Review

The bioenergetics mechanisms and applications of sulfate-reducing bacteria in remediation of pollutants in drainage: A review

Xin Li[a,b,*], Shi-ming Lan[a,b], Zhong-ping Zhu[c], Chang Zhang[a,b], Guang-ming Zeng[a,b], Yun-guo Liu[a,b], Wei-cheng Cao[a,b], Biao Song[a,b], Hong Yang[a,b], Sheng-fan Wang[a,b], Shao-hua Wu[a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] School of Minerals processing and Bioengineering, Central South University, No. 932 South Lushan road, Changsha, Hunan 410083, PR China

ABSTRACT

Sulfate-reducing bacteria (SRB), a group of anaerobic prokaryotes, can use sulfur species as a terminal electron acceptor for the oxidation of organic compounds. They not only have significant ecological functions, but also play an important role in bioremediation of contaminated sites. Although numerous studies on metabolism and applications of SRB have been conducted, they still remain incompletely understood and even controversial. Fully understanding the metabolism of SRB paves the way for allowing the microorganisms to provide more beneficial services in bioremediation. Here we review progress in bioenergetics mechanisms and application of SRB including: (1) electron acceptors and donors for SRB; (2) pathway for sulfate reduction; (3) electron transfer in sulfate reduction; (4) application of SRB for economical and concomitant treatment of heavy metal, organic contaminants and sulfates. Moreover, current knowledge gaps and further research needs are identified.

1. Introduction

Sulfate-reducing bacteria (SRB), a group of anaerobic prokaryotes, widely exist in a variety of anoxic habitats such as lakes, marshes, paddy fields, petroleum deposits, underground pipelines and some industry wastewater (Li et al., 2017b, 2016; Martins et al., 2009; Zhou et al., 2013). However, SRB activity is not confined to permanently anoxic environment. It has been reported that SRB in aerobic zones of numerous biotopes have higher abundance and metabolic activity than that in surrounding anoxic zones (Ramel et al., 2013). There are more than 40 SRB species including *Desulfovibrio*, *Desulfomicrobium*, *Desulfobacter* and *Desulfotomaculum*, and others (Hussain et al., 2016; Leloup et al., 2010; Mizuno, 2012). In nature, they can use sulfur species (sulfite, sulfate and thiosulfate) as terminal electron acceptor for the oxidation of organic compounds (Simon and Kroneck, 2013). Therefore, SRB are major contributors to the biological sulfur cycles (Heidelberg et al., 2004; Oliveira et al., 2008). In addition, for biological carbon cycles, SRB are component of microbial consortia that completely mineralize organic carbon in anaerobic environments, particularly in marine sediments. It has been estimated that sulfate reduction can account for more than 50% of the organic carbon mineralization in marine sediments (Bo, 1982). Beyond these ecological functions, SRB

also play an important role in bioremediation. Sulfate can be biologically reduced to hydrogen sulfide by SRB. This biogenic hydrogen sulfide can react with dissolved heavy metal ions and transform them into high chemical stability metals sulfides (e.g., Cd(II), Cu(II), Ni(II), Pb(II), U(IV) and Sb(V)) (Kiran et al., 2017; Sani et al., 2004; Zhang et al., 2016; Zhu et al., 2018). This process has some advantages over traditional chemical processes. Most metal sulfides are more stable than the hydroxides produced by chemical treatment. In addition, metal sulfides can be recycled and reused (Jalali and Baldwin, 2000). Furthermore, SRB are commonly known as the culprit of bio-corrosion, which is one of common corrosion types for buried and deep-water pipelines. The bio-corrosion usually results in costly repair and corrosion of pipe materials (Delaunois et al., 2014; Duncan et al., 2017; Mohd Ali et al., 2016). That is why SRB have been studied extensively.

