RECOVERY OF LITHIUM AND RUBIDIUM FROM WASTE AQUEOUSLEACHATES BY MICROALGAE

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ABSTRACT

Bioaccumulation of rubidium (Rb) and lithium (Li) from waste alkaline leachates obtained by calcinations of mineral zinnwaldite was studied in a laboratory setting using three strains of freshwater microalgae (*Chlorella vulgaris*, *Desmodesmus quadricauda* and *Scenedesmus obliquus*). Concentrations of Li and Rb were in the range of 0 to 5 mg/L. Bioaccumulation of Li was negligible in all tested strains. Bioaccumulation of Rb was the highest for *C. vulgaris*; four days after the addition of the metal leachate the accumulation reached 53% of the original amount. Addition of leachate (containing 4.8 mg/L of Rb and 3.0 mg/L of Li) to *C. vulgaris* practically did not affect the growth rate of the algae. The most important conclusion is the observation that bioaccumulation of Li and Rb, unlike adsorption on traditional sorbents, is selective. This finding has potential practical utilization.

Keywords: Rubidium, Lithium, Freshwater microalgae, Bioaccumulation, Selectivity

1. Introduction

In the Czech Republic, Rb could be obtained as a minor byproduct of the processing of zinnwaldite, $KLiFeAl[(F,OH)_2|AlSi_3O_{10}]$, and wastes contain 0.21 % Li and 0.20 % Rb. Up till today, such wastes still represent an unsolved ecological problem as they remained from dressings of Sn-W ores that were mined in the Czech Republic in the locality of Zinnwald in the past. According to the plans of some investors, extraction of Li in the Zinnwald location should be restored in 2016.

At present, soluble Rb ions are recovered from wastewaters using specific chemical procedures and ion exchange techniques. However, for solutions with low concentrations of Rb, these conventional methods have significant disadvantages. None of these methods achieves complete and selective recovery of metal ions. The methods have high reagent and/or energy requirements, generate waste products, and have high capital costs. Thus, it is essential to develop more economical and effective ways to recover Rb from diluted wastewaters.

It has been known for several decades that various green algal strains have high tolerance towards heavy metal ions and have shown properties that could be used for heavy metal removal. Although the idea of utilizing microalgae in bioaccumulation of heavy metal ions was proposed many years ago, its practical utilization has been considered only recently (Mehta and Gaur 2005; Priyadarshani et al. 2011; Ajayan et al. 2011).

Live algal biomass exhibits an affinity for heavy metal cations due to its high negative surface charge. Heavy metals enter algal cells either by means of active transport or by endocytosis through chelating proteins. Subsequently they are usually transported via protein carriers into the cellular interior.

For applications in large-scale productions involving live algae, a continuous process is relatively simple. Continuously flowing water containing Rb and Li remains in contact with the algal biomass during its entire residence time in the bioreactor. When saturated with the metals, the algae are continuously separated from the water. Given the mechanism of bioaccumulation the separation of metal ions into live biomass can be more selective than their simple adsorption.

The majority of studies concerning metal ions bioaccumulation into algae are focused on metals that are generally known to have adverse health effects on living organisms (such as Cd, Pb, Zn, Cr, Cu, Ni, and As. Literature provides only few references about bioaccumulation of Rb in biomass. Studies on the effectiveness of separation of Rb from dilute aqueous solutions via bioaccumulation in microalgae are therefore highly desirable. In this work, we focused on the study of the extraction of Rb with the help of selective bioacumulation from very dilute aqueous solutions containing residual concentrations of Rb and Li. This is the most frequently occurring combination of metals remaining in the waste from the treatment of Li ores. Possibilities of separating residual Rb from wastes generated by known technologies (Jandová et al. 2012b; Jandová et al. 2012a) especially zinnwaldite processing were examined experimentally. Experiments were done with 3 different strains of freshwater microalgae to determine the extraction efficiency (bioaccumulation) from the Rb leachate. The extents of adverse effects of Rb and Li on metabolic activity of algae were determined with the help of growth curves of the selected microalgae strains for various concentrations of Rb and Li in the nutrient medium.

2. Materials and methods

Preparation of leachate Conditions of roasting the zinnwaldite concentrate with $CaCO_3$ and leaching the calcine were based on the results of our previous research (Jandová et al. 2010). The leachate was then diluted with an appropriate amount of water and the resulting solution of defined concentration was used for subsequent bioaccumulation experiments involving 3 live algal strains.

