Sulphates Removal from Acid Mine Drainage

Alena Luptáková [1], Eva Mačingová [1], Ingrida Kotuličová [1], Dominika Rudzanová[1]

[1] Slovak Academy of Sciences, Institute of Geotechnics, Watsonova 45, 040 01 Košice, Slovak Republic

E-mail address: macingova@saske.sk

Abstract. Acid mine drainage (AMD) are a worldwide problem leading to ecological destruction in river basins and the contamination of water sources. AMD are characterized by low pH and high content of heavy metals and sulphates. In order to minimize negative impacts of AMD appropriate treatment techniques has to be chosen. Treatment processes are focused on neutralizing, stabilizing and removing pollutants. From this reason efficient and environmental friendly methods are needed to be developed in order to reduce heavy metals as well as sulphates. Various methods are used for remediation of acid mine drainage, but any of them have been applied under commercial-scale conditions. Their application depends on geochemical, technical, natural, financial, and other factors. The aim of the present work was to interpret the study of biological methods for sulphates removal from AMD out-flowing from the shaft Pech of the deposit Smolník in Slovak Republic. In the experimental works AMD were used after removal of heavy metals by precipitation and sorption using the synthetic sorbent Slovakite. The base of the studied method for the sulphates elimination was the anaerobic bacterial sulphate reduction using sulphate-reducing bacteria (SRB) genera *Desulfovibrio*. SRB represent a group of bacteria that uses sulphates as a terminal electron acceptor for their metabolism. These bacteria realize the conversion of sulphate to hydrogen sulphide under anaerobic conditions. For the purposes of experiments a few variants of the selective medium DSM-63 culture media were used in term of the sulphates and sodium lactate contents in the selective medium as well as sulphates in the studied AMD.

1. Introduction

Sulphates are found in almost all natural water, where the raised concentration can originate from landfill leaching. Sulphate and metal containing wastewater from the mining and metallurgical industry are a major source of natural water bodies pollution, but high sulphate loads can be the result of prolonged high atmospheric deposition, application of sulphate-containing fertilizers and a wide range of industrial processes including power generation, tanneries, paper and pulp production.

Sulphates present are not considered to be toxic, but negatively affect the taste of water and concentration higher than 600 mg/L usually results in a laxative effect [1]. However, sulphide produced from sulphate at anaerobic condition has toxic effects in the aquatic environment causing lack of oxygen resulting fish, plant and plankton deaths. Hydrogen sulphide can also increase eutrophication in natural water bodies by generating chemical cycle that release phosphate [2, 3]. Moreover, waters rich in sulphate have a high corrosive and scaling potential and induces an unbalance in the natural sulphur cycle [4].

Most jurisdictions have limits set in respect of waters intended for drinking water abstraction and finished drinking water, but not for aquatic life protection. Currently Government Regulation No 269/2010 of Slovak Republic Code includes general requirements for water quality, where the recommended concentration of sulphates is 250 mg/L for surface waters, 150 mg/L (recommended value) or 250 mg/L (marginal value) for waters intended for drinking water abstraction and 250 mg/L for irrigation waters.

Acid mine drainage (AMD), water draining active and, in particular, abandoned mines is largely acid with elevated concentration of metals and sulphates. Sulphates may be present in AMD at concentration ranging from few hundred to several thousand milligrams per litter. Different treatment processes for sulphates removal from AMD have been proposed. Established methods include the following: chemical treatment coupled with precipitation, membrane technologies, ion exchange techniques and biological remediation [1]. The biological removal of sulphates from AMD is possible to realize by way of anaerobic reduction to sulphide using sulphate-reducing bacteria (SRB). SRB represent a morphologically and phylogenetically heterogeneous group of microorganisms. They are generally strict anaerobes that oxidize simple organic compounds or hydrogen using sulphate, thiosulphate or sulphite as a terminal electron acceptor [5]. Sulphate rich AMD is usually deficient in electron donors and require their external addition in order to achieve a sulphate reduction.

The main advantages of biological sulphate reduction are the low volume of sludge produced and removal of sulphates from AMD to levels that comply with environmental regulations. The nascent biogenic sulphide may be successfully applied for metal precipitation or elementary sulphur production using different strains of bacteria [6].

