# Biological perchlorate reduction: which electron donor we can choose?

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## Abstract

Biological reduction is an effective method for removal of perchlorate ($ClO_4^-$), where perchlorate is transformed into chloride by perchlorate-reducing bacteria (PRB). An external electron donor is required for autotrophic and heterotrophic reduction of perchlorate. Therefore, plenty of suitable electron donors including organic (e.g., acetate, ethanol, carbohydrate, glycerol, methane) and inorganic (e.g., hydrogen, zero-valent iron, element sulfur, anthrahydroquinone) as well as the cathode have been used in biological reduction of perchlorate. This paper reviews the application of various electron donors in biological perchlorate reduction and their influences on treatment efficiency of perchlorate and biological activity of PRB. We discussed the criteria for selection of appropriate electron donor to provide a flexible strategy of electron donor choice for the bioremediation of perchlorate-contaminated water.

**Keywords** Biological reduction · Perchlorate · Electron donor · Selection

## Introduction

Perchlorate ($ClO_4^-$) is widespread in the production of pulp and paper, textiles, explosives, and rocket propellants (Crump and Gibbs 2005; Dasgupta et al. 2005; Xu et al. 2015a). As an emerging persistent pollutant, it has received great attention over the past few decades because it interferes with thyroid hormone secretion and causes damage to humans (Logan 2001; Luo et al. 2015; Ma et al. 2016). Perchlorate has low adsorption to natural solids, sluggish reactivity, and high solubility, so its amount is increasing year by year in environment (Choe et al. 2013; Song et al. 2017). Generally, the concentration of perchlorate is under 100 μg L$^{-1}$ in groundwater, but it was reported that the value reached 630–3700 mg L$^{-1}$ in the groundwater in Las Vegas and Nevada in the USA (Bardiya and Bae 2011).

Common methods for the remediation of perchlorate-contaminated water include physical separation, chemical/electrochemical reduction, and biological reduction (Logan 2001; Coates and Achenbach 2004; Zhao et al. 2011). Ion exchange (IX) is the most common in physical separation of perchlorate from wastewater. However, its application is limited because the concentrated residual waste brines are difficult to disposal. Meanwhile, the spent resins also need the regeneration (Hatzinger 2005; Chitrakar et al. 2012; Ye et al. 2012; Lin et al. 2014). The chemical reduction of perchlorate is difficult due to its special tetrahedral structure, where the central chlorine atom is surrounded by four oxygen atoms. The unique structure makes the chemical reduction of perchlorate need high activation energy (Srinivasan and Sorial 2009). The electrochemical reduction exhibited perfect efficiency and selectivity for perchlorate removal, but the high cost is a

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significant problem (Yang et al. 2016; Yao et al. 2017). Among the approached for the perchlorate-contaminated water treatment, biological reduction is more suitable because of its low cost, high efficiency, and free secondary pollution (Son et al. 2011; Wang et al. 2013; Lai et al. 2018). During this process, perchlorate is utilized by functional microorganisms as respiratory chain electron acceptor and reduced to chloride and oxygen when a suitable electron donor is present in anaerobic environment (Wen et al. 2016; Wen et al. 2017). So the suitable electron donor is necessary to provide the electrons to perchlorate molecules for their reduction. These functional microorganisms are defined as perchlorate-reducing bacteria (PRB), which can be classified into autotrophic PRB, using inorganic electron donors (Shrout et al. 2005a; Yu et al. 2006; Yu et al. 2007; Son et al. 2011) and heterotrophic PRB, using organic electron donors (Okeke and Frankenberger 2005; Wang et al. 2008; Xu et al. 2015b).

PRB are ubiquitous in natural environment and can grow with the processes of perchlorate bioreduction. Figure 1 shows the mechanism of the biological perchlorate reduction by PRB. These biological processes have been proved to be an enzymatic reaction (Steinberg et al. 2005; Van Trump and Coates 2009; Hutchison et al. 2013). With the assistance of (per)chlorate reductase (*pcr*), perchlorate is reduced by PRB to chlorate ($ClO_3^-$) and chlorite ($ClO_2^-$) successively and ends with the dismutation of $ClO_2^-$ into chloride ($Cl^-$) and molecular oxygen ($O_2$) catalyzed by chlorite dismutase (*Cld*). Furthermore, most of PRB are facultative anaerobes (Coates and Achenbach 2004; Nerenberg et al. 2008; Ma et al. 2016), molecular oxygen produced from biological reduction of perchlorate should be rapidly consumed by the reducing

equivalents provided by electron donor to avoid its accumulation in the system (Choi and Silverstein 2008; Zhao et al. 2013b; Xu et al. 2015b). Thus, maintenance of the suitable electron donor at useful levels is the key factor for efficient biological reduction of perchlorate.

There are plenty of published reviews on perchlorate, but their topic mainly focus on the fate, toxicity, and remediation of perchlorate (Srinivasan and Viraraghavan 2009; Srinivasan and Sorial 2009; Van der Zee and Cervantes 2009; Zhu et al. 2010). To the best of our knowledge, the systematical review on the role of electron donors for biological perchlorate reduction is rare. This article comprehensively summarized the type of electron donors used in bioreduction of perchlorate, the mechanistic reactions involved, and the major functional microorganisms. Then, the criteria of selection for the appropriate electron donor were discussed to provide a flexible strategy for selection of an electron donor for the bioremediation of perchlorate-contaminated water. Finally, the future research directions were prospected.

