Bioleaching of Zn, Ni and Fe from contaminated sediments of water reservoir Ružín I with using heterotrophic bacterial strains

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This study investigates the bioleaching of the zinc polluted sediment from water reservoir Ružín I using heterotrophic bacterial strains ubiquitous in sediment environment. The effect of bacterial activity, pH, iron solubilization and precipitation and bioleaching medium were evaluated. The pH value controls the bacterial activity during the leaching process. Addition of glucose to the bioleaching medium accelerated the bioleaching rate. The results indicates, that the leachibility of zinc depend on the geochemical forms and surface interaction between metal and sediment fraction. Sequential chemical extraction confirm, that Zn was predominantly bound to the iron-manganese oxides.

Key words: *Zinc, iron, bioleaching, Bacillus sp, heterotrophic bacteria, sediment*

Introduction

Aquatic sediments contaminated with heavy metals are still an unsolved problem in numerous industry sites in Europe. Water reservoir Ružín I located in east Slovakia is one of the most contaminated sites by heavy metals coming from mining and metallurgical industry. In this work, we investigated the leachibility of zinc, nickel and iron from contaminated sediment, because they present one of the contaminants exceeding the limit of the MoE SR No. 549/98-2. Therefore the bioleaching process, in which zinc and nickel are removed from contaminated sediment samples by flask bioleaching, has been developed. Aqueous metal cations show a high affinity to bacterial surfaces (Fowle et al., 2000), hence it is likely caused by the mobility of certain aqueous metal contaminants in aquatic systems, which is closely tied to the bacteria (Johnson et al., 1996). The mobility of bacteria in soil and aquifer systems is influenced by a variety of chemical and physical factors. Heterotrophic leaching may be particularly appropriate for waste of neutral and high pH such as sediments (Gadd, 1999). Previous studies have shown that surface chemistry can control bacterial transport through porous media, and that bacterial attachment is strongly influenced by mineralogy, solution, and ionic strength (Yee et al., 2000). It was demonstrated that is why the dissolution of silicates by heterotrophs is a consequence of the complexation of the cationic elements present in different silicated minerals (Webley et al., 1963). Due to these facts, above mentioned species produce organic acids (oxalic and citric) (Ehrlich et al., 1990).

The mobility, transport and fractionation of heavy metals are the function of the chemical forms of the elements, which in turn is controlled by the physicochemical and biological characteristics of the system. If heavy metals reach the aquatic sediments, they could be bound to hydrated oxides of iron and manganese, organic compounds, clay minerals, etc., and may be associated with them in different ways. For the determination of various binding fractions of heavy metals in sediments, a sequential extraction procedure is often employed (Li et al., 2001, Bacon et al., 2008). The geochemical characterisation of the sediments has the primary importance in bioremediation technologies (Schipers et al., 2002).

Materials and methods

Sediment samples were obtained from water reservoir Ružín I in the inlet of the largest tributary the Hornád river. Samples were taken from the depth of 20 cm, stabilized by freezing at – 15 °C.

Mineralogical composition was determined by X-ray diffraction, X`Pert, Philips, SW – binary diffractometer with CuKα radiation (40 kV, 50 mA), Germany. The content of Zn and Fe in the sediment matrix and liquid phases was detected by atomic absorption spectrometry (AAS, spectrometer, Varian, AA-30, Australia). Changes in pH values during bioleaching process were measured by potentiometry at RADEKIS (Hungary) and PHM 210 METERLAB (France).

The five-step sequential extraction was applied to understand mobility and chemical binding of Zn in sediment samples before bioleaching treatment. 1 g of solid sediment was extracted with 10 ml of the extractant in 50 ml polyethylene container. Extracts were centrifuged at 2000 rpm during 30 min, filtered and spectrophotometric analysed.

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Extraction solutions used in sequential extraction:
Step 1. (Exchangeable fraction) 1M $MgCl_2$, pH 7
Step 2. (Carbonate fraction) 1M NaOAc, HOAc, pH 5
Step 3. (Fe-Mn oxides) 0,04M $NH_2OH.HCl$ in 25 %HOAc, pH 3
Step 4. (Organic fraction) 0,02M HNO_3 in 30 % H_2O_2, pH 2
Step 5 (Residual fraction) mixture 5:1 HF and $HClO_4$ pH ~1

Bioleaching experiments were carried out in Erlenmeyer flasks, which contained 30 g of sediment and 600 ml of bioleaching medium. Two types of bioleaching medium were compared. The first was mineral Ashby medium 1.0 g $(NH_4)_2SO_4$, 2 g K_2HPO_4, 0.5 g $MgSO_4$ $.7H_2O$, 2 g NaCl and the second was Ashby`s, enriched with 20 g of glucose (per liter) for the activation of autochthonic heterotrophic bacteria. The flasks were incubated under static condition for 35 days at 25 °C. The changes of Zn and Fe concentration in liquid phase were measured by atomic absorption spectrometry.

