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Salvinia natans L. as an Extractor of Rhenium from Aqueous and Industrial Solutions

O. D. Bozhkov* and Chr. Tz. Tzvetkova

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,
Acad. G. Bontchev Str., bl. 11, 1113 Sofia, Bulgaria
*E-mail: bozhkov@svr.igic.bas.bg

Abstract

The dynamics and the capacity of water fern (*Salvinia natans L.*) for rhenium uptake from aqueous and acidic industrial solutions were investigated. It was established that the plant accumulates rhenium by two mechanisms- physical sorption and intracellular metabolite uptake. The roots accumulate 93.2% of the rhenium by sorption and 6.8% - by the metabolite mode, while the leaves accumulate 68% of the rhenium by sorption and 32% by metabolite uptake. It was established that intracellular uptake of rhenium from acidic industrial solutions reached the maximum after 4 hours and did not change during the following 24 hours. The physical sorption of rhenium is slower than the metabolite uptake- the maximum of physically accumulated rhenium was reached after 24 hours. This value did not undergo any changes over 7 days. It is of interest that the dried (dead) *Salvinia natans L.* accumulates by sorption significant amounts of rhenium from aqueous solutions. The rhenium thus sorbed is easily washed out with water from the plant mass. After drying, the water fern could be reused for rhenium sorption.

Key words: Rhenium, Phytoextraction, *Salvinia natans L.*, Aqueous and industrial solutions.

Introduction

Rhenium- one of the most expensive metals in the world market (4 500$ for 1 kg Re) is produced as a byproduct of pyro- and hydrometallurgical processing of molybdenum and copper concentrates. During these processes, part of rhenium is lost and dispersed as volatile Re_2O_7, and as ReO_4^- ions in surrounding soils and waters (Abisheva *et al*, 2011). How could the scattered rhenium be collected? Plant biosphere has been found to be a natural extractor and concentrator of Re from soils and waters (Bozhkov *et al*, 2006), (Bozhkov *at al*, 2007). Obviously, the plant biosphere is a source for rhenium recovery. The extraction of metals by plants is known as phytomining (Sheoran *at al*, 2009). The phytomining is profitable when the used plant species accumulate 1 000 ore more g of metal per 1 t of dry mass. These are the so-called hyperaccumulators. The authors found four rhenium hyperaccumulators, which are suitable for extraction of rhenium from soils of copper ore dressing and work processing regions (Bozhkov *at al*, 2011), (Bozhkov *at al*, 2012). For the direct extraction of rhenium from waste waters and industrial solutions, it is necessary to find an aquatic plant that is able to accumulate the metal. Our preliminary investigations showed that the water fern *Salvinia natans L.* could be used for such purposes (Tzvetkova and Bozhkov, 2009). The plant is a free floating freshwater macrophyte with many green leaves, which grows rapidly in ponds, lakes and wastewater bodies. It possesses several advantages, such as high productivity and heat tolerance in a broad range and could be easily collected. Some species of *Salvinia* have been successfully applied for the removal of Pb (II), Cd (II), Hg (II), Cu (II), As (V), etc. from waste waters (Dhir, 2009). The metal uptake by *Salvinia* occurs through a biological or/and physical mode. The metal uptake by physical processes is fast and involves adsorption, ionic exchange and chelation. The high sorption capacity of the plant attributed to its large specific surface (264 m^2 /g) and the high content of carbohydrates (48.50%) and carboxyl groups (0.95 mmol/g) (Sanchez-Galvan, 2008). It was also shown that the non-living biomass of *Salvinia* exhibits a high potential to remove heavy metals (Sune, 2007). Water fern is capable of sorbing both cations and anions. The different mechanisms of sorption are discussed in the review (Rahman and Hasegava, 2011). Biological processes, such as intracellular uptake (transport through plasmalemma into cells), are comparatively slow, but they help in the subsequent translocation of metals (cations and anions) from roots to leaves (Rahman and Hasegava, 2011).