This paper presents the results of biological removal of sulphates from real AMD at laboratory condition. Before the processes the metals were removed from AMD by precipitation of iron and by sorption using the synthetic sorbent Slovakite.

2. Materials and Methods

2.1. Mine water

The mine water used in experiments was sampled in the shaft Pech, which receives waters draining the abandoned Smolnik sulphide deposit (Slovak Republic). The historical Smolnik mine was exploited for Au, Ag, Cu and Fe from the 14th century to 1990. The flooding in the period 1990-1994 led to massive AMD discharge. The range of majority dissolved metals concentration, content of sulphates and values of pH are presented in the Table 1.

Table 1. Monitored parameters of AMD in the period 2006 – 2015

pH	Fe_{total}	Cu	Al	Mn	Zn	SO_4^{2-}
				[mg/L]		
3.5 - 3.9	260 - 460	1.7 – 3.2	50 - 100	23 - 36	7.9 – 12.6	1800 - 3200

In the experiments pretreated AMD was used. As first the iron was removed from AMD by oxidation using 31% H_2O_2 and subsequent precipitation with 0.1 M NaOH. In the next step the metals were removed from AMD by sorption using inorganic composite sorbent Slovakite [7]. Samples of AMD obtained in this process were marked as S/AMD.

2.2. Microorganisms

In the experiments culture of sulphate-reducing bacteria has been used, isolated from a mixed culture of SRB obtained from the mineral water Gajdovka (Kosice – North, Slovak Republic). For isolation and cultivation, the selective culture media DSM-63 was used at anaerobic conditions and temperature 30° C. The sodium sulphate was used as the sulphates source and the sodium lactate was used as the energetic substrate for the growth of SRB. The composition of culture media creates optimal conditions for the growth of SRB genera *Desulfovibrio* [5].

2.3. Analytical Methods

Samples were analyzed for concentration of sulphates, lactate and acetate by ion chromatography Dionex ICS 5000 (Sunnyvale, CA, USA), equipped with an IonPac AS11-HC anion column and suppressed conductivity detector.

2.4. Removal of Sulphates

Batch studies on biological sulphate removal from pretreated AMD with concentration of sulphates 2420 mg/L (sample S/AMD/1), 1681 mg/L (sample S/AMD/2) and 1500 mg/L (sample S/AMD/3) were realised. Differences in the initial concentration of sulphates at the particular samples were caused by sampling of AMD at various dates. For the experiments modified selective nutrient DSM-63 media were prepared - without sulphates contents and standard amount, double amount and triple amount of sodium lactate. The pretreated mine water (S/AMD) served as a source of sulphates for dissimilatory sulphate reduction. The abiotic samples (S/AMD-C) were prepared at identical conditions for control. Experiments were realized in the reagent bottles under anaerobic conditions at 30 ºC for 14 days. The samples were collected daily over two weeks to monitor the concentration of sulphates, lactate and acetate. Composition of biotic and abiotic samples in the process of the sulphates removal is described in Table 2.

Table 2. Composition of liquid phase of samples

Sample	Amount of Sodium Lactate	AMD	DSM-63 (without of sulphates) [ml]	Inoculum of SRB [ml]
S/AMD/1	standard	100	80	20
S/AMD/1-C			100	-
S/AMD/2	double		80	20
S/AMD/2-C			100	-
S/AMD/3	triple		80	20
S/AMD/3-C			100	-

3. Results and Discussions

In this work the biological sulphates removal from pre-treated AMD using SRB (Figure 1) was studied. The base of bacterial reduction was the heterotrophic oxidation of organic substrate (sodium lactate) in which the final product is acetate (Equation 1):

$$2\ CH_3CHOHCOO^- + SO_4^{2-} \xrightarrow{\text{SRB}} 2\ CH_3COO^- + 2\ HCO_3^- + H_2S \quad (1)$$

Successful process of the bacterial sulphates reduction was confirmed at the all biotic samples on the basis of monitored parameters:

- The formation of hydrogen sulphide according the orientation test (equation 2) when the hydrogen sulphide reacts with Cu^{2+} under acidic conditions (Figure 2). The intensive brown colouring is proportional to the hydrogen sulphide volume [8].

$$Cu^{2+} + H_2S \rightarrow CuS + 2\ H^+ \quad (2)$$

- The decrease of sulphate concentrations (Figure 3). None or the minimal decreasing of concentration of sulphates in abiotic controls was observed.

