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Sulfate reduction at low pH to remediate acid mine drainage

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HIGHLIGHTS

- Acid mine drainage (AMD) is an important environmental concern.
- Remediation through biological sulfate reduction and metal recovery can be applied for AMD.
- Microbial community composition has a major impact on the performance of bioreactors to treat AMD.
- Acidophilic SRB are strongly influenced by proton, sulfide and organic acids concentration.

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ABSTRACT

Industrial activities and the natural oxidation of metallic sulfide-ores produce sulfate-rich waters with low pH and high heavy metals content, generally termed acid mine drainage (AMD). This is of great environmental concern as some heavy metals are highly toxic. Within a number of possibilities, biological treatment applying sulfate-reducing bacteria (SRB) is an attractive option to treat AMD and to recover metals. The process produces alkalinity, neutralizing the AMD simultaneously. The sulfide that is produced reacts with the metal in solution and precipitates them as metal sulfides. Here, important factors for biotechnological application of SRB such as the inocula, the pH of the process, the substrates and the reactor design are discussed. Microbial communities of sulfidogenic reactors treating AMD which comprise fermentative-, acetogenic- and SRB as well as methanogenic archaea are reviewed.

1. The sulfur cycle and generation of acid mine drainage

Sulfur is one of the most abundant elements on Earth. The largest sulfur reservoirs are in sediments and rocks (7800×10^{18} g) in the form of iron sulfides, mainly pyrite (FeS_2), and gypsum ($CaSO_4$) or as sulfate in seawater (1280×10^{18} g) [1]. Sulfur occurs in different oxidation states (from −2 to +6, see Fig. 1) and chemical forms (cysteine, sulfide, sulfate, etc.) in the environment. These compounds can be transformed both chemically and biologically.

- *Chemical sulfur processes*: The environmental sulfur cycle comprises both atmospheric and terrestrial redox processes. In the terrestrial part, the weathering of rocks releases stored sulfur. Sulfate (SO_4^{2-}) is usually the final oxidation product, which accumulates in minerals (e.g. $CaSO_4$) and in the ocean. There is also a variety of sources that emit sulfur directly into the atmosphere. These sources can be either natural such as volcanic eruptions and evaporation of water or anthropogenic. For instance, burning of fuels releases large quantities of sulfur dioxide into the environment, contributing significantly to air pollution and causing acid rain [2].
- *Biological sulfur processes*: Microorganisms play an essential role in the sulfur cycle, catalyzing both oxidation and reduction reactions of sulfur compounds (Fig. 1). These reactions include: (1) dissimilatory sulfate reduction, the reduction of sulfate to sulfide is coupled to energy conservation and growth (see Section 3); (2) dissimilatory sulfur reduction, the electron acceptor is elemental sulfur; (3) assimilatory sulfate reduction, the reduced sulfide is assimilated in biomass, proteins, amino-acids and cofactors by plants, fungi and microorganisms; (4) mineralization of organic compounds with hydrogen sulfide release; (5) sulfide oxidation by O_2, NO_3^-, Fe^{3+} or Mn^{4+} as electron acceptors by lithotrophic and phototrophic bacteria, producing sulfur and subsequently

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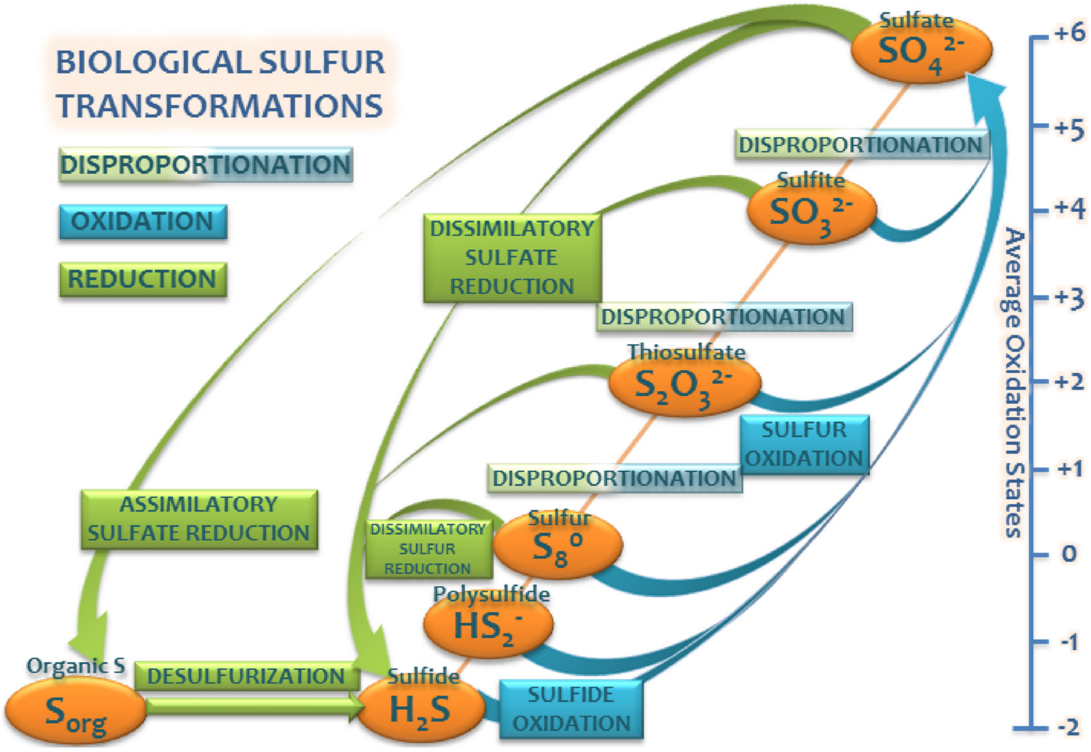

