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Biological Sulfate Reduction Using Gaseous Substrates To Treat Acid Mine Drainage

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Abstract

Purpose of Review Acid mine drainage (AMD) is a serious environmental problem due to its high sulfate and heavy metal content. In comparison with the conventionally used physico-chemical methods, biological methods involving sulfate-reducing bacteria (SRB) offer a green and sustainable way to treat AMD. Biological sulfate reduction requires an efficient and low-cost electron donor. This paper overviews different gaseous substrates as electron donor that can be used for sulfate reduction to treat AMD.

Recent Findings The use of gaseous substrates as electron donor for sulfate reduction is advantageous as it avoids dilution of wastewater and avoids secondary pollution problems arising from unutilized electron donor. Among the different gaseous substrates for sulfate reduction, hydrogen (H_2) is more energetically favourable to the sulfate-reducing microorganisms. Carbon monoxide (CO) is a low-cost waste gas substrate for sulfate reduction, but its toxicity limits its applications. Only a limited number of specialized slow-growing microorganisms can utilize methane (CH_4) coupled to sulfate reduction under anaerobic conditions.

Summary Different gases (H_2, CO and CH_4) are evaluated as potential electron donor for biological sulfate reduction to treat AMD. Several bacterial and archaeal species can use these gases as the sole electron donor for reducing sulfate to sulfide. Heavy metals present in the AMD can be removed by sulfidic precipitation although high concentrations of heavy metals can inhibit SRB activity, thus reducing the process efficiency. In addition, proper choice of the bioreactor system has a great influence on the AMD treatment efficiency by biological sulfate reduction using gaseous substrates.

Keywords Sulfate reduction · Acid mine drainage · Gaseous substrates · Bioreactor · Sulfate-reducing bacteria · Resource recovery

Introduction

Mining activities generate acid mine drainage (AMD) which causes severe damage to the environment [1]. AMD is characterized by a high sulfate and heavy metal content as well as a low pH, which when released into the environment without proper treatment can severely pollute the water resources and soils [2]. A common treatment method for AMD involves chemical precipitation using limestone or sodium hydroxide [3]. Although this process is inexpensive and easy to apply, generation of a large amount of toxic sludge and high requirement of chemicals make it unsustainable (Table 1) [4].

Biological treatment methods using sulfate-reducing bacteria (SRB) are more sustainable than chemical precipitation for treating AMD [1]. In addition, the biological process is highly suitable for treating AMD with a low content of sulfate and heavy metals, which is unsuitable for the chemical precipitation method [5]. In this process, SRBs reduce sulfate to sulfide, which upon reacting with heavy metals present in the AMD form insoluble precipitates of metal sulfides [6]. A prerequisite for the biological sulfate reduction process is the presence of an electron donor and a carbon source. As the organic content in AMD is often low, its treatment by SRB-based technologies depends on the supply of an external electron donor and carbon source [7]. Comparative advantages

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Table 1 Comparison between chemical precipitation and biological sulfate reduction methods for AMD treatment

Method	Advantages	Disadvantages
Chemical precipitation	• Ease of operation and use of inexpensive equipment • Effective even at high concentrations of heavy metals • Often achieves desired discharge standard	• Requires solid/liquid separation operation • Use of large quantities of toxic and corrosive chemicals • Generally large amount of toxic sludge generated and subsequent sludge disposal problem • Sulfate removal at concentrations below 1500 mg/L is not possible
Biological sulfate reduction	• Simultaneous removal of organic compounds, sulfate and heavy metals is possible • Produces minimum sludge for disposal • Highly efficient for treating wastewater with low concentrations of sulfate and heavy metal • Considered as green and sustainable technology • Allows recovery of resources in the form of metal sulfides and elemental sulfur	• Requires an external carbon source and electron donor • Low removal efficiency at high sulfate and heavy metal concentrations • Process parameters such as acidity, temperature, oxidation–reduction potential (ORP), sulfide concentration, hydraulic retention time (HRT) greatly influence the process efficiency

and disadvantages of chemical precipitation and biological sulfate reduction-based methods for AMD treatment are provided in Table 1.

An ideal electron donor for biological treatment of sulfate-rich wastewater has low cost and is easily available and non-toxic [1]. Organic electron donors support heterotrophic sulfate reduction while providing also the carbon source for the SRB, whereas for inorganic electron donors (e.g. H_2), a carbon source still has to be supplemented [5, 8]. This can be CO_2 or carbon from organic substrates. Many different electron donors, including lactate, acetate, glucose, ethanol, methanol, hydrogen, carbon monoxide and methane, have been used for biological sulfate reduction [7]. Among these, the gaseous electron donors hydrogen, carbon monoxide, methane or their gas mixtures such as hydrogen–carbon dioxide and syngas (mixture of CO, H_2 and CO_2) are attractive. The major advantages of using gaseous substrates are that the sulfate reduction rates are often very high (particularly in case of H_2) and they do not cause secondary pollution problems due to unutilized substrates remaining in the wastewater, which is a major concern with complex soluble organic substrates [8, 9].

Despite their advantages over soluble substrates for biological sulfate reduction, gaseous substrates for AMD treatment by biological sulfate reduction are not well-reported in the literature. Most of the previously published reviews in this area have solely focused on soluble substrates, and currently, there is no review paper available on AMD treatment by biological sulfate reduction using gaseous substrates as the carbon source and electron donor. Hence, this paper aims to provide an overview of the different gaseous substrates for sulfate reduction, SRB species capable of utilizing gaseous substrates and sulfidogenic bioreactor systems suited to use gaseous substrates.

Biological Sulfate Reduction for Treatment of Mining Wastewater

Mining Wastewater: Sources and Effects

AMD is primarily generated by activities associated with mining of coal and different metals, such as zinc, copper and nickel [1]. Oxidation of metal sulfides present in mine rocks due to contact with air and water produces an acidic (low pH) solution containing sulfate and soluble metal ions [10]. Though chemical processes play a key role in AMD generation, oxidizing bacteria belonging to *Thiobacillus* sp. can significantly contribute to its generation [11]. The acidic solution further reacts with the surrounding environment, thus further dissolving metals and releasing cations in the process.

The commonly found heavy metals in AMD are iron, copper, zinc, lead, cadmium, aluminium and manganese [4]. In addition, nickel, cobalt, chromium and uranium can also prevail in mining effluents depending on the geological composition of the ore [12]. The composition and characteristics of the AMD depends on various conditions such as physical, chemical and biological factors as well as the geographical location [13]. In addition to these parameters, rock permeability strongly influences the rate of AMD generation [3].

In most cases, as AMD is generated from abandoned mining sites, the absence of industrial treatment of the wastewater has led to environmental pollution, in particular the aquatic environment is largely affected when AMD flows into a water stream or surface water body from the location where it is generated [13]. As a result, AMD causes a severe impact on the ecosystem by reducing the dissolved oxygen content, inducing acidic conditions, and bioaccumulation of potentially toxic heavy metals [14]. In addition, it has the potential to contaminate the nearby soil and groundwater table [15]. Heavy metals present in AMD can damage internal organs, tissues and the central nervous system and are potentially carcinogenic [16]. They can as well lead to developmental

disorders in humans and animals [17]. The toxic effects of heavy metals are more severe due to their persistent nature in the environment which leads to bioaccumulation in aquatic plants and animals, thereby increasing the risk of exposure and harmful effects to humans [18]. Apart from affecting humans and animals, heavy metals present in acidic AMD also adversely affect plants by damaging the cells and tissues, thereby leading to loss of vegetation [13, 19]. The soil characteristics also change due to the low pH of AMD, which interferes with the uptake of essential nutrients (nitrogen, phosphate and potassium) by plants [13]. As per the World Health Organization (WHO), the permissible limits of heavy metals in drinking water are 2, 3, 0.01, 0.02, 0.003, 0.2 and 0.5 mg/L for copper, zinc, lead, nickel, cadmium, aluminium and manganese are, respectively, whereas there is no such limits proposed for iron [20]. Unlike heavy metals, sulfate present in AMD neither poses serious environmental challenges nor causes toxic effects on humans, plants and animals. As per the WHO regulation, the permissible limit of sulfate in drinking water is 250 mg/L [9]. Besides, high concentrations of sulfate in the environment can lead to several secondary pollution problems, e.g. formation of sulfide which in turn causes odour and corrosion problems in sewer and water supply systems [9]. Hence, in order to avoid contamination of drinking water resources by AMD and to achieve permissible standard concentrations, effective treatment technologies need to be applied.

Treatment of Mining Wastewater

Physico-chemical Methods

Conventionally, AMD is treated by addition of alkaline chemicals, viz. lime stone, sodium hydroxide or sodium carbonate, which increases the pH of AMD and precipitates heavy metals [13, 14]. Although the method is effective for treating high concentrations of metals and easy to apply, several disadvantages such as the use of costly chemicals, generation of toxic sludge and associated sludge disposal problems are of concern [1]. Membrane filtration processes are also used to treat heavy metal-laden AMD and in most cases the treatment efficiency is very high [21]. However, disadvantages of membrane separation are high installation cost, clogging and need for frequent replacement of the membrane module.

Adsorption using various lignocellulosic compounds [22], waste materials and nanoparticles [23] are reported ubiquitously in the literature for AMD treatment, including a few pilot-scale studies [24]. The drawbacks of adsorption-based treatment are the requirement of additional treatment to recover the heavy metals from the adsorbent as well as the need of costly and corrosive chemicals for adsorbent preparation and regeneration [13]. Furthermore, the removal efficiency of the adsorbents declines after a few cycles of regeneration and reuse of the adsorbent, necessitating the use of fresh adsorbents in the treatment process.

Other advanced physico-chemical methods, such as reverse osmosis [25], ion exchange [26] and electrodialysis [27], have been applied to treat AMD, but their large-scale application is limited owing to their high costs of installation and operation. Hence, drawbacks associated with the physico-chemical methods have led to the search for alternative AMD treatment methods. In this context, biological treatment systems could be more suited to overcome the disadvantages of physico-chemical methods.

Biological Methods

Biological treatment of AMD can be achieved by using microorganisms (mainly SRB), algae and plants. Phytoremediation using different hyperaccumulating plants has been successfully used for treating AMD, which can, however, cause secondary pollution upon disposal of the metal-accumulated plants [28]. Besides, high metal concentrations and acidic pH can cause difficulties with plant-based treatment methods, as most of the plants will not be able to survive in such harsh conditions [29]. Algae are known to remove heavy metals from AMD by adsorption and, to a smaller extent, bioaccumulation [15], but drawbacks such as need for secondary treatment to recover metals and disposal of metal-adsorbed algal biomass pose challenges towards their successful application in wastewater treatment systems [30].

Biological treatment systems can be broadly classified as either passive treatment systems such as anoxic ponds and constructed wetland or active treatment technologies using sulfidogenic bioreactors [1]. Anoxic ponds are water bodies amended with organic substrates (often manure or liquid organic waste) in which SBRs are used to treat AMD [31]. In constructed wetland systems, a combination of different methods including adsorption, sedimentation, phytoremediation (uptake by plants) and precipitation of metals help achieve a high treatment efficiency [1]. However, the main disadvantages of these passive systems are large area requirement, prolonged treatment time, possibility of metal leaching into the ground and surface water reserves and non-suitability in arid and semiarid regions [32]. In comparison with the passive treatment systems, active treatment systems involving SRB offer a promising solution for treating heavy metal and sulfate containing AMD on-site [14].