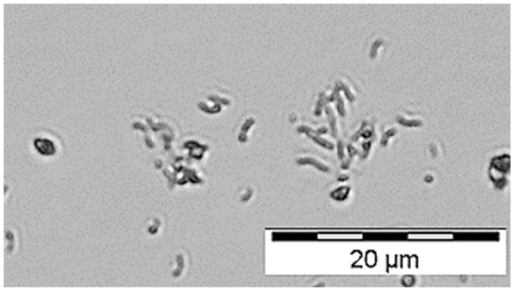

Figure 1. Scanning electron micrograph of sulphate-reducing bacteria *Desulfovibrio* sp.

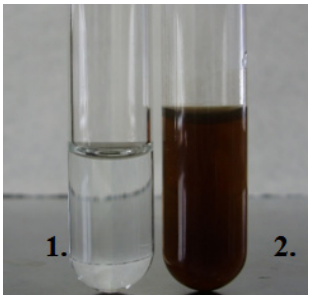

Figure 2. Evidence of the hydrogen sulphide presence (1 – S/AMD-C, 2 – S/AMD)

The kinetic of bacterial sulphate reduction depends on the several factors - quality and quantity of the SRB bacterial cultures, quality and quantity of the energetic substrate, value of pH, the concentration of bacterially produced hydrogen sulphide. The ratio of substrate quantity and sulphate concentration in the feed is an important parameter related to electron flow in anaerobic metabolism [9]. Experimental data showed that a lower or higher ratio results in the sulphate removal value. The higher substrate quantities led to higher efficiency of the sulphates removal (Figure 4).

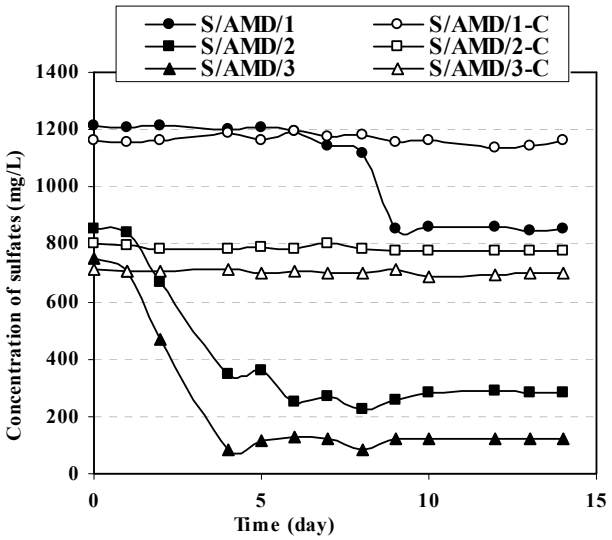

Figure 3. Kinetics of bacterial sulphate reduction observed in the experiment

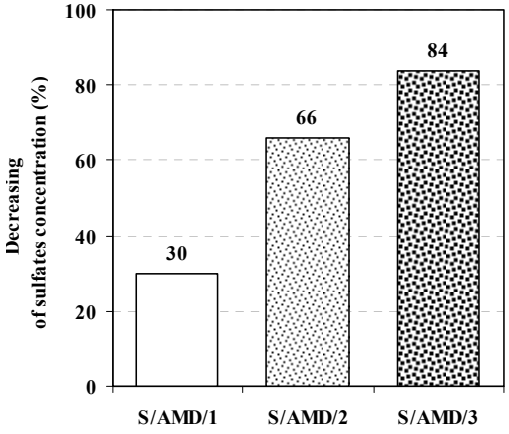

Figure 4. Efficiency of sulphates reduction by SRB at different amount of substrates

Figures 3 and 4 documented the satisfactory reduction of sulphates meeting the limit for surface waters established by Slovak legislation of 250 mg/L only in the case of sample S/AMD/3. Total elimination of sulphates was not achieved. Analyses of the lactate and acetate concentration confirm the lactate consumption at the acetate formation according of the equation 1 (Figure 5).