Results and discussion

Mineralogical composition of sediment: chlorite 6 %, illite 5 %, kaolinite 8 %, albite 7 %, montmorillonite 15A 5 %, montmorillonite 22A 5 %, quartz 64 %.

Physico-chemical properties of sediment samples are in Table 1.

Tab. 1. Physico – chemical properties of sediment.

Sample	pH	Eh [mV]	TOC [%]	Ni [mg.kg^{-1}]	Zn [mg.kg^{-1}]	Fe [mg.kg^{-1}]
Ružín I	7.13	341.4	3.31	87	427	44 600
TV MoE SR No 549/98-2	-	-	-	35	140	-

Legend: TV – target value

Five steps scheme was used to define the distribution of selected elements between phases present in sediment samples. The sequential extraction procedure was performed triplicate. The metal speciation in the investigated sediment is illustrated in Fig. 1. The mobile fraction of Ni in the material before bioleaching treatment was bound to the fraction of Fe/Mn oxide (36 %). Above the 18 % was confirmed in the carbonate minerals. The highest concentration of Ni was observed in the residual fraction (alumosilicate and clay minerals). The carbonate minerals as well as the residual fraction, bound the large mobile fraction of Zn (28 %) and the Fe/Mn oxide fraction contains 50 % of the total Zn concentration. Chemical extraction of Fe was carried out in order to suppose its dominant presence in the amorphous Fe/Mn oxides. (Fig. 1).

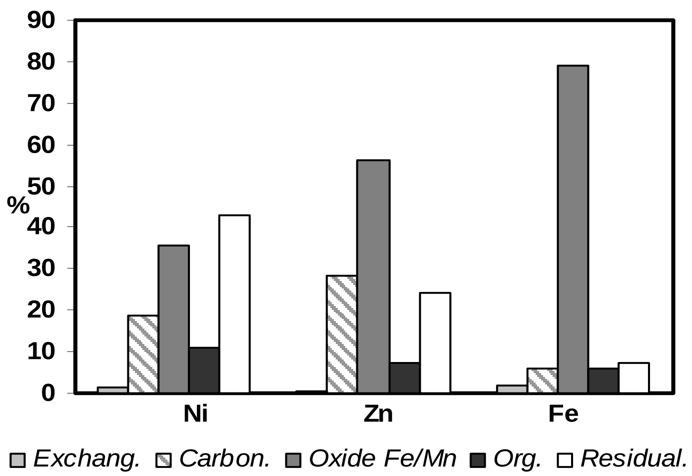

Fig. 1. Fractionation of Ni, Zn and Fe in sediment after sequential extraction

The bioleaching experiments examined the effect of two different bioleaching media at the extraction of Zn and Fe as the part of Fe/Mn oxides, through activation of autochthonous, heterotrophic bacteria. If the sedimentary environment is neutral and there is a sufficient quantity of minerals and organic substances, it may activate heterotrophic bacterial species in the sediment. These substances increase mobility of heavy metals in aquatic environment. Fe from Fe_2O_3 can be solubilized and recovered by direct or indirect actions of heterotrophic microorganisms that thrive under microaerobic or anaerobic conditions (Abbruzzese et al., 1990)