Biological Sulfate Reduction

Biological sulfate reduction is an economical and green method for AMD treatment in comparison with the available physico-chemical treatment methods [1, 14]. The removal of heavy metals as insoluble metal sulfide due to their reaction

with the biologically produced sulfide is the key mechanism involved in this process. SRB are capable of reducing sulfate to sulfide by utilizing organic compounds as carbon source and electron donor [33]. Following sulfate reduction, metals combine with the biologically produced sulfide to form metal sulfide precipitates. However, the degree of precipitation of different heavy metals with sulfide depends upon their solubility product and the solution pH [6].

The key requirement of biological sulfate reduction is the electron donor. For reducing sulfate (S^{6+}) to sulfide (S^{2-}), eight electrons are required [7]. Some sulfate-rich wastewaters such as those from the pulp and paper industry [34], food-processing industry [35] and edible oil production industry [36] contain high concentrations of organics, which can be utilized by SRB for sulfate reduction. AMD, in contrast, generally does not contain organic compounds, which makes biological treatment challenging. Various pure compounds, such as sugars (glucose and sucrose) [37, 38], alcohols (ethanol and methanol) [39, 40] or short-chain fatty acids (lactate, acetate and butyrate) [6, 41], have been previously supplemented to the AMD to support biological sulfate reduction [7]. The use of these pure compounds for several other applications and their high costs make these compounds mostly unsuitable for AMD treatment [1, 42].

Other low-cost materials including waste substrates such as manure [43], wood chips, sawdust, agriculture residues [44], compost [45] and organic wastewater [46] have also been explored for this purpose, but secondary pollution due to these substrates in the wastewater is a major drawback [7]. Besides, some of these solid waste substrates are difficult to degrade and be utilized by SRBs for sulfate reduction. These are, nevertheless, often used as matrix material in constructed wetlands [4, 47].

Several gaseous substrates, mainly H_2, CO and CH_4 can serve as electron donor for biological sulfate reduction and thus treatment of AMD. Furthermore, the gases can be generated from waste substrates by using different biochemical or thermochemical routes, which further reduces the costs and facilitates on-site treatment of AMD without the need for transporting and storing these gaseous compounds.

Biological Sulfate Reduction Using Gaseous Substrates

Hydrogen

Hydrogen is an attractive, non-toxic substrate for sulfate reduction because among the different hydrogenotrophic anaerobic processes, namely sulfate reduction, methanogenesis and acetogenesis, hydrogenotrophic sulfate reduction is more energetically favourable [48]. The high growth rate of SRB also helps them in outcompeting methanogens and homoacetogens in H_2 utilization. van Houten et al. [49] suggested hydrogen to be the best electron donor for sulfate reduction at large-scale operation in comparison with other substrates.

Many mesophilic and thermophilic SRB can use H_2 for sulfate reduction (Table 2). However, in several cases, the presence of CO_2 along with H_2 is essential for achieving a high sulfate reduction efficiency, as CO_2 is a carbon source for the sulfate reducers. The biochemical reaction involved in hydrogenotrophic sulfate reduction is:

$$4H_2 + SO_4^{2-} + H^+ \rightleftharpoons HS^- + H_2O \quad (1)$$

Sulfate reduction using acetate, often formed by hydrogenotrophic acetogens present in the sludge, occurs as per the following reactions:

$$4H_2 + 2CO_2 \rightleftharpoons CH_3COO^- + 2H_2O \quad (2)$$

$$CH_3COO^- + SO_4^{2-} \rightleftharpoons HS^- + 2HCO_3^- \quad (3)$$

Species capable of utilizing H_2 as electron donor for sulfate reduction are, among others, *Desulfovibrio hydrothermalis* [58], *Desulfovibrio paquesii* [57], *Desulfovibrio vulgaris* [59], *Desulfovibrio hydrothermalis* AM13^T [60] and *Desulfovibrio desulfuricans* strain G11 [61]. *Candidatus Desulfofervidus auxilii* isolated from enriched anaerobic methane oxidizing consortia from the Guaymas Basin (Gulf of California) is capable of chemolithotrophic sulfate reduction under thermophilic (50–70 °C) conditions using H_2 and CO_2, respectively, as the electron donor and carbon source [62].

Other than pure cultures, SRB are usually present in consortia in anaerobic sludge from wastewater treatment plants (Table 2). In these mixed culture systems, different classes of bacteria work in symbiotic relations when one group of organisms utilizes intermediates formed by another microbial group to degrade the target pollutant. Figure 1a shows the possible utilization of the H_2/CO_2 gas mixture by different species of microorganisms present in anaerobic microbial consortia. Hydrogenotrophic sulfate reduction can play a key role by interspecies H_2 transfer in co-cultures of SRB (such as *Desulfovibrio vulgaris*, *Desulfovibrio salexigens* and *Desulfovibrio gibsoniae*) with *Mesotoga prima* strain PhosAc3 [63]. The study showed enhanced H_2 production from sugar by *M. prima* when co-cultured with SRBs, the latter used the in situ produced H_2 during acetogenesis from the sugar.

The H_2 utilization efficiency of pure SRB cultures is often low due to the poor bioavailability of H_2. Xu et al. [59] used ethanol-permeabilized cells of *Desulfovibrio vulgaris* Hildenborough to improve its hydrogenotrophic sulfate reduction efficiency. The lipopolysaccharide layer present on the outer membrane of Gram-negative bacteria can be a permeability barrier to the H_2. The cell membrane can be made more

Table 2 Biological sulfate reduction using hydrogen as the electron donor

Inoculum	Bioreactor configuration	Temp (°C)	pH	Electron donor (conc./ loading condition)	Sulfate concentration used	Sulfate reduction efficiency/ removal rate	Reference
Anaerobic digester sludge	Membrane biofilm reactor	21 ± 3	7.7–8.3	80% H_2 + 20% CO_2	15 mM	99% sulfate removal	[50]
Anaerobic biomass acclimatized to sulfate and thiosulfate reduction using H_2 and CO_2	Gas lift reactor	35	9	5 ml/min H_2 flow rate to the reactor	50 mM sodium sulfate	18 mmol/L/day	[51]
Desulfovibrio desulfuricans (NCIMB 8372)	Stirred tank reactor	30	6.95–7.05	95% H_2 + 5% CO_2	–	3.4 g/L/day	[52]
Anaerobic sludge	Gas lift reactor	30	5.0–5.5	90% H_2 + 10% CO_2	10.4 mM sodium sulfate	> 80%	[53]
Anaerobic sludge biomass	Gas lift reactor	30–35	7–7.5	H_2	5–30 g/L sulfate	295 kg sulfate/h	[54]
Anaerobic aggregated biomass	Gas lift reactor	30	7	80% H_2 + 20% CO_2 80% H_2 + 15% CO_2 + 5% CO	18 g SO_4^{2-}/L/day	12–14 g SO_4^{2-}/L/day and 6–8 g SO_4^{2-}/L/day	[49]
Granular anaerobic biomass	Gas lift reactor	30	5	H_2 (90–100 mL/min) + CO_2 (0–10 mL/min)	–	99% of sulfate removal/51 mM sulfate/day	[55]
Sulfidogenic enrichment culture at low temperature	Gas lift reactor	9	7.5	90% H_2 + 10% CO_2	0.58–3.0 g/L/day	500–600 mg/L/day	[56]
Desulfovibrio paquesii	Serum bottles	10–45	6.5–8.5	H_2/CO_2 (ratio 4:1, pressure 1.7 kPa)	20 mM	–	[57]
Desulfovibrio hydrothermalis	Serum bottles	35	7.8	H_2/CO_2	20 mM	–	[58]

permeable by treating it with organic solvents or surfactants, which results in an accelerated substrate transfer inside the cell, which often leads to increased enzyme activity. Cell permeabilization was found to almost double the sulfate reduction efficiency with pure H_2, due to the enhanced hydrogenase and metabolic activity of the SRB [59].

Carbon Monoxide

A number of SRB are capable of utilizing CO as the sole carbon and energy source (Table 3). Although some SRB species can utilize CO, it is toxic for most sulfate-reducing bacteria [72]. Both thermophilic and mesophilic carboxydotrophic sulfate reducers are described in the literature, e.g. *Desulfotomaculum thermoacetoxidans* strain CAMZ, *Thermodesulfovibrio yellowstonii*, *Desulfotomaculum kuznetsovii* and *Desulfotomaculum thermobenzoicum* sub sp. *thermosyntrophicum*, are moderately thermophilic with an optimum temperature in the range 55–60 °C [71]. *Archaeoglobus fulgidus* VC16 is an extremophile with an optimum temperature between 75 and 80 °C and able to utilize CO as the carbon source and electron donor for sulfate reduction [66]. The optimum temperature of most mesophilic carboxydotrophic sulfate-reducing strains is in the range 30–37 °C, e.g. *Desulfovibrio vulgaris* str. Madison, *Desulfovibrio baarsii 2st14*, *Desulfovibrio desulfuricans*, *Desulfovibrio baculatus*, *Desulfovibrio africanus* and *Desulfosporosinus orientis* [73].

Sulfate reduction using CO occurs according the following stoichiometry:

$$4CO + SO_4^{2-} + 4H_2O \rightleftharpoons 4HCO_3^- + HS^- + 3H^+ \quad (4)$$

In addition to this direct biochemical conversion, CO can be metabolized by non-SRB in mixed consortia, and the sulfate-reducing bacteria metabolize the produced H_2 (Eq. 5) or acetate [8]. Figure 1b depicts the CO utilization and its bioconversion to different by-products and end products by different groups of microorganisms present in anaerobic mixed cultures.

Both pure cultures and co-cultures can use CO for efficient sulfate reduction (Table 3). However, co-culture systems using anaerobic consortia can avoid CO toxicity and achieve a high CO utilization efficiency. For instance, Parshina et al. [71] observed that *Desulfotomaculum kuznetsovii* and *Desulfotomaculum thermobenzoicum* sub sp. *thermosyntrophicum* can grow at 100% CO when co-cultivated with the hydrogenogenic carboxydotrophic bacterium *C. hydrogenoformans*. In contrast, pure cultures of *D. kuznetsovii* and *D. thermobenzoicum* subsp. *thermosyntrophicum* tolerate only up to 50–70% CO. Sipma et al. [68] reported that the toxic effects of CO on SRB can be alleviated by culturing them with other CO-utilizing bacteria,

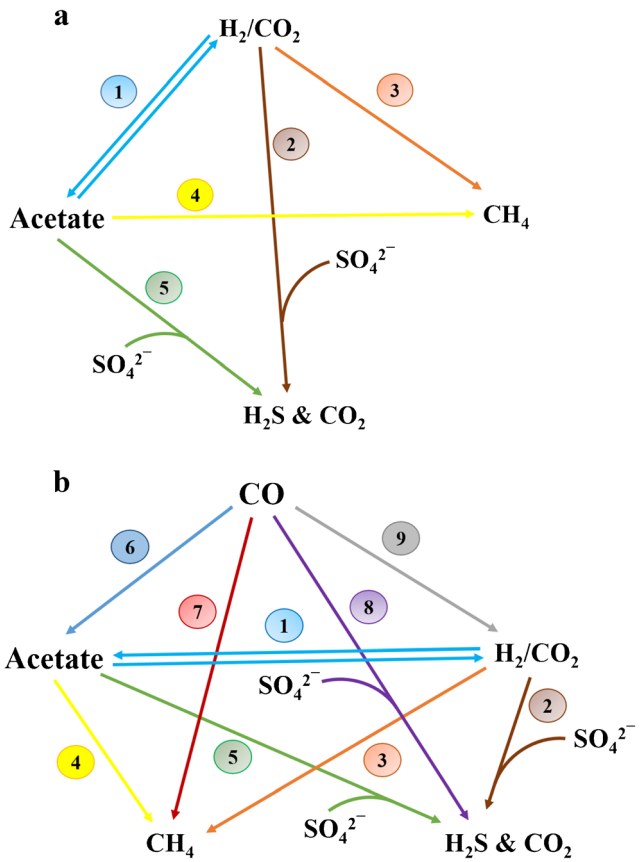

Fig. 1 The **a** hydrogen and **b** carbon monoxide utilization by different groups of microorganism present in anaerobic microbial consortia. (1) Homoacetogen/syntrophic acetate oxidizer, (2) hydrogenotrophic sulfate reducer, (3) hydrogenotrophic methanogen, (4) acetoclastic methanogen, (5) acetoclastic sulfate reducer, (6) carboxydotrophic acetogen, (7) carboxydotrophic methanogen, (8) carboxydotrophic sulfate reducer and (9) carboxydotrophic hydrogenogen

for example homo-acetogenic bacteria, that are capable of performing the biological water–gas shift reaction [74]:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad (5)$$

Therefore, in such mixed culture system, the microbial consortium can efficiently reduce sulfate to sulfide by utilizing CO as the sole carbon substrate. In another study, the use of a layered biomass structure such as granular sludge biomass or a bacterial biofilm with acetogenic bacteria at the periphery and SRB located inside was shown to lower the CO toxicity to SRB [49].