Several reviews have summarized fundamental biologic characteristics of SRB and mechanism of heavy metal removal (Hussain et al., 2016; Jamil and Clarke, 2013; Kiran et al., 2017; Papirio et al., 2013). For example, Hussain et al. (2016) reviewed the application and nutritional aspects of SRB. Papirio et al. (2013) conducted a detailed review of the effects of environmental conditions (such as pH, organic substrate and temperature) on SRB. However, electron transfer and substrate transformation in sulfate reduction by SRB remain partly

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Table 1
Typical literature about electron donors and acceptors for SRB in recent years.

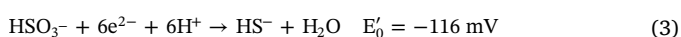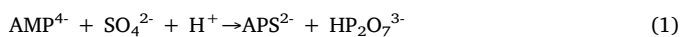| Respiration type	Genera	Electron donors	Electron acceptors	Reference
Autotrophic		H_2		(Lens and Kuenen, 2001)
Heterotrophic	*Desulfovibrio desulfuricans* strain PA2805	lactate	Dimethylsulphoxide	(Jonkers et al., 2010)
	Desulfovibrio strain IC1	Ethanol	Isethionate	(Lie et al., 1996)
	Desulfovibrio and *Desulfomicrobium* species	Formate, ethanol, lactate, methanol, acetate, carbohydrate based polymers, molasses, fatty acids mixture, glucose,fructose and agricultural waste	Sulfur species (sulfite, sulfate and thiosulfate), nitrate, iron(Fe(III)), uranium (U(VI)), chromate(Cr(VI)) and arsenate(As (VI))	(Hussain et al., 2016, 2014a; Hussain and Qazi, 2016; Muyzer and Stams, 2008; Papirio et al., 2013; Reyes-Alvarado et al., 2017; Zhou et al., 2014b)
	Desulfovibrio desulfuricans-HAQ3	Bovine and poultry manures	Sulfate	(Hussain et al., 2014b)

understood and even controversial (Zhou et al., 2017). In this review, indirect electron transfer through hydrogen cycling and direct electron transfer through menaquinone (MQ) mediation are detailed reviewed. Those studies are very important in developing bioremediation for the applications of heavy metal removal.

2. Electron acceptors and donors for SRB

There are different genera of SRB, and they may be different respiration-type of life (such as autotrophic, litho-autotrophic and heterotrophic) under anaerobiosis condition (Hussain et al., 2016). In general, autotrophic SRB can use CO_2 as substrates and oxidize H_2 to obtain electrons and energy for growth, while heterotrophic must use organic matters (Lens and Kuenen, 2001). It has been confirmed that SRB could utilize a wide variety of chemical substance as electron acceptors and donors (Hussain and Qazi, 2012; Hussain et al., 2014b) (more from Table 1). Some SRB can completely oxidize organic substrates to CO_2, while some others can only oxidize them to acetate incompletely (Sahinkaya et al., 2007). In addition to the chemical substance above, aromatic hydrocarbons, alkanes and alkenes are also fermented by a number of SRB (Aeckersberg et al., 1998; Morasch et al., 2004; Vincent Grossi et al., 2007). However, not all of this chemical substance is perfect for SRB growth. Some reviews have concluded the advantages and disadvantages of main organic electron donors for SRB (for detail, see refs.(Papirio et al., 2013)). In summary, low-molecular weight organic compounds are better electron donor for SRB (Hussain et al., 2016; Zhou et al., 2017).