Bioleaching is affected by the production of organic acids which are excreted into the bioleaching medium and dissolve heavy metals by direct displacement from the sediment matrix of soluble metal complexes and chelates.(Bosecker, 1988, Wagner et al., 1967). These experiments demonstrate that, even without the inoculation is possible to mobilize heavy metals, because of the presence of heterotrophic bacterial species. It was observed, that using mineral medium with the addition of glucose as carbon source intensifies the bioleaching process. Active microorganisms from Pseudomonas, Erwinia and Bacillus genus produce 2 – ketogluconic acid when grown on a glucose medium (Henderson et al., 1963). It is also known, that Bacillus mucilaginosus is able to accelerate the releasing of silicon from quartz. The data obtained suggest an indirect mechanism in which the siloxan binding is disrupted by the action of exopolysaccharides (Avakyan, 1985). Bioleaching with Ashby mineral medium was in the first 10 days increasing, but after the depletion of accessible organic matter in the sediments, a decrease of the amount of metals was detected in the solution. Using bioleaching medium containing glucose we obtained the maximum metal extraction in 27 days. The concentration of metals in this case was several times higher than in the case of using medium without glucose. After the accumulation of acidic microbial metabolites - fatty acids in bioleaching medium, a reduced microbial activity and a decrease of the concentration of metals was detected in the solution. We also observed some changes in pH in the bioleaching system during the experiments (Fig. 5.). The pH of the bioleaching solution decreases from 7.0 to 4.7 during the first days and thereafter to the end of the experiment to pH 2.7. The knowledge of heavy metal dissolution kinetics permits the timing for the exchange of bioleaching media by discontinuous bioleaching of sediments.

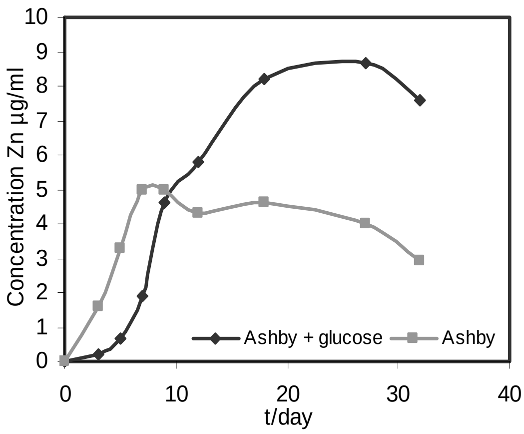

Fig. 2. Comparison of the kinetics of Zn bioleaching.

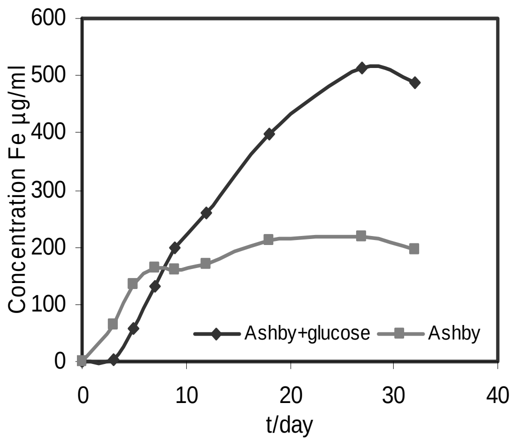

Fig. 3. Comparison of the kinetics of Fe bioleaching.

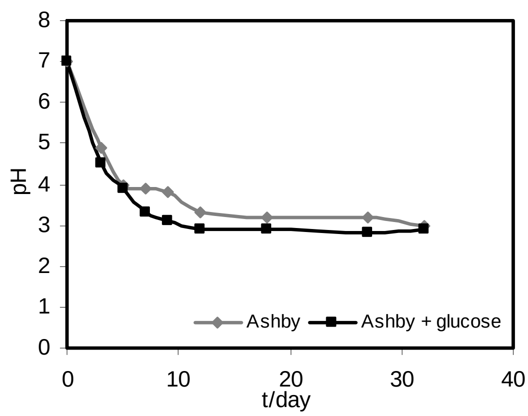

Fig. 5. Comparison of the kinetics of pH in the bioleaching system.

Conclusion

The distribution of Ni and Zn in sediments confirms the ability of Fe/Mn oxides with sorption properties preferentially for heavy metals. Amorphous Fe and Mn oxides are also presented in alumosilicate components of sediments in the form of fine coatings. They are taking part on the indirect reactions between the bacterial cells and the mineral surface of alumosilicates, in which structure various heavy metals are bounded. The organic matter presented at the matrix of the sediments initialize the activity of heterotrophic bacterial species, which indirectly participate on the mobility of Zn and Fe in bioleaching system. With the adjunct of the organic matter in the form of glucose, were also detected the increase of the activity of microorganisms, which was also expressed as an increasing amount of metals in bioleaching medium. Bacterial leaching methods which use autochthonous, heterotrophic bacteria in the presence of sufficient amount of organic matter, are presumptions for the mobilization of metals in contaminated sediments with an intent of exploitation of these processes in in-situ decontamination and remediation of contaminated sites.

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