A high tolerance towards CO was reported for an anaerobic sludge during sulfate reduction using CO with 50.6% sulfate reduction and 85.6% CO utilization efficiencies [65]. The CO utilization data fitted well with the Haldane's kinetic model with an inhibitory concentration of 3.354 mmol/L. The optimum conditions for sulfate reduction using CO were 45 °C, 60 kPa initial CO partial pressure and 10% (v/v) inoculum. In the presence of sulfate, no methanogenic activity was observed [65].

Application of carboxydotrophic sulfate reducers for heavy metal removal using sulfide precipitation has been recently reported [12]. The heavy metal removal efficiency was high (> 70%) for the four heavy metals (Cu, Cd, Zn and Pb) investigated, which indicates the possibility of using CO as the electron donor for AMD treatment by carboxydotrophic sulfate reduction. The presence of heavy metals lowered the sulfate reduction and CO utilization efficiencies due to their inhibitory effect on the SRB activity. For example, the sulfate removal efficiency dropped to 50.3% and 59.4% in the presence of 100 mg/L of Pb and Cd, respectively, in comparison with control experiments where heavy metals were absent (88.6% sulfate reduction). Similarly, the CO utilization efficiency lowered from 95.2% (control experiment) to 80%, 77.8%, 63.2% and 59.5% in the presence of 100 mg/L of Cu, Zn, Cd and Pd, respectively [12].

Methane

Biological sulfate reduction can be coupled to anaerobic oxidation of methane (AOM), a process that occurs in deep-sea sediments (Table 4). For example, it prevails in sediments from eastern Mediterranean seafloor [79], Eckernförde Bay sediment [78], hydrothermal sediments of Guaymas Basin [80] and sediments from the upwelling area off Namibia [81].

The reaction stoichiometry of sulfate reduction using methane as the electron donor is given as:

$$CH_4 + SO_4^{2-} + 4H_2O \rightleftharpoons HCO_3^- + HS^- + H_2O \quad (6)$$

Various environmental factors such as temperature [80], pressure [76], pH, salinity and sulfide concentration [78] affect the sulfate reduction efficiency. Kallmeyer and Boetius [80] reported the best sulfate reduction rate of 6660 nmol/cm^3/day at 4.5×10^7 Pa pressure and 95 °C using AMO sediments collected from a hydrothermal vent in the Guaymas Basin. Cassarini et al. [76] reported the key role played by the methane partial pressure (studied in the range 0.1–40 MPa) on shaping the ANME-SRB microbial community. At low pressure conditions (0.1 MPa), a high number of SRB species such as *Desulfosarcina* and *Desulfococcus* were enriched in the microbial consortia collected from the marine lake Grevelingen sediment [76].

Omoregie et al. [79] reported sulfate reduction combined with methane oxidation in sediments below the seafloor in the eastern Mediterranean Sea. The sulfate reduction rate was higher than the anaerobic methane oxidation rate, indicating possibilities of other electron donors for sulfate reduction as well. Most AOM microorganisms are sensitive to sulfide: Meulepas et al. [78] observed that even at 2.4 mM of sulfide, both AOM and the associated sulfate reduction were completely inhibited. In the case of deep-sea sediments, a part of the sulfide produced in the process is carried to the surface

Table 3 Biological sulfate reduction using carbon monoxide as the electron donor

Inoculum	Bioreactor configuration	Temp (°C)	pH	Electron donor (conc./loading condition)	Sulfate concentration used	Sulfate reduction efficiency/ removal rate	Reference
Anaerobic sludge biomass	Gas lift reactor	30	7	100% CO	250–1000 mg/L sulfate	62.5–97.5%	[8]
Anaerobic sludge biomass	Moving bed biofilm reactor	30	7	100% CO	250–1000 mg/L sulfate	67.1–95.2%	[64]
Anaerobic sludge biomass immobilized in PVA and sodium alginate	Packed bed reactor	30	7	100% CO	250–1000 mg/L sulfate	61–94%	[9]
Anaerobic granular sludge	Batch serum bottle	30	7	100% CO	1000 mg/L sulfate	50.65%	[65]
Archaeoglobus fulgidus	Batch serum bottle	80	6.8	80% CO	2.2 g/L sodium sulfate	–	[66]
Carboxydothermus pertinax	Batch serum bottle	65	6–6.5	100% CO	–	–	[67]
Anaerobic granular sludge	Gas lift reactor	55	7	CO (100–250 mmol/L/day)	30–37 mmol/L/day	–	[68]
Anaerobic granular sludge	Gas lift reactor	55	6.9	CO (18–110 mmol/L/day)	20–60 mmol/L/day	17 mmol/L/day	[69]
Desulfotomaculum carboxydivorans	Batch serum bottle	55	6.8–7.2	100% CO	–	–	[70]
Co-culture of *Desulfotomaculum thermoacetoxidans*, *Thermodesulfovibrio yellowstonii*, *Desulfotomaculum kuznetsovii*, *Desulfotomaculum thermobenzoicum* subsp. *Thermosyntrophicum*, *Carboxydothermus hydrogenoformans*	Batch serum bottle	60	7	100% CO	20 mM	–	[71]

where it gets oxidized to sulfur or sulfate, thus avoiding sulfide accumulation and corresponding inhibition [48].

CH_4 as an electron donor for sulfate reduction provides many advantages over other gaseous substrates such as H_2 or CO. In terms of electron transfer, CH_4 can supply four electrons which is twice that by H_2. Hence, to achieve the same sulfate reduction efficiency with CH_4, a lower volume of the gas will be required in comparison with H_2. The solubility (at 101.325 kPa pressure and 20 °C temperature) of CH_4 (0.023 g CH_4 per kilogramme of water) is also higher than H_2 (0.0016 g H_2 per kilogramme of water), which increases its bioavailability to SRB (consortia) for achieving high sulfate

Table 4 Biological sulfate reduction using methane as the electron donor

Inoculum	Bioreactor configuration	Temp (°C)	pH	Electron donor (conc./ loading condition)	Sulfate concentration used	Sulfate reduction efficiency/ removal rate	Reference
Sediments from Gulf of Cadiz (Spain)	Biotrickling filter	20 ± 2	7	CH_4 (4.7 mM/day)	10 mM	0.05–0.26 mM/day	[75]
Marine lake Grevelingen sediment	Pressure vessels	15	–	6.4 mM CH_4	2–2.5 mM	297.0 ± 43.0 μmol/g-VSS/day	[76]
Sediments from Ginsburg mud volcano (Gulf of Cadiz, Spain)	Biotrickling filter	20 ± 2	7	CH_4 (2 mL/min)	10–18 mM	0.36 mM/day (maximum)	[77]
Eckernförde Bay Enrichment	Serum bottle	20	7.5	CH_4 (0.00 to 0.15 MPa)	0.5–20 mM	~ 0.06 mM/day	[78]
Sediments in cold seeps of the deep eastern Mediterranean sea	Glass vial	14	–	CH_4	–	0.1–66 mmol/m^2/day	[79]
Hydrothermal sediments of Guaymas Basin	Sealed glass flask	95	–	CH_4 (4.5×10^7 Pa)	–	6660 nmol/cm^3/day	[80]

reduction efficiencies [48]. Also, loss of substrate due to the formation of undesired by-products that are commonly observed with H_2 and CO_2 are avoided by using CH_4 as the electron donor for sulfate reduction [48]. However, the major problem with CH_4 is that only a limited number of microorganisms can perform anaerobic methane oxidation combined with sulfate reduction. The slow growth rate of the microorganisms also limits their applicability in wastewater treatment systems [77].

Bioreactors for Sulfate Reduction Using Gaseous Substrates

Bioreactor Considerations

Proper design of a bioreactor and its operation mode is one of the main concerns for successful scale-up of these lab-based technologies for AMD treatment using gaseous substrates [82]. In order to select a suitable bioreactor system for AMD treatment using gaseous substrates, the volumetric mass transfer rate for the proposed system needs to be determined. This is important because the key parameters necessary for considering a suitable bioreactor are mainly related to gas–liquid mass transfer, which includes temperature–pressure conditions and bioreaction kinetics. In addition, agitation speed, impeller design and related power consumption also need to be considered for agitated bioreactor types. The volumetric mass transfer rate is defined as the product of the volumetric mass transfer coefficient (KLa) and the mass transfer driving force ($C^* - \overline{C}$), where $\overline{C}$ is the liquid-phase concentration of the transferred gas and C^* is the liquid-phase concentration that is in equilibrium with the gas phase concentration [83].

The transport of supplied gaseous substrates to the biomass involves transport of gas from the gas phase into the liquid phase, followed by its transport from the liquid phase to the biomass surface and finally its diffusions into the biomass layer and its consumption by the active biomass (Fig. 2). Various factors influences this gas transport and gas–liquid mass transfer coefficient, among these the physico-chemical properties of the gaseous substrate are most important [84]. The gas solubility in water majorly decides its gas–liquid mass transfer. The media (wastewater) properties such as its viscosity, dissolved salt concentration and organic content also influence the solubility of gases and the gas–liquid mass transfer coefficient [85]. The specific characteristics of a reactor such as the fluid flow behaviour inside the reactor and available surface area has the ability to improve or deteriorate the gas–liquid mass transfer [86]. All of the above-mentioned parameters are intrinsic in nature and can hardly be changed without changing the gaseous substrate, the liquid phase or the reactor configuration itself. However, the bioreactor operating conditions such as temperature, pressure, gas and liquid flow rate (velocity) are some of other important parameters that provide ample opportunity for the operator to improve the gas–liquid mass transfer within a given system [87].

Gas Lift Reactor

A gas lift or airlift reactor is similar to a bubble column reactor, except that it contains a draft tube (Fig. 3(a)). The draft tube is either an inner (called gas lift reactor with internal loop) or an external (called gas lift reactor with external loop) tube [88]. The gas stream facilitates the exchange of material between the gas phase and the media, thus enhancing the overall mass transfer. Moreover, dissolution of the gas in the liquid lowers its density, and the density difference of the water in the gas sparged and non-sparged reactor parts induces circulation of water [82]. It thus enhances liquid circulation and also improves gas–liquid mass transfer and equalizes shear forces in the reactor. The major advantages of a gas lift bioreactor are the simple design with no moving parts or agitators, and the homogeneous distribution of nutrients and shear force. However, in order to overcome the pressure drop in this type of reactor, a greater effort need to be applied to bring the gas in reactor column which increases the energy requirement and running cost [8].