The bioavailable (water-soluble) species of Re in soils and waters is perrhenate anion (ReO_4^-) (Bozhkov *et al*, 2006). In this respect, rhenium resembles arsenic, which is present in aqueous solutions in the anionic forms AsO_4^{3-} and AsO_3^{3-}. Besides intracellular uptake in aquatic plants, the arsenic is accumulated by physicochemical adsorption on root surface, from which it can be easily washed out (Robinson et al, 2006). Our investigations on Re uptake by *Salvinia natans L.* showed that the rhenium content in unwashed plant samples exceeds that in washed samples immersed in the same solution. Our hypothesis that part of Re is surface-bound (like arsenic) comes from the observation that some quantity of Re was rapidly removed by rinsing the plant mass. This got us to thinking that part of Re is accumulated in water fern by sorption. Further, the authors consider that unwashed plant samples contain the total amount of accumulated rhenium, while the washed samples contain the intracellular accumulated rhenium. The differences between total and metabolic accumulated rhenium gives the amount of rhenium accumulated by sorption.

In our previous work we studied the intracellular uptake of Re in *Salvinia natans L.* from aqueous solutions spiked with Re and from waste acidic rhenium containing industrial solutions from the copper mine Asarel, Bulgaria (Tzvetkova and Bozhkov, 2009). The results showed that maximum accumulation of Re in water fern from aqueous solutions was reached in 18 days and didn’t undergo more changes in time. The dynamic of Re accumulation in water fern from acidic industrial solutions is faster than from aqueous media. The maximum of Re concentration in *Salvinia* was reached after 24 h, then gradually decreases after a certain period of time, as the plant died and released the accumulated rhenium in the surrounding solution. The aim of present study is to investigate the total uptake of Re in *Salvinia natans L.* (by sorption and by metabolic path) from aqueous and industrial solutions.

Experimental

The studies of the bioaccumulation of rhenium in the water fern were performed under static conditions, close to the real terms for phytoextraction in the nature.

Procedures for studying the dynamics of rhenium accumulation by sorption and by intracellular uptake in *Salvinia natans L.* from aqueous and industrial solutions

Two separate portions of well developed water fern, previously cultivated in a green house, were placed in two glasses, each one containing 250 ml solution with rhenium concentration as follows:

1. An aqueous solution with C_{Re}=40 µg Re/ml, prepared by diluting of 10 ml aliquot of a stock solution of rhenium with C_{Re}= 1000 µg Re/ml with 240 ml tap water.

2. A waste solution from the mine Asarel with C_{Re}= 0.420 µg Re/ml and pH=2

The volume of the solutions was kept constant during the experiments by the addition of tap water in the first case and waste solution in the second case. Two portions of the plant samples were removed from each of the solutions after different periods of time. The first portion of water fern was drained on a Buchner funnel and then it was dried at 70^{o}C in a drying oven to constant weight. So treated plant sample contains the total amount of rhenium accumulated by sorption and by intracellular uptake. The second portion of *Salvinia natans L.* was placed in a glass funnel and was rinsed with 6 portions of 5 ml distilled water in order to wash away the rhenium accumulated by sorption. Then the plant mass was drained on a Buchner funnel and was dried at 70^{o}C to constant weight. This sample should contain the rhenium accumulated only by metabolic uptake. The two portions of the dried plant samples were incinerated at 480^{o}C and rhenium was extracted from the ash by an alkaline solution (Bozhkov and Borisova, 2003). The rhenium content in both leaching solutions was determined according to a semiquantitative highly sensitive and selective catalytic method for rhenium determination with N, N-dimethyldithiooxamide (DMDTO) (Bozhkov and Borisova, 1996). The difference between the concentrations of total and metabolic accumulated rhenium gives the Re accumulated by sorption.

Procedure for studying the distribution of accumulated rhenium in roots and leaves of *Salvinia natans L.*

A portion of water fern was placed in aqueous solution with C_{Re}=40 µg Re/ml. After seven- day stay, the plant samples were removed from the solution and the roots of water fern were separated from the leaves. In order to determine the amount of accumulated rhenium by sorption and by metabolic uptake in the two parts of the plant, the roots samples and the leave samples were treated according то to the above mentioned procedures. The rhenium concentration in the roots (resp. leaves) rinsed with water shows the intracellular accumulated rhenium, while the samples incinerated without preliminary rinsing contain the total amount of accumulated rhenium - by sorption and by metabolic uptake.

Procedure for studying of the sorption capacity of the dried (dead) *Salvinia natans L.* for Re

Salvinia natans L. was removed from the aquarium and was dried in an oven at 70^{o} C to a constant weight. Dried water fern was placed in an aqueous solution with C_{Re} = 40 µg Re / ml. After 24 h stay, the samples were taken out and dried to constant weight as described above. Then, two portions of the dried samples were accurately weighed. One was rinsed with 6 portions of 5 ml of water each, followed by its ashing. The other was directly incinerated without rinsing. The quantity of Re was determined as described above.

