


Fig. 2. ^{137}Cs content (%) in the sorbent (*C. islandica*) as a function of the number of successive desorption (n_x) with solutions A at pH 2.87 and B at pH 3.75 according to Eq. (1).

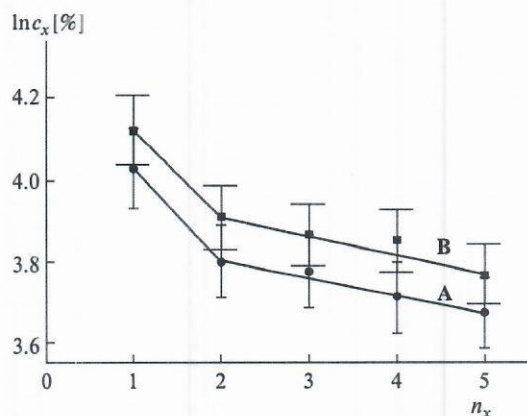


Fig. 3. ^{137}Cs content (%) in the sorbent (*C. islandica*) as a function of the number of successive desorptions (n_x) with solutions A at pH 2.87 and B at pH 2.58, according to Eq. (1).

The amount of absorbed water from solutions A and (B) used for desorption of *C. islandica* lichen in relation to the starting volume ($20 \pm 1.5\%$) shows that the solution concentration effect is not present, and all noted changes are within the margin of error. Table 3 gives measured pH values of the thallus after treatment with desorption solutions A and B. The pH value of non-treated lichen thallus is 4.83. These results show that lichen act as neutralizing agents since in all cases the thallus pH is higher than the pH value of the solution used. Processes leading to this could be neutralization with inorganic or organic bases, but also possible utilization of acid from desorption solutions in decomposition processes of organic compounds in the lichen tissue.

CONCLUSIONS

The obtained results indicate that lichen can be considered sorbents which, due to their complex structure in relation to inorganic or synthetic organic sorbents, can have two or more sorption centers of different affinities towards the $^{137}\text{Cs}^+$ cation.

Desorption of ^{137}Cs using acid solutions indicates that lichen with previously accumulated ^{137}Cs become secondary sources of pollution with acid rain, all the more as the rain is more acid. This desorption process does not damage lichen to a degree that could be established, as the amount of sorbed water does not change significantly with changes of the solution pH and the number of desorptions.

Since ^{137}Cs is one of the alkaline elements and they behave similarly, the conclusions reached in this work from experiments using ^{137}Cs can be applied to other alkaline element cations.

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