A very high sulfate reduction rate (18 mmol/L/day) was obtained using a H_2-fed gas lift reactor (GLR) operated under haloalkaline conditions [51]. The haloalkaline conditions hampered the formation of microbial aggregates inside the reactor. Denaturing gradient gel electrophoresis (DGGE) analysis of the biomass revealed haloalkaliphilic SRB bacteria, i.e. *Desulfonatronospira delicata*, *Desulfonatronospira thiodismutans* and *Desulfonatronovibrio* sp., were present in the gas lift reactor.

Hydrogenogenic CO conversion for biological sulfate reduction was studied in a gas lift reactor and the effect of the hydraulic retention time (HRT) was investigated at thermophilic (55 °C) conditions [69]. At a high retention time (> 5.5 h), the H_2 produced from CO conversion was utilized for methane production, whereas at a short HRT (3 h), 87% of the H_2 produced was utilized by SRB for sulfate reduction. A CO conversion efficiency of 85% and a high sulfate reduction rate (17 mmol/L/day) was achieved at a short HRT (3 h) [69]. In another study, a high sulfate reduction efficiency (76–97%) was obtained at mesophilic conditions (30 °C) using a CO-fed GLR [8]. The sulfate reduction and CO utilization were further improved by adding zero-valent iron nanoparticles, even for high influent sulfate concentrations in the system.

Sulfate reduction using syngas (H_2, CO_2 and CO) as the electron donor was demonstrated in a gas lift reactor [49]. The presence of CO in the H_2/CO_2 gas mixture was inhibitory to the sulfate reduction process when used in more than 20% in the gas mixture (by volume). However, due to the presence of CO in the feed gas, the biomass aggregates formed in the

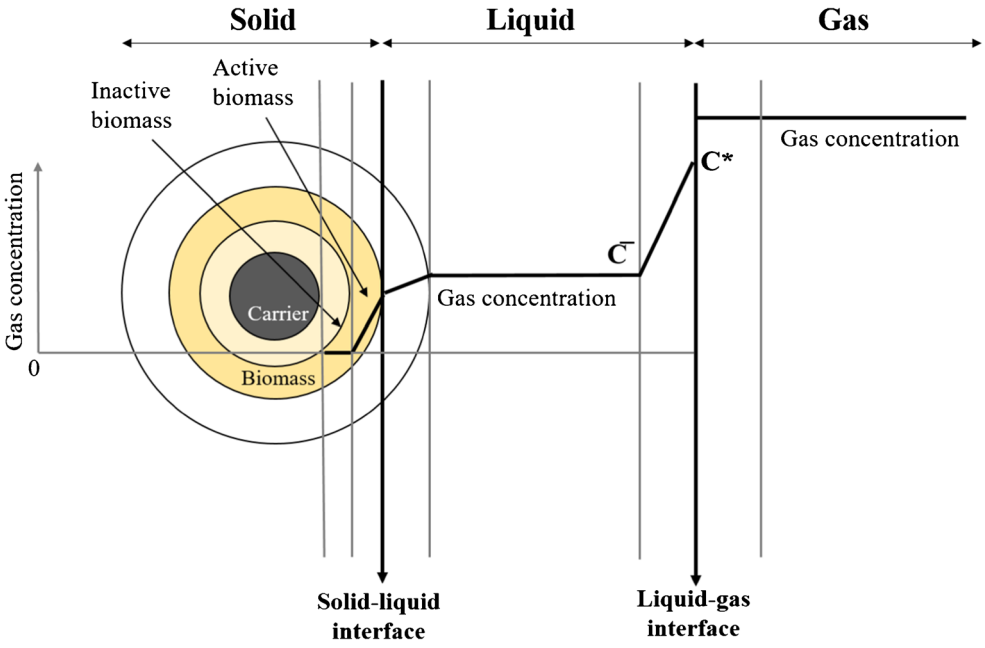

Fig. 2 The mass transfer from the gas phase to the liquid and the solid (biomass) phase

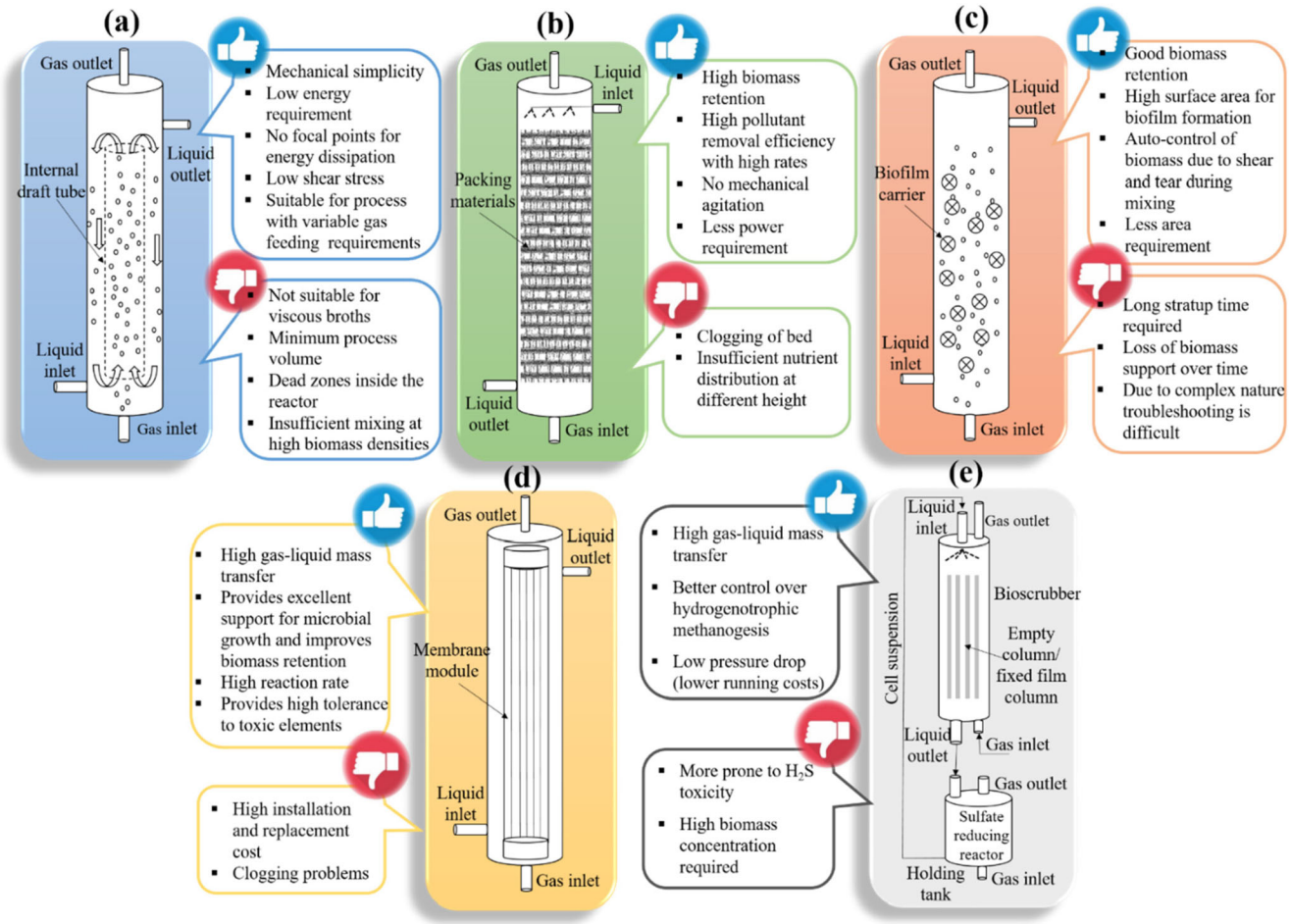

Fig. 3 Bioreactor systems used for acid mine drainage treatment using gaseous substrates along with their advantages and disadvantages. (a) Gas lift reactor, (b) packed bed reactor, (c) moving bed biofilm reactor, (d) membrane bioreactor and (e) cell suspension bioreactor

reactor had a layered structure with *Acetobacteria* sp. located mainly on the outer surface and *Desulfovibrio* sp. located in the innermost parts of the aggregates. In another study, high sulfate reduction rates (295 kg sulfate/h, weekly average) could be achieved using a H_2 and CO_2-fed GLR even in the presence of zinc and manganese as co-pollutants [54]. The methanogenic activity was controlled in this study by lowering the CO_2 percentage in the feed gas from 20–22 to 3–6%.

A 99% sulfate reduction efficiency was achieved at pH 5.0 and 24 h HRT using a H_2 and CO_2 gas-fed GLR [55]. In order to assess the potential of H_2-fed GLR to treat AMD, nickel was fed with sulfate both individually and in combination with iron [53]. This sulfidogenic GLR had a high recovery potential (~ 99%) of nickel as NiS, present as partially crystalline precipitates with a Ni content of 83%. The iron recovery was low (< 15%) at this pH, thereby demonstrating a good potential for selective recovery of Ni from AMD. Apart from these lab-scale studies, a H_2-fed GLR for treating zinc and sulfate-containing wastewater from a zinc refinery is already operational at Budel (Netherlands) [48], further indicating its industrial applicability.

Membrane Bioreactors

Membrane bioreactors (MBR) or membrane biofilm reactors consist of membrane modules that are partially or completely submerged in the AMD [89]. The feed gas diffuses through the pores of the membranes without forming bubbles (Fig. 3(d)). The biomass grows on the outer wall of the membranes as a biofilm [89]. Several recent studies on hollow fibre membrane (HFM) bioreactors suggest that MBR have the potential to replace the commonly used bioreactors to overcome gas–liquid mass transfer limitations [90]. A good number of membrane materials are available, among which hydrophobic membrane materials such as polypropylene (PP), polyethylene (PE) and polyvinylidene fluoride (PVDF) are the most commonly used. The advantage of MBR over traditional reactor systems is the high gas–liquid mass transfer efficiency and low energy consumption [89]. Moreover, it provides a high substrate utilization rate and increased tolerance to toxic compounds, e.g. tar, acetylene and NO_x. Besides, this reactor type can operate under high-pressure conditions [91]. The disadvantages are clogging and biofouling of the membranes due to excessive biomass growth or bioprecipitation on the membrane surface. In addition, installation costs and cost of replacing membrane modules are high, which is another drawback of this technology [90].

The potential of H_2-fed membrane biofilm reactors was demonstrated for treating AMD and achieved a very high sulfate reduction efficiency even at large scale [92]. However, the AMD fed to the reactor was pretreated with H_2S and alkali, which resulted in wastewater containing very low metal (< 1 mg/L) and high sulfate (5400 mg/L) concentrations. This study proposed a two-stage process for AMD treatment, with a H_2-based MBR for the initial sulfate reduction to sulfide, followed by metal precipitation using the produced sulfide. Suárez et al. [93] investigated treatment of copper mine wastewater (from central Chile) using a H_2-fed membrane biofilm reactor. A very high sulfate reduction efficiency (95–99%) was attained, but the pH control was difficult due to the continuous increase in pH as a result of sulfate reduction. Addition of 20% (v/v) CO_2 to the feed gas in the reactor was successful in maintaining the pH within a neutral range.

Hollow fibre membrane biofilm reactors, particularly by feeding H_2, have been successfully applied not only for sulfate reduction but also for the simultaneous treatment of multiple pollutants such as perchlorate, nitrate, selenate and chromate [89]. This H_2-fed MBR is suitable for treating sulfate, perchlorate and nitrate simultaneously, although an excess H_2 concentration enhances the sulfate reduction efficiency by increasing SRB activity in the biofilm [94]. In addition, the biofilm thickness significantly influenced the pollutant removal efficiency in the system.