Results and Discussion

The studies of the dynamics of Re accumulation in *Salvinia natans L.* by metabolic and sorption uptake from aqueous solution with C_{Re}= 40 µg Re/ml at different treatment of the samples were performed as described in the procedure. The results are shown in Table 1. As the results show, after 7 days most of the rhenium in *Salvinia natans L.* is accumulated by sorption. Sorption processes are much faster than the intracellular uptake. The maximum of Re accumulated by sorption is reached after 24 hours and does not change significantly over the course of 7 days. Probably, the sorption capacity of *Salvinia natans L.* is limited by the availability of adsorption sites. The experiments showed that rhenium accumulated by sorption can be easily washed from the surface of the plant with water. This indicates a weak connection between the perrhenate ions and the sorption sites on the surface of the water fern. Metabolic accumulation of rhenium gradually increases with increasing contact time between *Salvinia natans L.* and solution and reaches a 37.3 µg Re/g dry mass after 7 days. This is logical, since the perrhenate ions have to pass through the plant roots, then part of them should be transported through the plasmalemma into the leave cells. It is known that movement of the metals in the plants takes place by the so-called active transport involving its binding with various specific proteins, which serve as a vehicle. For this reason, the intracellular uptake of the metals is comparatively slow (Greger, 2004).

The distribution of rhenium accumulated by sorption and by metabolic uptake for 7 days in the roots and leaves of *Salvinia natans L.* from a solution with C_{Re}=40 µg Re/ml is shown in Table 2. The results of Table 2 show that rhenium preferably accumulates in roots by sorption (93.2% of total accumulated rhenium in roots). This can be explained by the large surface area of the root hairs of *Salvinia Natans L.*, which are fully submerged in the solution. Only 6.8% of rhenium accumulates by intracellular uptake in the roots, because, as is known from our previous investigations, the perrhenate ions prefer to accumulate in the green parts of the plants, such as the leaves of the water fern. The results of the experiments show that the amount of metabolic accumulated rhenium in leaves is 4 times higher than in the roots. On the other hand, the lower part of the leaves, which is in contact with the solution, also has a large surface available for sorption. Therefore, 68% of total accumulated rhenium is sorbed in the leaves. Total accumulated amount of rhenium in the roots and leaves is 153.2 g dry mass after a 7 day stay in an aqueous solution with a concentration of 40 µg Re/ml, which is consistent with the results of Table 1.

Table 1Dynamics of Re accumulation in *Salvinia natans L.* by metabolic and sorption uptake from aqueous solution with C_{Re}= 40 µg Re/ml at different treatment of the samples.

Sample	Contact time	Sample pretreatment	Type of accumulated Re	C_{Re} in µg /g dry mass	% of accumulated Re
P1a	3 h	unwashed	total	87.4	100
P1b	3 h	washed	metabolic	4.6	5.3
P1c	3 h		sorbed*	82.8	94.7
P2a	5 h	unwashed	total	105.3	100
P2b	5 h	washed	metabolic	5.4	5.6
P2c	5h		sorbed	99.4	94.4
P3a	24 h	unwashed	total	130.0	100
P3b	24 h	washed	metabolic	14.6	11.2
P3c	24 h		sorbed	115.4	88.8
P4a	5 days	unwashed	total	151.6	100
P4b	5 days	washed	metabolic	35.5	23.4
P4c	5 days		sorbed	116.1	76.6
P5a	7 days	unwashed	total	153.2	100
P5b	7days	washed	metabolic	37.3	24.3
P5c	7 days		sorbed	115.9	75.7

*C_{Re} sorbed= C_{Re} total- C_{Re}metabolic

Table 2 Results for metabolic and sorption accumulated Re in roots and leaves of *Salvinia natans L.*

Type of sample	Sample pretreatment	Type of accumulated Re	C_{Re} in µg /g dry mass	% of accumulated Re
Roots	unwashed	total	83.4	100
	washed	metabolic	5.7	6.8
		sorbed	77.7	93.2
Leaves	unwashed	total	69.8	100
	washed	metabolic	22.3	32.0
		sorbed	47.5	68.0

