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Biological transformation of alkaline earth metal sulphates

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Abstract

The aim of this paper is to verify experimentally the possibility of the biological transformation of the alkaline earth metal sulphates ($CaSO_4$ and $BaSO_4$) to carbonates by sulphate-reducing bacteria. These carbonates can be used in some industrial technologies (e.g. the energetic industry – the recycling of desulphurization agent (limestone) for the thermal power plant, the electrical industry – the production of colour display).

Key words: gypsum, barite, sulphate-reducing bacteria, biological transformation

Introduction

In nature the sulphur can be found as a pure element or in the form of sulphide and sulphate minerals. Common naturally occurring sulphur compounds include the sulphide minerals, such as pyrite (FeS_2), cinnabar (HgS), galena (PbS), sphalerite (ZnS) and stibnite (Sb_2S_3); and the sulphates, such as gypsum ($CaSO_4$), alunite ($KAl(SO_4)_2$), celestite ($SrSO_4$) and barite ($BaSO_4$). The biological circulation of sulphur and its compounds in the biosphere is considered as one of the basic biological systems on the Earth (Lide, 1998). The participating populations of different species of microorganisms (MO) are able to transform organic substances into inorganic ones and vice versa supporting the circulation of sulphur in the nature. The natural biological circulation of sulphur consists of assimilation and dissimilation parts. The microbial population of the dissimilation part is called sulphuretum (Postgate, 1984). In addition to other MO also the sulphate-reducing bacteria (SRB) take part in the sulphuretum. They realize the conversion of sulphate to hydrogen sulphide under anaerobic conditions (Odom and Singleton, 1993). Gaseous hydrogen or organic substrates (lactate, malate, etc.) are the electron donor and sulphate is the electron acceptor (equations 1 and 2). In this process produced gaseous hydrogen sulphide reacts easily in the water medium with heavy metal cations forming sparingly soluble sulphides of the given metals (equation 3):

$$4\,H_2 + SO_4^{2-} \xrightarrow{SRB} H_2S + 2\,H_2O + 2\,OH^- \qquad (1)$$

$$4\,CH_3COCOONa + 5\,MgSO_4 \xrightarrow{SRB} 5\,MgCO_3 + 2\,Na_2CO_3 + 5\,H_2S + 5\,CO_2 + H_2O \qquad (2)$$

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \text{ (}Me^{2+}\text{ – metal cation)} \qquad (3)$$

The above-listed equations show the possibility of using SRB for the removal of soluble heavy metals and sulphates from acid mine drainage (AMD) (Skousen et al., 1998; Luptáková et al., 2002; Kaksonen and Puhakka, 2007) or other industrial waste waters (Cork and Cusanovich, 1979). In addition, the equation 2 suggests the usage of bacterial sulphate reduction by SRB on the treatment process for sulphate-contained sludge (Cork, 1985; Baldi et al., 1996; Kennedy and Everett, 2001; Luptáková et al., 2003) being the basis of the biological transformation of sulphates to carbonates.

The objective of our study is to verify experimentally the possibility of the biological transformation of the alkaline earth of metals sulphates – $CaSO_4$ and $BaSO_4$ by SRB. Under the appropriate conditions the SRB are able to convert with a high efficiency the alkaline earth metal sulphates in corresponding carbonates. These can be utilized by some industrial technologies (e.g. in the energetic industry – the recycling of desulphurization agent (limestone) for the thermal power plant, in the electrical industry – the production of colour display).

Materials and methods

In the experiment a culture of SRB (genera *Desulfovibrio* and *Desulfotomaculum*) was used. It was obtained from drinking mineral water Gajdovka (locality Košice-north, Slovak Republic). Culture was grown in a Postgate lactate medium that was prepared sulphate-free. The pH was adjusted to 7.2 – 7.5 with 5 M NaOH solution. Culture medium contained gypsum or barite as the solid-phase electron acceptors. SRB were grown at 30 °C under static and anaerobic conditions. The inoculum of SRB was 10 % (v/v). For the series of anaerobic tests SRB adapted or non-adapted were used on the presence of gypsum or barite. At the adaptation procedure SRB were transferred three times into the media which contained the test compound as the sole electron acceptor. The abiotic controls were carried out without the SRB application at the same conditions. The nefelometric method was used to determine the concentration of sulphates at 490 nm using the Spectromom 195 spectrophotometer. Soluble sulphide was analysed using a methylene blue method based on a colourimetric determination of dissolved H_2S and HS^- using *N*, *N*-dimethyl-*p*-phenylenediamine. The pH of the cultivation medium was determined using the PHM 210 MeterLab pH meter.