In H_2-based membrane biofilm reactors treating sulfate and nitrate, competition between SRB and denitrifying bacteria occurs [95]. The optimum conditions for sulfate reduction in this system are > 3.4 atm pressure and a nitrate loading rate of < 0.13 g N/m^2/day. However, in most cases, the presence of such co-pollutants lowered the sulfate reduction efficiency [96]. Though the perchlorate reduction efficiency exceeded 96%, a low sulfate reduction efficiency of only 10–60% could be achieved due the insufficient H_2 available for sulfate reduction.

Packed Bed Bioreactor

A packed bed reactor (PBR) or trickle bed reactor (TBR) consists of a cylinder with solid support for biomass to grow and attach onto (Fig. 3(b)) [97]. In general, this type of reactor is operated under counter current flow of liquid to gas, with the gas rising upwards and the liquid flowing down through the packed bed [9]. However, PBR can also be operated in co-current mode. Special care needs to be taken to maintain a low water flow rate to prevent flooding in the column. The liquid flow is mainly provided to keep the biomass moist along with nutrient supplementation for cell growth [1, 82]. This is one of the most economical wastewater treatment systems and other than controlling the biofilm growth to prevent bed clogging, it does not require much maintenance [97]. The main advantage of this reactor configuration is the increased gas transfer area with a minimal pressure drop. In addition, it is easy to improve the mass transfer by controlling the liquid flow rates [9].

Using a CH_4-fed biotrickling filter, around 70% sulfate reduction efficiency was achieved [77]. The highest sulfide production of 7 mmol/L was obtained, which did not inhibit the sulfate reduction or methane oxidation. In a similar study, Cassarini et al. [75] studied sulfate reduction coupled to

anaerobic methane oxidation using a biotrickling filter packed with polyurethane foam and pall rings as biofilm support. The sulfate reduction rates were 0.29 (± 0.03) mmol/L/day along with high methane oxidation rates (0.34 ± 0.06 mmol/L/day). However, the sulfate reduction rates were too low compared with the rates obtained using lactate or H_2, which is a challenge for its successful application in large-scale AMD treatment.

In addition to passive immobilization of biomass on support materials, anaerobic biomass can be actively immobilized inside polyvinyl alcohol (PVA) and sodium alginate beads [9]. High sulfate reduction (94.4%) and CO utilization (90%) efficiencies were achieved at a 48-h HRT using a CO-fed PBR [9]. The superior performance of the PBR containing SRB immobilized beads was attributed to an excellent gas–liquid mass transfer due to counter current flow of the AMD influent and the feed gas. Besides, the use of biomass immobilized in polyvinyl alcohol and sodium alginate beads could prevent CO toxicity to SRB by avoiding direct exposure of the biomass to high CO concentrations [9].

Moving Bed Biofilm Reactor

The moving bed biofilm reactor (MBBR; Fig. 3(c)) is another biofilm-based reactor configuration with specially designed biofilm carriers, known as Kaldness® biosupport material, with a large surface area for biofilm formation [64]. Advantages of the MBBR include high biomass retention, high treatment efficiency, resistance to shock loading conditions and small footprint [97]. In addition, bed clogging, which is mostly observed with other attached growth bioreactor configurations, is uncommon in a MBBR due to continuous mixing.

The MBBR configuration is mostly used in aerobic treatment for concentrated organic wastewaters and air is used to keep the biomass carrying support materials suspended [98]. In the case of anaerobic operation, the requirement for a feed gas supply to keep the biofilm carriers in suspended form is considered uneconomical. However, this problem can be overcome in anaerobic MBBR with gaseous substrates as electron donor.

A limited number of studies on biogenic sulfate reduction using gas-fed MBBR have been reported in the literature. In a recent study, stable sulfate reduction over a long period of time using a MBBR fed with CO as the sole substrate was reported [64]. A high sulfate reduction efficiency could be achieved even under high sulfate loading rates by increasing the CO loading to the reactor. However, the CO utilization efficiency decreased at high CO loading rates due to the high CO flow rate and low gas retention time in the MBBR reactor. Furthermore, the high gas flow rate beyond a certain value (50 mL/min of CO) caused biofilm detachment from the support material, leading to biomass washout and deterioration in the reactor performance.

Cell Suspension Bioreactors

A cell suspension bioreactor (CSBR) is a less explored bioreactor system that can be used for AMD treatment using gas phase substrates for the SRB. A CSBR system consists of a continuously stirred tank bioreactor (CSTR) and a bioscrubber column (Fig. 3(e)). In the CSTR vessel, microorganisms are grown under suspended mode to treat the sulfate-rich wastewater using gaseous substrates. This cell suspension is percolated through the bioscrubber column to load the water with the gaseous substrates. The reactor operates in a closed loop with the treated bioscrubber liquid (i.e. treated AMD) recycled back to the CSTR (Fig. 3(e)).

This system has so far not been reported for AMD treatment, however, is a previous study to achieve flue gas desulfurization, a H_2-fed cell suspension bioreactor was used [99]. The system achieved a 300% increase in the specific hydrogenotrophic sulfate reduction rate in comparison with granular sludge and crushed granular sludge systems. The main advantage of the CSBR system is its better gas–liquid mass transfer compared with the attached growth biofilm based bioreactors, as the mass transfer only involves gas transport from the gas to the liquid phase [99]. In addition, this bioreactor permits better control of the competition between hydrogenotrophic SRB and methanogens, which helps in improving SRB activity in the reactor [100]. The need to have a high cell concentration and possibility of H_2S toxicity are some of the disadvantages of the CSBR system.

Potential for Resource Recovery

The two main resources that can be recovered from AMD treatment systems using biological sulfate reduction with gaseous substrates are metal sulfides and elemental sulfur [101]. Both compounds have wide ranging application in different fields; however, as they are recovered from waste resources and due to possible contamination, their use in the biomedical field is limited. Biosulfur recovered from AMD can be utilized in agriculture as fertilizer and antifungal agent [102], in addition to its application in nitrate-rich wastewater treatment [103]. The metal sulfides can be processed in the smelter together with the ores [48] or in electronics [104]. Alternatively, they can be used as adsorbent [95] and photo-catalyst in wastewater treatment [105]. In a simplified setup, biological sulfate reduction and metal sulfide precipitation can take place in a single reactor [106], followed by recovery of the metal sulfide precipitates from the bioreactor effluent in a settling tank (Fig. 4a). The excess sulfide present in the effluent can then be oxidized to elemental sulfur (S^0) by passing it through an aeration tank followed by separation of the S^0 from the treated effluent.

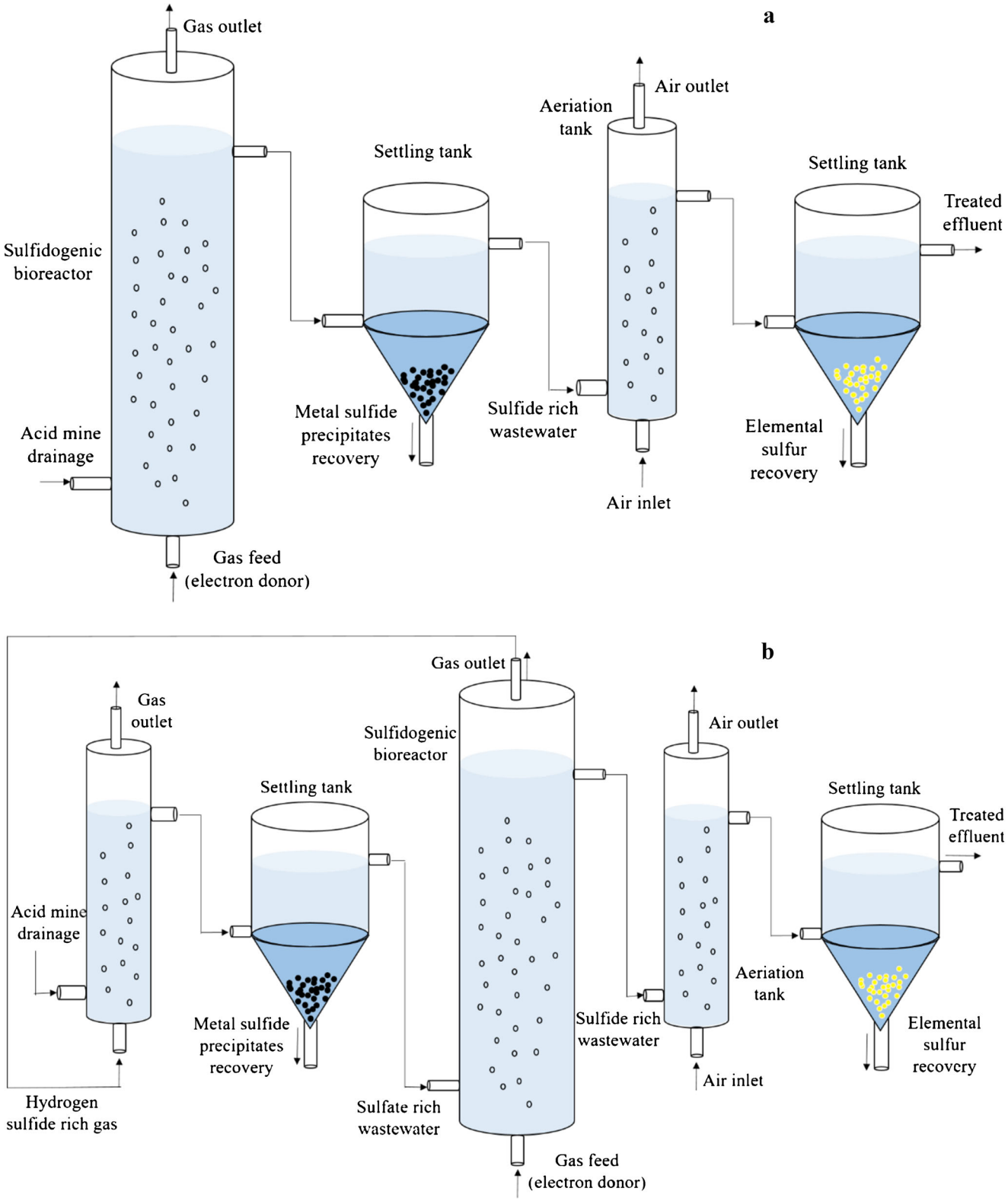

Fig. 4 Bioreactor setup for resource recovery from acid mine drainage using biological sulfate reduction. **a** Single-stage bioreactor for simultaneous metal and sulfate removal. **b** Sequential stages for removal of metal and sulfate

In another strategy, metals can be removed from AMD using sulfide in a separate reactor upstream to the bioreactor where biological sulfate reduction takes place (Fig. 4b). This strategy is applied because heavy metal toxicity negatively

affects the sulfate reduction performance in a single-stage operation strategy. This inhibitory effect can be avoided by removing the heavy metals prior to the biological sulfate reduction step [92]. This strategy is also useful for sulfidogenic systems that use gaseous substrates as most of the sulfide produced in these systems exit the bioreactor along with the effluent gas stream and require treatment before being released into the environment [8, 64]. This sulfide-containing effluent gas stream can be used for metal precipitation. In addition, selective removal and recovery of specific single metals can be achieved by changing the pH in a multistage system [107]. In this strategy, multiple mixing tanks and settlers can be introduced for individual metal precipitation in each stage prior to the bioreactor operation [108]. The S^0 formation and its recovery by settling is similar to that described previously for single-stage systems.

Challenges and Future Research Perspective

From the various aspects discussed in this review, it is clear that the prospects of AMD treatment by biological sulfate reduction using gaseous substrates is highly promising, but several hurdles, including suitable microorganisms, gas–liquid mass transfer problems, bioreactor type selection and the presence of co-pollutants need to be addressed for achieving its commercial success. Robust and sturdy microorganisms are essential for industrial scale-up and commercial success of this technology. From the reported literature, it is evident that a limited number of microbes are available for performing sulfate reduction using gaseous substrates, especially for CO and CH_4. A number of recent studies indicate the potential of new organisms from extreme environments like hot springs [66], acidic environments [52] or deep-sea surfaces [78], which may be better suited for sulfate reduction using the gaseous substrates CO or CH_4. Apart from that, long-term enrichment can enable a selective group of microorganisms to perform sulfate reduction using desired substrates [62, 75].