3. Pathway for sulfate reduction

SRB cannot utilize directly sulfate as the electron donors for growth. Sulfate is an unsuitable electron donor for SRB, because it is a thermodynamically stable oxidized form of sulfur. The E_0' of the redox couple sulfate-sulfite is $-516\,mV$, which is difficult to directly reduce by the intracellular electron mediators ferredoxin or nicotinamide adenine dinucleotide phosphate (NADH) (Muyzer and Stams, 2008). The pathways of sulfate reduction are presented in the equations below (Eqs. 1–3) (Keller and Wall, 2011). In general, sulfate reduction includes three main steps: (1) sulfate activation to adenosine 5′- phosphosulfate (APS) (Eq. 1); (2) APS reduction to sulfite (Eqs. 2); and (3) sulfite reduction to sulfide (Eq. 3) (Broco et al., 2005). Sulfate reduction is an intracellular process requiring active transport of sulfate. First, before reduction, the sulfate must be activated by ATP sulphurylase to yield APS and pyrophosphate, thereby shifting the E_0'(APS/AMP + HSO_3^-) to $-60\,mV$ (Muyzer and Stams, 2008).

$$AMP^{4-} + SO_4^{2-} + H^+ \rightarrow APS^{2-} + HP_2O_7^{3-} \tag{1}$$

$$APS^{2-} + 2e^{2-} + H^+ \rightarrow HSO_3^- + AMP^{2-} \quad E_0' = -60\,mV \tag{2}$$

$$HSO_3^- + 6e^{2-} + 6H^+ \rightarrow HS^- + H_2O \quad E_0' = -116\,mV \tag{3}$$

The formation of APS is endergonic process. Hence, addition of suitable carbon source for sulfate reduction is often necessary. Second, APS can be exergonic reduced to sulfite by APS reductase (Broco et al., 2005). The third step (Eq. 3) is still a point of contention with two mechanisms proposed. A pathway through trithionate and thiosulphate would allow a reduction in three two-electron reduction steps (trithionate pathway). However, a reduction in direct six-electron reduction step still cannot be excluded (direct pathway)(Fig. 1) (Muyzer and Stams, 2008). It has been reported that neither thiosulfate nor trithionate was a normal intermediate in the reduction pathway (Chambers and Trudinger, 1975). So, it involves the reduction of sulfite to sulfide occurring in one step through the transfer of six-electrons (direct pathway). Another one suggests the formation of trithionate and thiosulfate as intermediates in the sulfite reduction(trithionate pathway) (Ishimoto, 1969). For complete reduction of sulfite to sulfide, some enzymes are involved, such as trithionate and thiosulfate reductases (Chambers and Trudinger, 1975). Some studies have shown that disruption of flavoredoxin gene strongly inhibited the reduction of thiosulfate (Broco et al., 2005).

4. Electron transfer in sulfate reduction

Electron transport chain is considered to be a principal component in sulfate reduction (Li et al., 2013). Intensive studies of electron transfer pathway in sulfate reduction have focused on members of the genus *Desulfovibrio* because of their rapid growth and ease of manipulation (Keller and Wall, 2011; Zhou et al., 2017). However, the pathway of electron flow in sulfate reduction remains controversial. Electron transfer models can be grouped broadly into two categories (model of hydrogen cycling and new model).
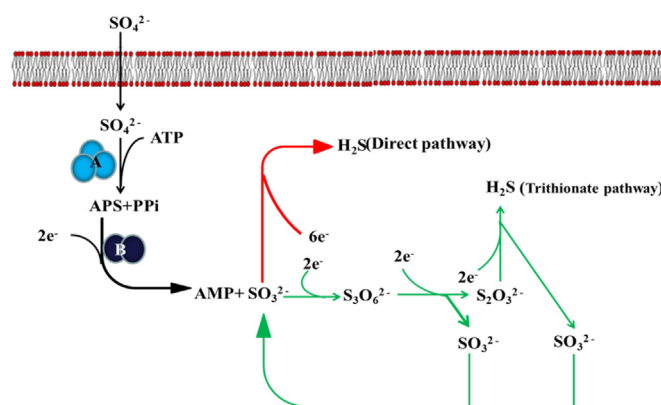

Fig. 1. The two previously proposed pathways for dissimilatory sulfate reduction(adapted from Broco et al. (2005); Muyzer and Stams (2008)). A represents ATP sulphurylase and B represents APS reductase. Red arrows represent direct pathway; green arrows represent trithionate pathway.