Bioaccumulation tests The three microalgal strains *Chlorella vulgaris* Beijerinck P12 (CCALA 924), *Desmodesmus quadricauda* GREIFSWALD/15 (CCALA 463) and *Scenedesmus obliquus* LHOTSKY O. 1966/7 (CCALA 453) were maintained according to previously described procedures (Brányíková et al. 2011; Sirmerova et al. 2013). Batch cultivation in the photobioreactor proceeded as reported in literature,i.e. glass tubes were placed in a water bath (30 °C) under continuous illumination with incident light intensity 100 μmol m^{-2} s^{-1} (PAR sensor QSL-2101, Biospherical instruments Inc., USA). Air enriched with 2% CO_2 (v/v) was introduced at 15 L/h per tube. Each tube contained 300 mL of mineral medium, with the initial composition (mg/L^{-1}): 1100 $(NH_2)_2CO$, 238 KH_2PO_4, 204 $MgSO_4.7H_2O$, 40 $C_{10}H_{12}O_8N_2NaFe$, 88 $CaCl_2$, 0.832 H_3BO_3, 0.946 $CuSO_4.5H_2O$, 3.294 $MnCl_2.4H_2O$, 0.172 $(NH_4)_6Mo_7O_{24}.4H_2O$, 2.678 $ZnSO_4.7H_2O$, 0.616 $CoSO_4.7H_2O$, and 0.0014 $(NH_4)_2VO_3$. The medium was treated as for outdoor culture so it was not sterilized, but distilled water was used nevertheless. After reaching the exponential growth phase (155 h cultivation time) concentrated metal leachate having the initial metal concentration 48 mg/L of Rb and 30 mg/L of Li was added directly to the medium in an amount to ensure its 10-fold dilution. From each algal species samples were taken at regular intervals to determine gravimetrically the biomass concentration. Simultaneously, 5mL of the algal suspension was centrifuged and the obtained supernatant was used for subsequent analysis via atomic absoprtion spectroscopy GBC AVANTA 932 plus.

3. Results

Cultivation of algae in the presence of Rb and Li Effects of Rb and Li ions on the growth curves of selected microalgae and bioaccumulation rate of Rb and Li are shown in Fig. 1 - 3. Bioaccumulation of Li was negligible in all tested strains. Bioaccumulation of Rb from solutions containing both Li and Rb is selective. This is significant for potential applications of this technique as a separation method. In comparison, in our ongoing experiments on separation of Rb with the help of commercial sorbents (activated carbon, alumina) we were not able to obtain selective separation.

Unlike of Rb bioaccumulation of Li was negligible in all tested strains. Bioaccumulation of Rb was the highest for *C. vulgaris*; four days after the addition of the metal leachate the accumulation reached 53% of the original amount. The most important conclusion is the observation that bioaccumulation of Li and Rb, unlike adsorption on traditional sorbents, is selective. *C.vulgaris* is thus a suitable candidate for the bioaccumulation of Rb from ore waste leachates. An earlier work with different photosynthetic organisms has shown that the uptake of Rb is often so similar to the uptake of K (Keith and Pitman 1967, Ritchie 1997). Hypothetically, biomagnification involves the co-uptake of Rb, which has smaller cation radii than K^+, via active transport H^+ and K^+ membrane channels in primary producers and the subsequent transfer and accumulation of Rb (Rowan and Rasmussen 1994, Rit). Due to the higher toxicity of Li, its transfer into algae is rather suppressed. Further research will be directed to the increase of bioaccumulation of Rb via adaptation of the candidate microalgae *Chlorella* to higher concentrations of Rb. The increase in the bioaccumulation is necessary to make this separation technique feasible.