The low gas–liquid mass transfer has long been identified as an important factor impeding the scale-up of this technology. In addition to the bioreactors available, designing novel bioreactor configurations with high gas–liquid mass transfer could solve this problem. A novel bioreactor named rotating horizontal packed bed reactor has been used for syngas fermentation [109], but not yet for sulfate reduction. A lot of studies on improving gas–liquid mass transfer using addition of electrolytes [110], surfactants [111] and nanoparticles [112, 113] for increase in syngas fermentation efficiency have been reported. However, the use of such methods in sulfate reduction driven by gaseous substrates is yet to be studied and provide a future research direction.

The use of pure gases for AMD treatment may impose additional cost on the industry [9] and gases such as H_2 or CH_4 in pure form are valuable renewable energy resources [72], which make their use in wastewater treatment challenging. Instead of procuring pure gases, the gaseous substrates can be produced by thermochemical or biochemical methods from various compounds including different waste resources [114]. This will not only help in reducing the cost by eliminating the transportation and storage expenses but also provide options for on-site treatment of AMD. In many industries, these processes are already in place and can be integrated with the wastewater treatment system to further improve the economic viability of the process [8, 9].

The online monitoring and modelling of AMD treatment using biological sulfate reduction using gaseous substrates is another essential area of research to understand the effect of key parameters influencing the process efficiency. Among the available tools, machine learning methods such as artificial neural network (ANN) has been used to model various bioprocesses, including sulfate reduction using gaseous substrates [8, 64]. The ability of this method in predicting output variables involving complex systems with multiple input variables have been well established and hence should be included as an important future prospect of this area of research.

Conclusions

AMD generated by mining activities can be treated by biological sulfate reduction using SRB. In addition to precipitation of metals present in the wastewater by the biogenic sulfide, the pH of the wastewater is increased due to the bicarbonate generated during the process. Gaseous electron donors such as H_2, CO and CH_4 are more beneficial than lactate or other conventional substrates for sulfate reduction owing to their easy availability and avoidance of secondary pollution problems that are common with incomplete utilization of soluble substrates. Selection of microorganisms or selective enrichments are crucial for the design and operation of a treatment system with gaseous substrates as not all microorganisms are capable of utilizing such substrates as electron donor and in some cases they are even toxic to the microorganisms. In addition, proper choice of a bioreactor system plays a key role in determining the process efficiency. The most commonly used bioreactor systems for biogenic sulfate reduction with gaseous substrates are the gas lift and the membrane biofilm reactor.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

Human and Animal Rights and Informed Consent This article does not contain any studies with human or animal subjects performed by any of the authors.

References

1. Kiran MG, Pakshirajan K, Das G. An overview of sulfidogenic biological reactors for the simultaneous treatment of sulfate and heavy metal rich wastewater. Chem Eng Sci. 2017;158:606–20. https://doi.org/10.1016/j.ces.2016.11.002.
2. Kefeni KK, Msagati TA, Mamba BB. Acid mine drainage: prevention, treatment options, and resource recovery: a review. J Clean Prod. 2017;151:475–93. https://doi.org/10.1016/j.jclepro.2017.03.082.
3. Akcil A, Koldas S. Acid mine drainage (AMD): causes, treatment and case studies. J Clean Prod. 2006;14:1139–45. https://doi.org/10.1016/j.jclepro.2004.09.006.
4. Skousen J, Zipper CE, Rose A, Ziemkiewicz PF, Nairn R, McDonald LM, et al. Review of passive systems for acid mine drainage treatment. Mine Water Environ. 2017;36:133–53. https://doi.org/10.1007/s10230-016-0417-1.
5. Wu G, Kang H, Zhang X, Shao H, Chu L, Ruan C. A critical review on the bio-removal of hazardous heavy metals from contaminated soils: issues, progress, eco-environmental concerns and opportunities. J Hazard Mater. 2010;174:1–8. https://doi.org/10.1016/j.jhazmat.2009.09.113.
6. Kiran MG, Pakshirajan K, Das G. Heavy metal removal from multicomponent system by sulfate reducing bacteria: mechanism and cell surface characterization. J Hazard Mater. 2017;324:62–70. https://doi.org/10.1016/j.jhazmat.2015.12.042.
7. Liamleam W, Annachhatre AP. Electron donors for biological sulfate reduction. Biotechnol Adv. 2007;25:452–63. https://doi.org/10.1016/j.biotechadv.2007.05.002.
8. Sinharoy A, Baskaran D, Pakshirajan K. Process integration and artificial neural network modeling of biological sulfate reduction using a carbon monoxide fed gas lift bioreactor. Chem Eng J. 2019;123518:123518. https://doi.org/10.1016/j.cej.2019.123518.
9. Kumar M, Sinharoy A, Pakshirajan K. Process integration for biological sulfate reduction in a carbon monoxide fed packed bed reactor. J Environ Manag. 2018;219:294–303. https://doi.org/10.1016/j.jenvman.2018.04.033.
10. Johnson DB, Hallberg KB. Acid mine drainage remediation options: a review. Sci Total Environ. 2005;338:3–14. https://doi.org/10.1016/j.scitotenv.2004.09.002.
11. Sağlam ES, Akçay M, Çolak DN, Bektaş Kİ, Beldüz AO. Generation of acid mine drainage around the Karaerik copper mine (Espiye, Giresun, NE Turkey): implications from the bacterial population in the Acısu effluent. Extremophiles. 2016;20:673–85. https://doi.org/10.1007/s00792-016-0857-3.
12. Sinharoy A, Pakshirajan K. Heavy metal sequestration by sulfate reduction using carbon monoxide as the sole carbon and energy source. Process Biochem. 2019;82:135–43. https://doi.org/10.1016/j.procbio.2019.04.002.
13. Simate GS, Ndlovu S. Acid mine drainage: challenges and opportunities. J Environ Chem Eng. 2014;2:1785–803. https://doi.org/10.1016/j.jece.2014.07.021.
14. Rambabu K, Banat F, Pham QM, Ho SH, Ren NQ, Show PL. Biological remediation of acid mine drainage: review of past trends and current outlook. Environ Sci Ecotechnol. 2020;100024:100024. https://doi.org/10.1016/j.ese.2020.100024.
15. Roy AS, Hazarika J, Manikandan NA, Pakshirajan K, Syiem MB. Heavy metal removal from multicomponent system by the cyanobacterium *Nostoc muscorum*: kinetics and interaction study. Appl Biochem Biotechnol. 2015;175:3863–74. https://doi.org/10.1007/s12010-015-1553-y.
16. Cobbina SJ, Chen Y, Zhou Z, Wu X, Zhao T, Zhang Z, et al. Toxicity assessment due to sub-chronic exposure to individual and mixtures of four toxic heavy metals. J Hazard Mater. 2015;294:109–20. https://doi.org/10.1016/j.jhazmat.2015.03.057.
17. Assi MA, Hezmee MNM, Haron AW, Sabri MYM, Rajion MA. The detrimental effects of lead on human and animal health. Vet World. 2016;9:660. https://doi.org/10.14202/vetworld.2016.660-671.
18. Khan A, Khan S, Khan MA, Qamar Z, Waqas M. The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review. Environ Sci Pollut Res. 2015;22:13772–99. https://doi.org/10.1007/s11356-015-4881-0.
19. Liao J, Wen Z, Ru X, Chen J, Wu H, Wei C. Distribution and migration of heavy metals in soil and crops affected by acid mine drainage: public health implications in Guangdong Province, China. Ecotox Environ Safe. 2016;124:460–9. https://doi.org/10.1016/j.ecoenv.2015.11.023.
20. World Health Organisation (WHO). Guidelines for drinking water quality, 4th ed.; WHO: Geneva, Switzerland, 2011. 38(4), 104–108.
21. Al-Zoubi H, Rieger A, Steinberger P, Pelz W, Haseneder R, Härtel G. Optimization study for treatment of acid mine drainage using membrane technology. Sep Sci Technol. 2010;45:2004–16. https://doi.org/10.1080/01496395.2010.480963.
22. Miretzky P, Cirelli AF. Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. J Hazard Mater. 2010;180:1–19. https://doi.org/10.1016/j.jhazmat.2010.04.060.
23. Kefeni KK, Msagati TM, Mamba BB. Synthesis and characterization of magnetic nanoparticles and study their removal capacity of metals from acid mine drainage. Chem Eng J. 2015;276:222–31. https://doi.org/10.1016/j.cej.2015.04.066.
24. Raulino GS, Vidal CB, Lima ACA, Melo DQ, Oliveira JT, Nascimento RF. Treatment influence on green coconut shells for removal of metal ions: pilot-scale fixed-bed column. Environ Technol. 2014;35:1711–20. https://doi.org/10.1080/09593330.2014.880747.
25. Zhong CM, Xu ZL, Fang XH, Cheng L. Treatment of acid mine drainage (AMD) by ultra-low-pressure reverse osmosis and nanofiltration. Environ Eng Sci. 2007;24:1297–306. https://doi.org/10.1089/ees.2006.0245.
26. Bertoli AC, Quintão MC, De Abreu HA, Ladeira ACQ, Duarte HA. Uranium separation from acid mine drainage using anionic resins–an experimental/theoretical investigation of its chemical speciation and the interaction mechanism. J Environ Chem Eng. 2019;7:102790. https://doi.org/10.1016/j.jece.2018.11.035.
27. Martí-Calatayud MC, Buzzi DC, García-Gabaldón M, Ortega E, Bernardes AM, Tenório JAS, et al. Sulfuric acid recovery from acid mine drainage by means of electrodialysis. Desalination. 2014;343:120–7. https://doi.org/10.1016/j.desal.2013.11.031.
28. Punia A. Innovative and sustainable approach for phytoremediation of mine tailings: a review. Waste Dispos Sustain Energy 2020:1:169–176. https://doi.org/10.1007/s42768-019-00022-y
29. Sinha V, Pakshirajan K, Chaturvedi R. Chromium tolerance, bioaccumulation and localization in plants: an overview. J Environ Manage. 2018;206:715–30. https://doi.org/10.1016/j.jenvman.2017.10.033.