Fig. 1. Biological sulfur transformations.

sulfate; and (6) disproportionation, the coupled oxidation and reduction of sulfur compounds (thiosulfate, sulfite and sulfur) to sulfate and sulfide. Table 1 shows the equations for some of the relevant biological processes with their energy release per reaction.

The generation of acid mine drainage (AMD), waters with low pH and high heavy metals content, is a combined physicochemical and biological process. It starts with the chemical attack (Fe^{3+}) of the ores and continues due to the microbiological regeneration of the Fe^{3+}. The chemical oxidation of the minerals can follow two mechanisms depending on the structure of the mineral substrate [4]. Three metal sulfides: pyrite (FeS_2), molybdenite (MoS_2) and tungstenite (WS_2), undergo through the so-called thiosulfate mechanism and the rest of the sulfides undergo through the polysulfide mechanism [5].

Table 1
Stoichiometry and Gibbs free energy changes of some of the relevant conversions in the biological sulfur cycle. Gibbs free energy changes were calculated from [3].

Reaction equations		$\Delta G^{\circ\prime}$ [kJ mol^{-1}]
Sulfide oxidation		
$HS^- + 3/2O_2 + H^+ \rightarrow S^0 + H_2O$	(1)	−210
$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	(2)	−709
$HS^- + Fe^{3+} \rightarrow S^0 + Fe^{2+} + H^+$	(3)	−47
$HS^- + 2/5NO_3^- \rightarrow S^0 + 1/5N_2 + 6/5H_2O$	(4)	−214
Sulfur oxidation		
$S^0 + 1.5O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+$	(5)	−499
$S^0 + 6/5NO_3^- + 2/5H_2O \rightarrow SO_4^{2-} + 3/5N_2 + 4/5H^+$	(6)	−510
Disproportionation		
$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + HS^- + H^+$	(7)	−22
$S^0 + H_2O \rightarrow 1/4SO_4^{2-} + 3/4HS^- + 5/4H^+$	(8)	9.5
$SO_3^{2-} + 2/3H^+ \rightarrow 2/3SO_4^{2-} + 1/3S^0 + 1/3H_2O$	(9)	−7.6
Sulfate reduction		
$CH_3COO^{-a} + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$	(10)	−48
$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$	(11)	−151.9
Sulfur reduction		
$1/4C_2H_3O_2^{-a} + H_2O + S^0 \rightarrow 1/2HCO_3^- + 5/4H^+ + HS^-$	(12)	−13
$H_2 + S^0 \rightarrow HS^- + H^+$	(13)	−27.8

[a] Acetate is used as a representative organic compound, but other organic compounds may be used as well.

Pyrite (FeS_2), the most abundant sulfide mineral in Earth's crust, can serve as example of the thiosulfate mechanism. When pyrite is exposed, its chemical oxidation occurs. Eq. (14) describes the oxidation of pyrite in the presence of oxygen and water [6].

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (14,\ \text{abiotic})$$

A critical factor is that ferric iron is able to oxidize pyrite even under anoxic aqueous conditions at a much faster rate (18–170 times faster) than molecular oxygen [7–9], according to Eq. (15).

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (15,\ \text{abiotic})$$

First, the ferric iron attacks the iron—disulfur bonds, oxidizing it partially to thiosulfate (Eq. (16)), which will be later completely oxidized to sulfate again by the ferric iron attack (Eq. (17)). In this mechanism, the end chemical product of the overall reaction is sulfuric acid [10].

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \qquad (16,\ \text{abiotic})$$

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \qquad (17,\ \text{abiotic})$$

The rest of the sulfides, e.g. chalcopyrite ($CuFeS_2$), sphalerite (ZnS) or galena (PbS), are oxidized through the other pathway, the polysulfide mechanism, with a combined attack from iron and protons [5]. In this mechanism, polysulfides are first generated (Eq. (18)) and then partially oxidized to elemental sulfur (Eq. (19)).

$$8MeS + 8Fe^{3+} + 8H^+ \rightarrow 8Me^{2+} + 4H_2S_n + 8Fe^{2+} \quad (n \geq 2) \qquad (18,\ \text{abiotic})$$

$$4H_2S_n + 8Fe^{3+} \rightarrow S_8{}^{o} + 8Fe^{2+} + 8H^+ \qquad (19,\ \text{abiotic})$$