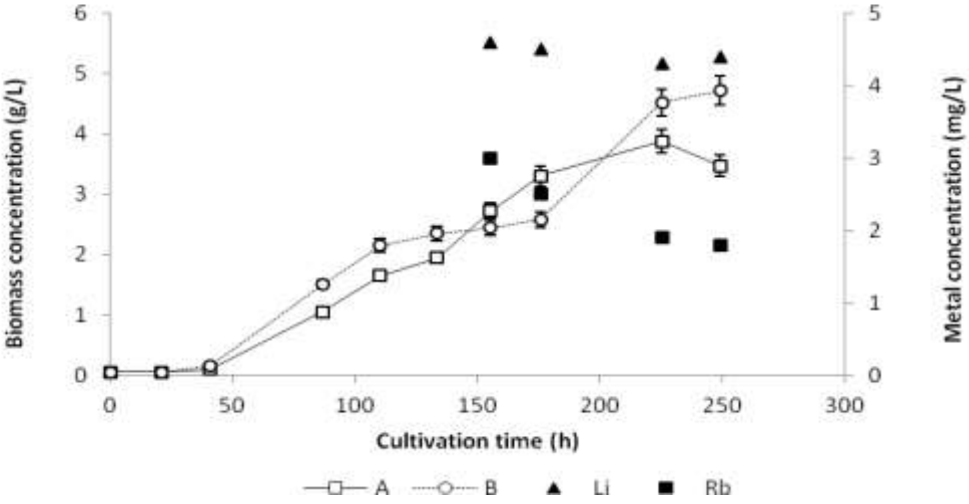

Figure 1: *D. quadricauda* growth in the presence of metal leachate added after 155 hours of cultivation (A) compared to control (B) with subsequent bioaccumulation of lithium (Li) and rubidium (Rb). Absorption of Rb by algae.

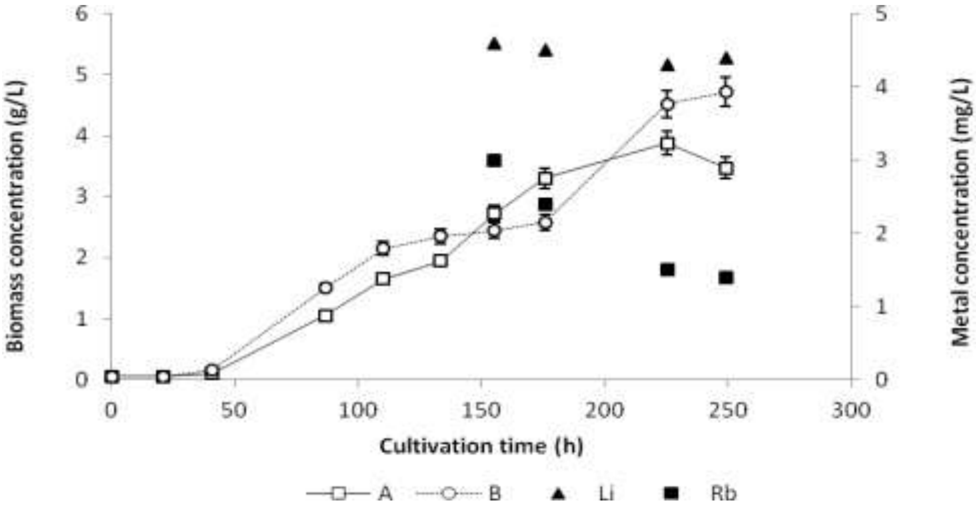

Figure 2: *C. vulgaris* growth in the presence of metal leachate added after 155 hours of cultivation (A) compared to control (B) with subsequent bioaccumulation of lithium (Li) and rubidium (Rb). Absorption of Rb by algae.

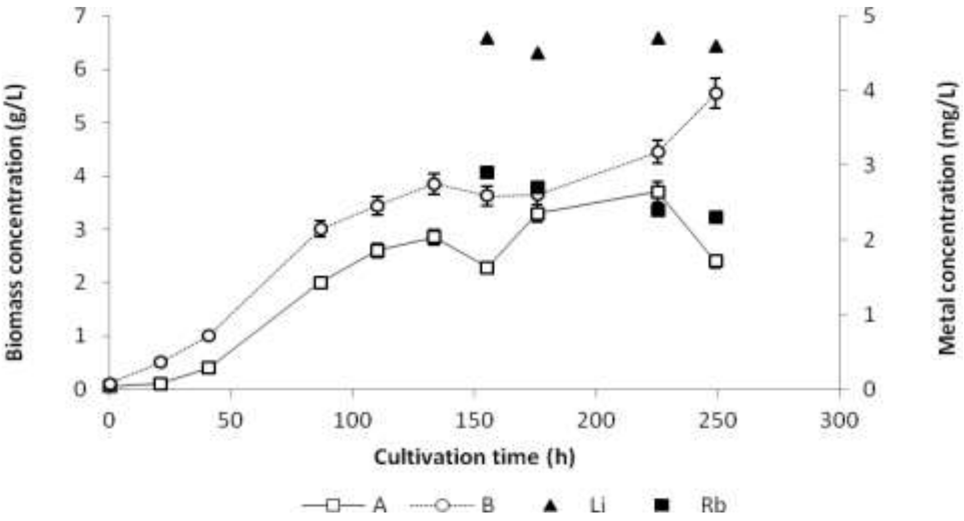

Figure 3: *S. obliquus* growth in the presence of metal leachate added after 155 hours of cultivation (A) compared to control (B) with subsequent bioaccumulation of lithium (Li) and rubidium (Rb). Absorption of Rb by algae.

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