30. Li H, Watson J, Zhang Y, Lu H, Liu Z. Environment-enhancing process for algal wastewater treatment, heavy metal control and hydrothermal biofuel production: a critical review. Bioresour Technol. 2020;298:122421. https://doi.org/10.1016/j.biortech.2019.122421.
31. Gazea B, Adam K, Kontopoulos A. A review of passive systems for the treatment of acid mine drainage. Miner Eng. 1996;9:23–42. https://doi.org/10.1016/0892-6875(95)00129-8.
32. Skousen J, Zipper CE, Rose A, Ziemkiewicz PF, Nairn R, McDonald LM, et al. Review of passive systems for acid mine drainage treatment. Mine Water Environ. 2017;36:133–53. https://doi.org/10.1007/s10230-016-0417-1.
33. Papirio S, Villa-Gomez DK, Esposito G, Pirozzi F, Lens PNL. Acid mine drainage treatment in fluidized-bed bioreactors by sulfate-reducing bacteria: a critical review. Crit Rev Environ Sci Technol. 2013;43:2545–80. https://doi.org/10.1080/10643389.2012.694328.
34. Kamali M, Khodaparast Z. Review on recent developments on pulp and paper mill wastewater treatment. Ecotoxicol Environ Saf. 2015;114:326–42. https://doi.org/10.1016/j.ecoenv.2014.05.005.
35. Chitapornpan S, Chiemchaisri C, Chiemchaisri W, Honda R, Yamamoto K. Organic carbon recovery and photosynthetic bacteria population in an anaerobic membrane photo-bioreactor treating food processing wastewater. Bioresour Technol. 2013;141:65–74. https://doi.org/10.1016/j.biortech.2013.02.048.
36. Wu TY, Mohammad AW, Jahim JM, Anuar N. Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. J Environ Manag. 2010;91:1467–90. https://doi.org/10.1016/j.jenvman.2010.02.008.
37. Polpresert C, Haas CN. Effect of sulfate on anaerobic processes fed with dual substrate. Water Sci Technol. 1995;31:101–7. https://doi.org/10.2166/wst.1995.0349.
38. Barber WP, Stuckey DC. Effect of sulfate reduction on chemical oxygen demand removal in an anaerobic baffled reactor. Water Environ Res. 2000;72:593–601 www.jstor.org/stable/25045425.
39. Kaksonen AH, Franzmann PD, Puhakka JA. Performance and ethanol oxidation kinetics of a sulfate-reducing fluidized-bed reactor treating acidic metal-containing wastewater. Biodegradation. 2003;14:207–17. https://doi.org/10.1023/A:1024262607099.
40. Weijma J, Stams AJ, Hulshoff Pol LW, Lettinga G. Thermophilic sulfate reduction and methanogenesis with methanol in a high rate anaerobic reactor. Biotechnol Bioeng. 2000;67:354–63. https://doi.org/10.1002/(SICI)1097-0290(20000205)67:3<354::AID-BIT12>3.0.CO;2-X.
41. Finke N, Vandieken V, Jørgensen BB. Acetate, lactate, propionate, and isobutyrate as electron donors for iron and sulfate reduction in Arctic marine sediments, Svalbard. FEMS Microbiol Ecol. 2007;59:10–22. https://doi.org/10.1111/j.1574-6941.2006.00214.x.
42. Sinharoy A, Saikia S, Pakshirajan K. Biological removal of selenite from wastewater and recovery as selenium nanoparticles using inverse fluidized bed bioreactor. J Water Process Eng. 2019;32:100988. https://doi.org/10.1016/j.jwpe.2019.100988.
43. Zhang M, Wang H. Organic wastes as carbon sources to promote sulfate reducing bacterial activity for biological remediation of acid mine drainage. Miner Eng. 2014;69:81–90. https://doi.org/10.1016/j.mineng.2014.07.010.
44. Chang IS, Shin PK, Kim BH. Biological treatment of acid mine drainage under sulphate-reducing conditions with solid waste materials as substrate. Water Res. 2000;34:1269–77. https://doi.org/10.1016/S0043-1354(99)00268-7.
45. Sahinkaya E. Microbial sulfate reduction at low (8 °C) temperature using waste sludge as a carbon and seed source. Int Biodeterior Biodegradation. 2009;63:245–51.
46. Das BK, Gauri SS, Bhattacharya J. Sweetmeat waste fractions as suitable organic carbon source for biological sulfate reduction. Int Biodeterior Biodegradation. 2013;82:215–23. https://doi.org/10.1016/j.ibiod.2013.03.027.
47. Hazarika J, Pakshirajan K, Sinharoy A, Syiem MB. Bioremoval of Cu (II), Zn (II), Pb (II) and Cd (II) by *Nostoc muscorum* isolated from a coal mining site. J Appl Phycol. 2015;27:1525–34. https://doi.org/10.1007/s10811-014-0475-3.
48. Meulepas RJ, Stams AJ, Lens PNL. Biotechnological aspects of sulfate reduction with methane as electron donor. Rev Environ Sci Bio. 2010;9:59–78. https://doi.org/10.1007/s11157-010-9193-8.
49. van Houten RT, Van der Spoel H, van Aelst AC, Hulshoff Pol LW, Lettinga G. Biological sulfate reduction using synthesis gas as energy and carbon source. Biotechnol Bioeng. 1996;50:136–44. https://doi.org/10.1002/(SICI)1097-0290(19960420)50:2<136::AID-BIT3>3.0.CO;2-N.
50. Suárez JI, Aybar M, Nancucheo I, Poch B, Martínez P, Rittmann BE, et al. Influence of operating conditions on sulfate reduction from real mining process water by membrane biofilm reactors. Chemosphere. 2020;244:125508. https://doi.org/10.1016/j.chemosphere.2019.125508.
51. Sousa JA, Plugge CM, Stams AJ, Bijmans MF. Sulfate reduction in a hydrogen fed bioreactor operated at haloalkaline conditions. Water Res. 2015;68:67–76. https://doi.org/10.1016/j.watres.2014.09.035.
52. Saez-Navarrete C, Rodriguez-Cordova L, Baraza X, Gelmi C, Herrera L. Hydrogen kinetics limitation of an autotrophic sulphate reduction reactor. Dyna. 2012;79:126–32.
53. Bijmans MF, van Helvoort PJ, Dar SA, Dopson M, Lens PNL, Buisman CJ. Selective recovery of nickel over iron from a nickel–iron solution using microbial sulfate reduction in a gas-lift bioreactor. Water Res. 2009;43:853–61. https://doi.org/10.1016/j.watres.2008.11.023.
54. van Houten BH, van Doesburg W, Dijkman H, Copini C, Smidt H, Stams AJ. Long-term performance and microbial community analysis of a full-scale synthesis gas fed reactor treating sulfate- and zinc-rich wastewater. Appl Microbiol Biotechnol. 2009;84:555–63. https://doi.org/10.1007/s00253-009-2075-8.
55. Bijmans MF, Dopson M, Ennin F, Lens PNL, Buisman CJ. Effect of sulfide removal on sulfate reduction at pH 5 in a hydrogen fed gas-lift bioreactor. J Microbiol Biotechnol. 2008;18:1809–18. https://doi.org/10.4014/jmb.0800.109.
56. Bijmans MF, Lens PNL, Kaksonen AH, Puhakka JA. Hydrogenotrophic sulfate reduction in a gas-lift bioreactor operated at 9°C. J Microbiol Biotechnol. 2010;20:615–21. https://doi.org/10.4014/jmb.0906.06016.
57. van Houten BH, Meulepas RJ, van Doesburg W, Smidt H, Muyzer G, Stams AJ. *Desulfovibrio paquesii* sp. nov., a hydrogenotrophic sulfate-reducing bacterium isolated from a synthesis-gas-fed bioreactor treating zinc-and sulfate-rich wastewater. Int J Syst Evol Micr. 2009;59:229–33. https://doi.org/10.1099/ijs.0.65616-0.
58. Alazard D, Dukan S, Urios A, Verhé F, Bouabida N, Morel F, et al. *Desulfovibrio hydrothermalis* sp. nov., a novel sulfate-reducing bacterium isolated from hydrothermal vents. Int J Syst Evol Micr. 2003;53:173–8. https://doi.org/10.1099/ijs.0.02323-0.
59. Xu H, Zhang X, Li L, Li G. Enhanced hydrogenotrophic sulfate reduction using *Desulfovibrio vulgaris* Hildenborough cells permeabilized with ethanol. J Chem Technol Biotechnol. 2009;84:1539–43. https://doi.org/10.1002/jctb.2217.
60. Ji B, Gimenez G, Barbe V, Vacherie B, Rouy Z, Amrani A, et al. Complete genome sequence of the piezophilic, mesophilic, sulfate-reducing bacterium *Desulfovibrio hydrothermalis* AM13T. Genome Announc. 2013;1:e00226–12. https://doi.org/10.1128/genomeA.00226-12.