Results and discussion

The hydrogen sulphide production from the gypsum as the solid-phase electron acceptors during a 7-day period of SRB cultivation at using adapted (SRB – A) or non-adapted bacteria (SRB – N) is described in Fig. 1. Positive influence of the adaptation procedure was observed. The hydrogen sulphide amount in the case of adapted SRB using, in comparison with the non-adapted SRB was above double. Sulphates from gypsum were reduced by SRB according to equation (4) forming hydrogen sulphide. In abiotic controls (SRB – A (abiotic) and SRB – N (abiotic)) the negligible hydrogen sulphide production was observed.

$$2C_3H_5O_3Na + CaSO_4 \xrightarrow{SRB} 2CH_3COONa + CO_2 + CaCO_3 + H_2S + H_2O \tag{4}$$

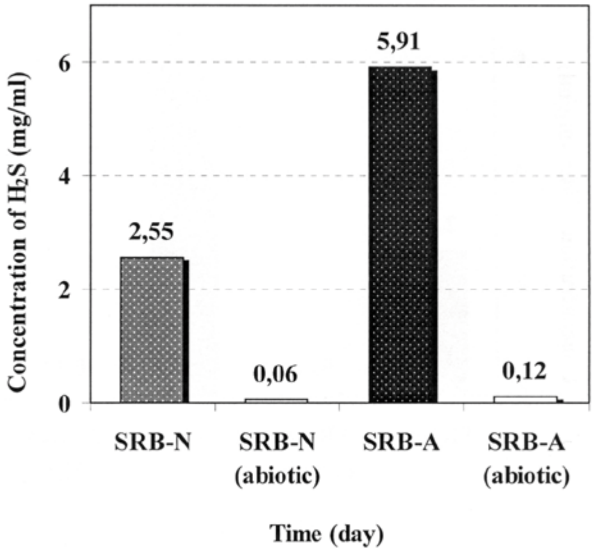

Fig. 1. Hydrogen sulphide production from gypsum by non-adapted sulphate-reducing bacteria (SRB-N) and adapted bacteria (SRB-A). SRB-A (abiotic), SRB-N (abiotic) – abiotic controls.

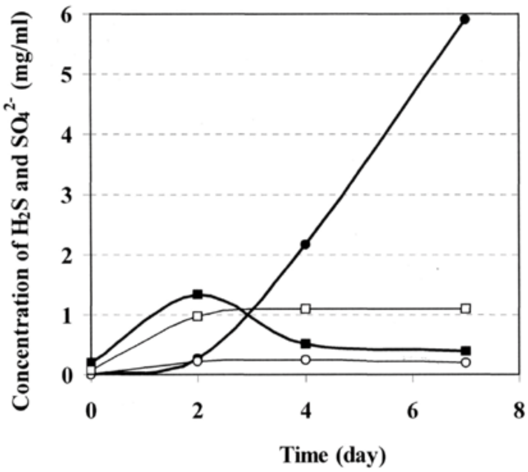

Fig. 2. Changes of sulphates (■)and hydrogen sulphide (●) concentration during adapted SRB cultivation and changes of sulphates (□) and hydrogen sulphide (○) in corresponding abiotic controls using gypsum as the solid-phase electron acceptors.

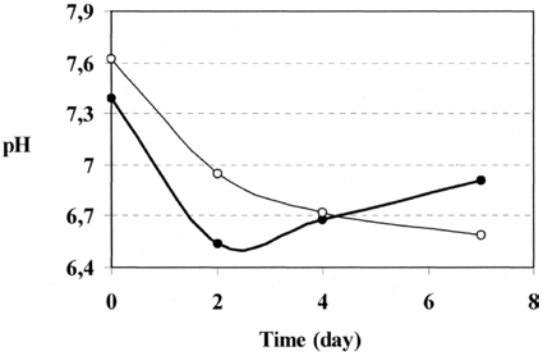

Fig. 3. Changes of pH values during adapted SRB cultivation (●) and corresponding abiotic control (○) using gypsum as the solid-phase electron acceptors.

The changes of sulphates and the hydrogen sulphide concentration at adapted SRB application and at abiotic control, when gypsum as the solid-phase electron acceptor was used is demonstrated in Fig. 2. Changes of corresponding pH values is shown in Fig. 3. The comparison of biotic and abiotic conditions documented the similar curve shape of changes of sulphates and hydrogen sulphide concentration, and pH values only during the first and second days (Figs. 2 and 3). Later the SRB presence caused the sulphates concentration decreasing and the hydrogen sulphide concentration increasing. In abiotic control after the second day sulphates and hydrogen sulphide concentrations changes were minimal. Also Fig. 2 documented the nutrient medium influence on the barite dissolving. Fig. 3 described the contrast of pH values changes between the SRB application and the abiotic control. Shift of pH values to alkaline zone was recorded at SRB presence. It corresponds with equation (4) because $CaCO_3$ as alkaline mater was produced. Abiotic conditions report consistent decreasing of pH.