SRB genera *Desulfovibrio* cannot utilize acetate as growth substrate [5]. Bacterial sulphate reduction was stopped at the influence of suitable organic substrate absence.

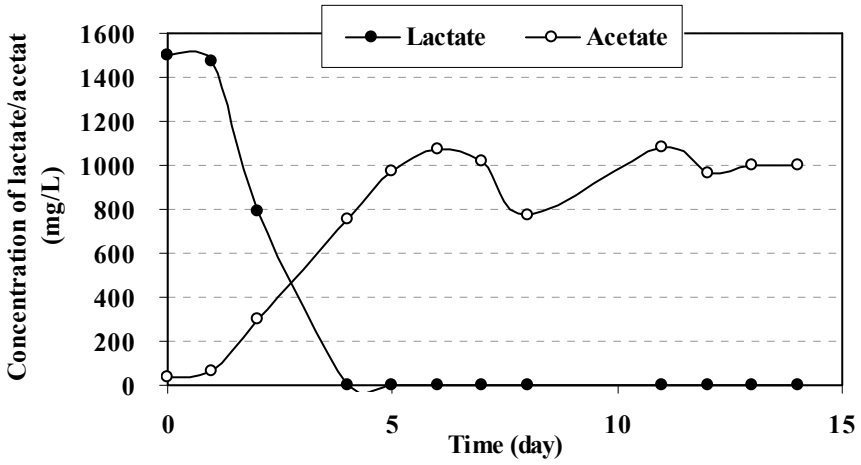

Figure 5. Lactate utilization and acetate production by SRB

4. Conclusions

Our study demonstrated the possibility of a biological treatment of mine water with high concentration of sulphates. Removing of sulphates by dissimilatory sulphate reduction has been reached with 30 %, 66% and 84% efficiency in depend of amount of used organic substrate – sodium lactate. The results of this work suggest that ratio of substrate quantity and sulphate concentration is one of the key parameter of sulphate reducing condition. Subsequent experiments will be focused on the use of the mixed bacterial culture of SRB containing genera which are able utilize acetate as growth substrate.

Acknowledgement

This work was supported by the Slovak Grant Agency for Science Grant No. 2/0145/15.

References

[1] INAP - International Network for Acid Prevention, 2003. Treatment of Sulphate in Mine Effluents, LORAX Environmental, Inc., 129 p.

[2] Geurts, J.J.M., Sarneel, J.M., Willers, B.J.C., Roelofs, J.G.M., Verhoeven, J.T.A., Lamers, L.P.M., 2009. Interacting effects of sulphate pollution, sulphide toxicity and eutrophication on vegetation developments in fens: A mesocosm experiment. *Environmental Pollution*, 157: 2072-2081

[3] Lamers, L.P.M., Tomassen, H.B.M., Roelofs, J.G.M., 1998. Sulfate-Induced Eutrophication and phytotoxicity in Freshwater. *Environmental Science & Technol*., 32: 99-205

[4] Sarti, A., Silva, A. J., Zaiat, M., Foresti, E., 2009. The treatment of sulfate-rich wastewater using an anaerobic sequencing batch biofilm pilot-scale reactor. Desalination, 249: 241-246

[5] Postgate, J.R., 1984: The sulphate-reducing bacteria. University Press, Cambridge, Second edition, 210 p.

[6] Tang, K., Baskaran, V., Mehdi, T., 2009. Bacteria of the sulphur cycle: An overview of microbiology, biokinetics and their role in petroleum and mining industries. *Biochemical Engineering Journal,* 44: 73-94

[7] Bálintová, M., Holub, M., Števulová, N., Cigašová, J., Tesarčíková, M., 2014. Sorption in Acidic Environment – Biosorbents in Comparison with Commercial Adsorbents. *Chemical Engineering Transaction,* 39: 625-630

[8] Luptáková, A., Kušnierová, M., Fečko, P., 2002. Minerálne biotechnológie II.Mineral technolgies, VŠB TU Ostrava, 152 p. (in Czech)

[9] Liamleam, W., Annachhatre, A.P., 2007. Electron donors for biological sulfate reduction. *Biotechnology Advances,* 25: 452-463