61. Sheik CS, Sieber JR, Badalamenti JP, Carden K, Olson A. Complete genome sequence of *Desulfovibrio desulfuricans* strain G11, a model sulfate-reducing, hydrogenotrophic, and syntrophic partner organism. Genome Announc. 2017;5:e01207–17. https://doi.org/10.1128/genomeA.01207-17.
62. Krukenberg V, Harding K, Richter M, Glöckner FO, Gruber-Vodicka HR, Adam B, et al. *Candidatus Desulfofervidus* auxilii, a hydrogenotrophic sulfate-reducing bacterium involved in the thermophilic anaerobic oxidation of methane. Environ Microbiol. 2016;18:3073–91. https://doi.org/10.1111/1462-2920.13283.
63. Fadhlaoui K, Ben Hania W, Armougom F, Bartoli M, Fardeau ML, Erauso G, et al. Obligate sugar oxidation in *Mesotoga* spp., phylum *Thermotogae*, in the presence of either elemental sulfur or hydrogenotrophic sulfate-reducers as electron acceptor. Environ Microbiol. 2018;20:281–92. https://doi.org/10.1111/1462-2920.13995.
64. Sinharoy A, Baskaran D, Pakshirajan K. A novel carbon monoxide fed moving bed biofilm reactor for sulfate rich wastewater treatment. J Environ Manag. 2019;249:109402. https://doi.org/10.1016/j.jenvman.2019.109402.
65. Sinharoy A, Manikandan NA, Pakshirajan K. A novel biological sulfate reduction method using hydrogenogenic carboxydotrophic mesophilic bacteria. Bioresour Technol. 2015;192:494–500. https://doi.org/10.1016/j.biortech.2015.05.085.
66. Hocking WP, Roalkvam I, Magnussen C, Stokke R, Steen IH. Assessment of the carbon monoxide metabolism of the hyperthermophilic sulfate-reducing archaeon *Archaeoglobus fulgidus* VC-16 by comparative transcriptome analyses. Archaea. 2015;235384:1–12. https://doi.org/10.1155/2015/235384.
67. Yoneda Y, Yoshida T, Kawaichi S, Daifuku T, Takabe K, Sako Y. *Carboxydothermus pertinax* sp. nov., a thermophilic, hydrogenogenic, Fe (III)-reducing, sulfur-reducing carboxydotrophic bacterium from an acidic hot spring. Int J Syst Evol Microbiol. 2012;62:1692–7. https://doi.org/10.1099/ijs.0.031583-0.
68. Sipma J, Lettinga G, Stams AJ, Lens PNL. Hydrogenogenic CO conversion in a moderately thermophilic (55 °C) sulfate-fed gas lift reactor: competition for CO-derived H_2. Biotechnol Prog. 2006;22:1327–34. https://doi.org/10.1021/bp0601084.
69. Sipma J, Osuna MB, Lettinga G, Stams AJM, Lens PNL. Effect of hydraulic retention time on sulfate reduction in a carbon monoxide fed thermophilic gas lift reactor. Water Res. 2007;41:1995–2003. https://doi.org/10.1016/j.watres.2007.01.030.
70. Parshina SN, Sipma J, Nakashimada Y, Henstra AM, Smidt H, Lysenko AM, et al. *Desulfotomaculum carboxydivorans* sp. nov., a novel sulfate-reducing bacterium capable of growth at 100% CO. Int J Syst Evol Microbiol. 2005;55:2159–65. https://doi.org/10.1099/ijs.0.63780-0.
71. Parshina SN, Kijlstra S, Henstra AM, Sipma J, Plugge CM, Stams AJM. Carbon monoxide conversion by thermophilic sulfate-reducing bacteria in pure culture and in co-culture with *Carboxydothermus hydrogenoformans*. Appl Microbiol Biotechnol. 2005;68:390–6. https://doi.org/10.1007/s00253-004-1878-x.
72. Sinharoy A, Baskaran D, Pakshirajan K. Sustainable biohydrogen production by dark fermentation using carbon monoxide as the sole carbon and energy source. Int J Hydrogen Energ. 2019;44:13114–25. https://doi.org/10.1016/j.ijhydene.2019.03.130.
73. Parshina SN, Sipma J, Henstra AM, Stams AJ. Carbon monoxide as an electron donor for the biological reduction of sulphate. Int J Microbiol. 2010;2010:1–9. https://doi.org/10.1155/2010/319527.
74. Svetlichny VA, Sokolova TG, Gerhardt M, Ringpfeil M, Kostrikina NA, Zavarzin GA. *Carboxydothermus hydrogenoformans* gen. nov., sp. nov., a CO-utilizing thermophilic anaerobic bacterium from hydrothermal environments of Kunashir Island. Syst Appl Microbiol. 1991;14:254–60. https://doi.org/10.1016/S0723-2020(11)80377-2.
75. Cassarini C, Rene ER, Bhattarai S, Vogt C, Musat N, Lens PN. Anaerobic methane oxidation coupled to sulfate reduction in a biotrickling filter: reactor performance and microbial community analysis. Chemosphere. 2019;236:124290. https://doi.org/10.1016/j.chemosphere.2019.07.021.
76. Cassarini C, Zhang Y, Lens PNL. Pressure selects dominant anaerobic methanotrophic phylotype and sulfate reducing bacteria in coastal marine Lake Grevelingen sediment. Front Environ Sci. 2019;6:162. https://doi.org/10.3389/fenvs.2018.00162.
77. Bhattarai S, Cassarini C, Rene ER, Zhang Y, Esposito G, Lens PNL. Enrichment of sulfate reducing anaerobic methane oxidizing community dominated by ANME-1 from Ginsburg mud volcano (Gulf of Cadiz) sediment in a biotrickling filter. Bioresour Technol. 2018;259:433–41. https://doi.org/10.1016/j.biortech.2018.03.018.
78. Meulepas RJ, Jagersma CG, Khadem AF, Buisman CJ, Stams AJ, Lens PNL. Effect of environmental conditions on sulfate reduction with methane as electron donor by an Eckernforde Bay Enrichment. Environ Sci Technol. 2009;43:6553–9. https://doi.org/10.1021/es900633c.
79. Omoregie EO, Niemann H, Mastalerz V, de Lange GJ, Stadnitskaia A, Mascle J, et al. Microbial methane oxidation and sulfate reduction at cold seeps of the deep eastern Mediterranean Sea. Mar Geol. 2009;261:114–27. https://doi.org/10.1016/j.margeo.2009.02.001.
80. Kallmeyer J, Boetius A. Effects of temperature and pressure on sulfate reduction and anaerobic oxidation of methane in hydrothermal sediments of Guaymas Basin. Appl Environ Microbiol. 2004;70:1231–3. https://doi.org/10.1128/AEM.70.2.1231-1233.2004.
81. Niewöhner C, Hensen C, Kasten S, Zabel M, Schulz HD. Deep sulfate reduction completely mediated by anaerobic methane oxidation in sediments of the upwelling area off Namibia. Geochim Cosmochim Acta. 1998;62:455–64. https://doi.org/10.1016/S0016-7037(98)00055-6.
82. Sinharoy A, Lens PNL. Biological removal of selenate and selenite from wastewater: options for selenium recovery as nanoparticles. Curr Pollution Rep. 2020;6:230–49. https://doi.org/10.1007/s40726-020-00146-4.
83. Bredwell MD, Srivastava P, Worden RM. Reactor design issues for synthesis-gas fermentations. Biotechnol Prog. 1999;15:834–44. https://doi.org/10.1021/bp990108m.
84. Kraakman NJ, Rocha-Rios J, van Loosdrecht MC. Review of mass transfer aspects for biological gas treatment. Appl Microbiol Biotechnol. 2011;91:873–86. https://doi.org/10.1007/s00253-011-3365-5.
85. Harms H, Bosma TNP. Mass transfer limitation of microbial growth and pollutant degradation. J Ind Microbiol Biot. 1997;18:97–105. https://doi.org/10.1038/sj.jim.2900259.
86. Paca J, Halecky M, Kozliac E. Styrene biofiltration using two packing materials with different adsorption properties. Environ Eng Sci. 2009;26:195–208. https://doi.org/10.1089/ees.2007.0252.
87. Yasin M, Jeong Y, Park S, Jeong J, Lee EY, Lovitt RW, et al. Microbial synthesis gas utilization and ways to resolve kinetic and mass-transfer limitations. Bioresour Technol. 2015;177:361–74.
88. Asimakopoulos K, Gavala HN, Skiadas IV. Reactor systems for syngas fermentation processes: a review. Chem Eng J. 2018;348:732–44. https://doi.org/10.1016/j.cej.2018.05.003.
89. Zhou C, Ontiveros-Valencia A, Nerenberg R, Tang Y, Friese D, Krajmalnik-Brown R, et al. Hydrogenotrophic microbial reduction of oxyanions with the membrane biofilm reactor. Front Microbiol. 2019;9:3268. https://doi.org/10.3389/fmicb.2018.03268.

90. Yasin M, Park S, Jeong Y, Lee EY, Lee J, Chang I.S. Effect of internal pressure and gas/liquid interface area on the CO mass transfer coefficient using hollow fibre membranes as a high mass transfer gas diffusing system for microbial syngas fermentation. Bioresour Technol 2014:169:637–643. https://doi.org/10.1016/j.biortech.2014.07.026.
91. Munasinghe PC, Khanal SK. Biomass-derived syngas fermentation into biofuels: opportunities and challenges. Bioresour Technol. 2010;101:5013–22. https://doi.org/10.1016/j.biortech.2009.12.098.
92. Tabak HH, Govind R. Advances in biotreatment of acid mine drainage and biorecovery of metals: 2. Membrane bioreactor system for sulfate reduction. Biodegradation. 2003;14:437–52. https://doi.org/10.1023/A:1027332918844.
93. Suárez JI, Aybar M, Nancucheo I, Poch B, Martínez P, Rittmann BE, et al. Influence of operating conditions on sulfate reduction from real mining process water by membrane biofilm reactors. Chemosphere. 2020;244:125508. https://doi.org/10.1016/j.chemosphere.2019.125508.
94. Chen X, Liu Y, Peng L, Ni BJ. Perchlorate, nitrate, and sulfate reduction in hydrogen-based membrane biofilm reactor: model-based evaluation. Chem Eng J. 2017;316:82–90. https://doi.org/10.1016/j.cej.2017.01.084.
95. Ontiveros-Valencia A, Ziv-El M, Zhao HP, Feng L, Rittmann BE, Krajmalnik-Brown R. Interactions between nitrate-reducing and sulfate-reducing bacteria coexisting in a hydrogen-fed biofilm. Environ Sci Technol. 2012;46:11289–98. https://doi.org/10.1021/es302370t.
96. Ontiveros-Valencia A, Tang Y, Krajmalnik-Brown R, Rittmann BE. Managing the interactions between sulfate-and perchlorate-reducing bacteria when using hydrogen-fed biofilms to treat a groundwater with a high perchlorate concentration. Water Res. 2014;55:215–24. https://doi.org/10.1016/j.watres.2014.02.020.
97. Kanaujiya DK, Paul T, Sinharoy A, Pakshirajan K. Biological treatment processes for the removal of organic micropollutants from wastewater: a review. Curr Pollut Rep. 2019;5:112–28. https://doi.org/10.1007/s40726-019-00110-x.
98. Barwal A, Chaudhary R. To study the performance of biocarriers in moving bed biofilm reactor (MBBR) technology and kinetics of biofilm for retrofitting the existing aerobic treatment systems: a review. Rev Environ Sci Bio. 2014;13:285–99. https://doi.org/10.1007/s11157-014-9333-7.
99. PNL, Gastesi R, Lettinga, G. Use of sulfate reducing cell suspension bioreactors for the treatment of SO_2 rich flue gases. Biodegradation 2003:14:229–240. https://doi.org/10.1023/A:1024222020924.
100. Lens PNL, Vallerol M, Esposito G, Zandvoort M. Perspectives of sulfate reducing bioreactors in environmental biotechnology. Rev Environ Sci Biotech. 2002;1:311–25. https://doi.org/10.1023/A:1023207921156.
101. Kumar M, Pakshirajan K. Novel insights into mechanism of biometal recovery from wastewater by sulfate reduction and its application in pollutant removal. Environ Technol Inno. 2020;17:100542. https://doi.org/10.1016/j.eti.2019.100542.
102. Boswell CC, Friesen DK. Elemental sulfur fertilizers and their use on crops and pastures. Fertil Res. 1993;35:127–49. https://doi.org/10.1007/BF00750226.
103. Sahinkaya E, Kilic A. Heterotrophic and elemental-sulfur-based autotrophic denitrification processes for simultaneous nitrate and Cr (VI) reduction. Water Res. 2014;50:278–86. https://doi.org/10.1016/j.watres.2013.12.005.
104. Kowshik M, Deshmukh N, Vogel W, Urban J, Kulkarni SK, Paknikar KM. Microbial synthesis of semiconductor CdS nanoparticles, their characterization, and their use in the fabrication of an ideal diode. Biotechnol Bioeng. 2002;78:583–8. https://doi.org/10.1002/bit.10233.
105. Chandrasekaran S, Yao L, Deng L, Bowen C, Zhang Y, Chen S, et al. Recent advances in metal sulfides: from controlled fabrication to electrocatalytic, photocatalytic and photoelectrochemical water splitting and beyond. Chem Soc Rev. 2019;48:4178–280. https://doi.org/10.1039/C8CS00664D.
106. Kiran MG, Pakshirajan K, Das G. A new application of anaerobic rotating biological contactor reactor for heavy metal removal under sulfate reducing condition. Chem Eng J. 2017;321:67–75. https://doi.org/10.1016/j.cej.2017.03.080.
107. Park SM, Yoo JC, Ji SW, Yang JS, Baek K. Selective recovery of dissolved Fe, Al, Cu, and Zn in acid mine drainage based on modeling to predict precipitation pH. Environ Sci Pollut Res. 2015;22:3013–22. https://doi.org/10.1007/s11356-014-3536-x.
108. Wang LP, Ponou J, Matsuo S, Okaya K, Dodbiba G, Nazuka T, et al. Integrating sulfidization with neutralization treatment for selective recovery of copper and zinc over iron from acid mine drainage. Miner Eng. 2013;45:100–7. https://doi.org/10.1016/j.mineng.2013.02.011.
109. Shen Y, Brown RC, Wen Z. Syngas fermentation by *Clostridium carboxidivorans* P7 in a horizontal rotating packed bed biofilm reactor with enhanced ethanol production. Appl Energy. 2017;187:585–94. https://doi.org/10.1016/j.apenergy.2016.11.084.
110. Zhu H, Shanks BH, Heindel T.J. Effect of electrolytes on CO–water mass transfer. Ind Eng Chem Res 2009:48:3206–3210. https://doi.org/10.1021/ie8012924.
111. Bredwell MD, Telgenhoff MD, Barnard S, Worden RM. Effect of surfactants on carbon monoxide fermentations by *Butyribacterium methylotrophicum*. Appl Biochem Biotechnol. 1997;63:637–47. https://doi.org/10.1007/BF02920462.
112. Zhu H, Shanks BH, Heindel TJ. Enhancing CO–water mass transfer by functionalized MCM41 nanoparticles. Ind Eng Chem Res. 2008;47:7881–7. https://doi.org/10.1021/ie800238w.
113. Sinharoy A, Pakshirajan K. A novel application of biologically synthesized nanoparticles for enhanced biohydrogen production and carbon monoxide bioconversion. Renew Energy. 2020;147:864–73. https://doi.org/10.1016/j.renene.2019.09.027.
114. Parthasarathy P, Narayanan KS. Hydrogen production from steam gasification of biomass: influence of process parameters on hydrogen yield–a review. Renew Energy. 2014;66:570–9. https://doi.org/10.1016/j.renene.2013.12.025.