The opposed results were observed at the adaptation of SRB using barite as the solid-phase electron acceptors (Fig. 4). Non-adapted SRB produced nearly decimal higher

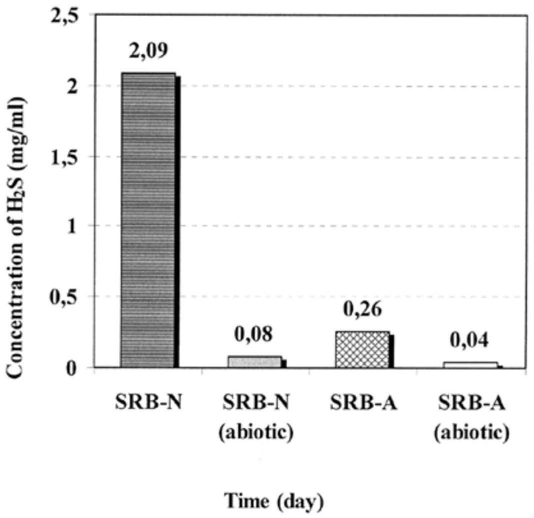

Fig. 4. Hydrogen sulphide production from barite by non-adapted sulphate-reducing bacteria (SRB-N) and adapted bacteria (SRB-A). SRB-A (abiotic), SRB-N (abiotic) – abiotic controls.

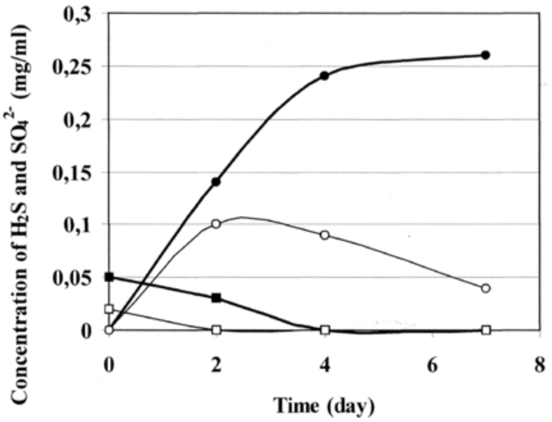

Fig. 5. Changes of sulphates (■) and hydrogen sulphide (●) concentration during adapted SRB cultivation and changes of sulphates (☐) and hydrogen sulphide (○) in corresponding abiotic controls using barite as the solid-phase electron acceptors.

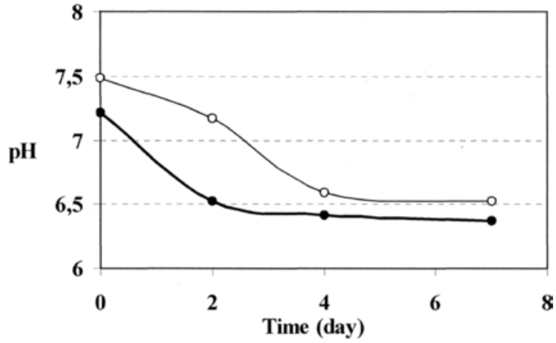

Fig. 6. Changes of pH values during adapted SRB cultivation (●) and corresponding abiotic control (○) using barite as the solid--phase electron acceptors.

concentration of hydrogen sulphide. At the moment we cannot explain of this fact. Probably the barium toxicity influenced on the SRB growth because the barium is generally toxic to bacteria, fungi, mosses and algae (Roza and Berman, 1971).

When the barium as the solid-phase electron acceptors was used the changes of sulphates and hydrogen sulphide concentration at adapted SRB application and at abiotic control shows Fig. 5. Changes of pH values at using SRB are shown in Fig. 6. The decrease of sulphate concentration and the increase of hydrogen sulphide concentration were observed in the case of SRB presence. At abiotic control allocated the decreasing of sulphates. After the initial minor increasing the hydrogen sulphide concentration showed the decreasing.

Equations (5) and (6) describe the biochemical reaction initiated by SRB in the presence of sodium lactate as an electron donor and $BaSO_4$ as an electron acceptor under anaerobic conditions at pH 7 according to Baldi et al. (1996).

$$\text{Na-lactate} + BaSO_4 \xrightarrow{\text{SRB}} \text{biomass} + BaCO_3 + BaS + CO_2 + H_2S \quad (5)$$

$$BaSO_4 + 2H_2S \rightarrow BaS + SO_2 + 2H_2O + S \quad (6)$$

Equation (5) suggests the biological decrease of the sulphate concentration and equation (6) the chemical trend, because produced hydrogen sulphide reduces $BaSO_4$ to BaS. These facts probably explain the zero concentration of sulphates in the Fig. 5. Experiments realized at biotic and abiotic conditions have documented the consistent decreasing of pH.

Conclusions

The study of the biological transformation of alkaline earth of metals sulphates ($CaSO_4$ and $BaSO_4$) confirmed that SRB obtained from the drinking mineral water Gajdovka could produce sulphide from the sulphate entity of gypsum and barite. The sulphate concentration decreased by the zero concentration in test cultures growing with $BaSO_4$ as the electron acceptor, possibly due to BaS precipitation by bacterially produced hydrogen sulphide. Hydrogen sulphide formation from the barite was the slowest when compared to gypsum as electron acceptor that is more soluble. Sulphate reduction with gypsum as the electron acceptor probably resulted in calcite formation ($CaCO_3$) but no precipitation of sulphide. With barite as the electron acceptor probably sulphide precipitated as BaS (galena), which is why the dissolved sulphide concentration remained low.

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