For the purpose of practical application of the water fern for the recovery of rhenium from industrial solutions, the dynamics and capacity of *Salvinia natans* for rhenium extraction from rhenium containing acidic waste solutions of mine Asarel were investigated. The results are shown in Table 3. As is seen, the rhenium uptake by water fern in acidic medium is quite different from that in aqueous solution. During the first hours after immersion of the plant in the acidic solution, accelerated accumulation of rhenium through metabolic pathway was observed. After 4- hour stay of the water fern in the solution, 88.4% of rhenium is accumulated by intracellular uptake. In the subsequent hours, the plant slowly died and gradually released Re in the surrounding solution. Within 7 days, the rhenium content accumulated by metabolism becomes zero. The authors suggest that upon placing the plant at extreme conditions (acidic medium) it seeks to survive. Proof of this is the production of seeds by the plant, which are released in the ambient solution. Accordingly, the plant increases its metabolism. It is known that the rate of Re phytoaccumulation directly depends on the plant metabolism (Bozhkov, 2006). Enhanced metabolism leads to rapid accumulation of perrhenate ions. It was noticed that after a longer stay of the plant in the acidic solution, it dies. The reason is that a lysis takes place in the plant cells as a result of their placement in a more concentrated medium than the cell sap.

Table 3 Dynamics of Re accumulation in *Salvinia natans L.* by metabolic and sorption uptake from waste industrial solution of mine Asarel, pH=2, C_{Re}= 420 ng Re/ml

Sample N	Contact time	Sample pretreatment and type of accumulated Re	C_{Re} ng Re/g dry mass	% of accumulated Re
P1a	2h	unwashed-total	1569	100
P1b	2h	washed-metabolic	1366	87.1
P1c	2h	sorbed	203	12.9
P2a	4h	unwashed-total	1768	100
P2b	4h	washed-metabolic	1563	88.4
P2c	4h	sorbed	205	11.6
P3a	24 h	unwashed-total	4361	100
P3b	24 h	washed-metabolic	1300	29.8
P3c	24h	sorbed	3061	70.2
P4a	7days	unwashed-total	3111	100
P4b	7days	washed-metabolic	0.0	0.0
P4c	7days	sorbed	3111	100

The resulting reaction of the cell is its shrinking because of the diffusion of water to the ambient solution. Over time, the cell wall is disrupted and the cell sap containing the perrhenate ions is poured into the acidic solution. As a result, the concentration of intracellular accumulated Re in water fern reaches zero (Tzvetkova, 2009). What is the kinetics of rhenium sorption? During the 4-hour stay of the plant in the solution, only 11.6% of rhenium accumulates by sorption on the plant surface. The authors assume that sorption and metabolic uptake of rhenium compete during the first few hours. Probably, the increased metabolism of the water fern leads to suppression of the rhenium sorption. Once the plant begins to die, the metabolic accumulation greatly slows down and fast sorption of rhenium starts onto the surface of the water fern. After 24 hours, the quantity of sorbed rhenium reaches its maximum value and undergoes almost no changes with time. It can be concluded from the results of Table 3 that the maximum accumulated quantity of Re in *Salvinia natans* by both mechanisms is reached after 24 hours. This is the optimal time for the recovery of rhenium from industrial acidic solutions.

The authors tested the sorption properties of the dried (dead) *Salvinia natans* for Re extraction from solutions. The results are shown in Table 4. It can be seen that dried water fern is a good sorbent of rhenium from aqueous solutions. If we compare the amount of Re accumulated by sorption in living and dead *Salvinia natans* for 24 hours, it appears that the amount of rhenium accumulated by sorption in the dried water fern exceeds that in the living plant more than 3 times (see the results from Table 1 and Table 3). Probably the lack of competition between sorption and metabolic accumulation of rhenium in the dried *Salvinia natans* is the reason for the higher sorption capacity of dead water fern. Moreover, the dried *Salvinia natans* accumulated for 1 day more rhenium than living water fern accumulated in 7 days by the two mechanisms. The high sorption capacity of dried *Salvinia natans*, its ability to be easily recovered and re-used as a simple sorption material and its easy storage is a big advantage, compared with the living plant.

Table 4 Sorption of Re on the dried *Salvinia natans N.* after 24 h stay in an aqueous solution with C_{Re}=40 µg Re/ml

Sample №	Sample pretreatment	C_{Re} µg/g dry mass	% of accumulated Re
P1	unwashed	389.4	100
P2	washed	1.57	0.4

Conclussions

The results obtained in this study show that *Salvinia natans L.* is an appropriate collector of rhenium from aqueous and industrial solutions. The plant can be used for the development of an environmentally friendly, cheap and profitable technology for rhenium recovery from aqueous and waste solutions.

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