# Electron donors for biological perchlorate reduction

The type of electron donors used in the biological perchlorate reduction is very abundant. Table 1 summarizes the performance of biological perchlorate reduction with various electron donors. For heterotrophic process, organic compounds such as acetate, methane, ethanol, glycerol, acetic acid, and glucose are the common carbon source and organic electron donor (Ahn et al. 2009; Xu et al.

**Fig. 1** The mechanism for the biological reduction of perchlorate by PRB. Adapted with permission from Song et al. (2017), Copyright 2017, Elsevier
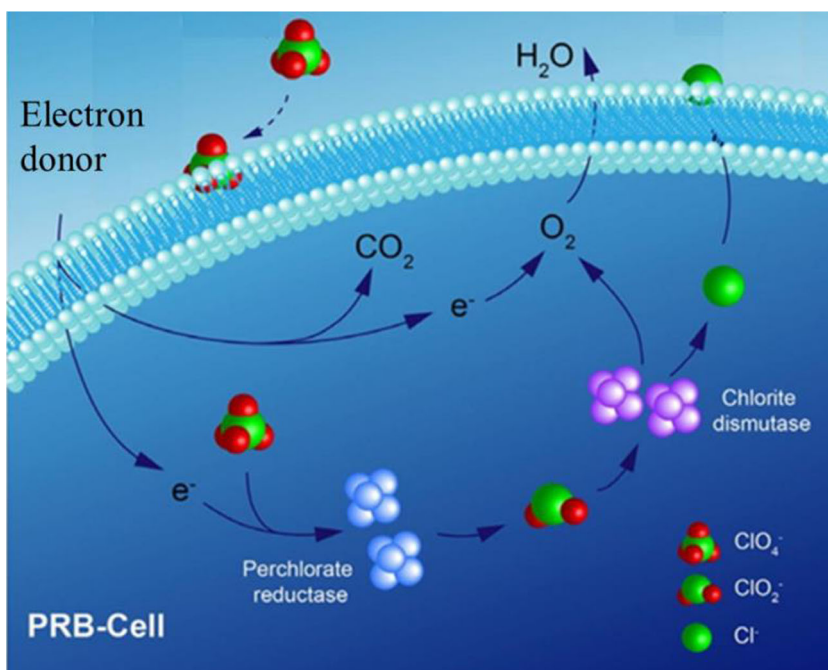
**Table 1**  The reduction rates of perchlorate and biomass yield with different electron donor

| Electron donor | Bioreactor type | Temperature | pH | $ClO_4^-$ removal rate (mg $L^{-1}$ $day^{-1}$) | Biomass yield (mg-VSS mg-perchlorate$^{-1}$) | Ref. |
|---|---|---|---|---|---|---|
| Acetate | Microbial fuel cell | NA | 8.5 | 32.79 | NA | Butler et al. (2010) |
| Acetate | Microbial fuel cell | NA | 6.5 | 24 | NA | Butler et al. (2010) |
| Acetate | Activated carbon reactor | $25 \pm 1$ °C | $7.5 \pm 0.2$ | 31.86 | NA | Zhu et al. (2016b) |
| Acetate | Sequencing batch reactor | $20 \pm 5$ °C | 7.0 | 2064[a] | NA | Ryu et al. (2012) |
| Acetate | Sequencing batch reactor | $20 \pm 5$ °C | 7.0 | 1152[b] | NA | Ryu et al. (2012) |
| Acetate | Batch experiments | NA | 5.0–9.0 | NA | 2.6–12 | Wang et al. (2008) |
| Ethanol | Ion exchange membrane bioreactor | $25 \pm 1$ °C | 7.0 | 0.289 | 3.64 | Ricardo et al. (2012) |
| Methane | Membrane biofilm reactor | $30 \pm 1$ °C | $7.4 \pm 0.2$ | 14.45 | NA | Xie et al. (2018) |
| Methane | Membrane biofilm reactor | $29 \pm 1$ °C | $7.0 \pm 0.2$ | 55.38 | NA | Chen et al. (2016) |
| Hydrogen | Hydrogen gas-lift reactor | 30 °C | 7.5 | 7638.53 | NA | Kroon and van Ginkel (2004) |
| Zero-valent iron | Flow-through reactor | $23 \pm 2$ °C | $6.9 \pm 0.1$ | 72 | NA | Yu et al. (2007) |
| Cathode | Bioelectrochemical reactor | $30 \pm 1$ °C | $7.8 \pm 0.2$ | 16.07 | NA | Xie et al. (2014) |
| Element sulfur | Sulfur-packed bed reactor | $27 \pm 2$ °C | 7.0 | 672 | NA | Wan et al. (2019) |
| Element sulfur | Batch experiments | $25 \pm 1$ °C | 7.2 | 90 | 2.47–11.4 | Gao et al. (2015) |

*NA* not available

[a] Salt tolerant perchlorate-reducing bacterial consortia (ST-PRBC)

[b] Non-salt-tolerant perchlorate-reducing bacterial consortia (N-PRBC)

2015b). However, these organic compounds can be utilized by other heterotrophic microorganisms as the carbon source, even superior to PRB, resulting in the deficiency of electron donors and the flourish of heterotrophic microorganisms. Therefore, the electron donor should be excessive in order to ensure that the perchlorate is completely removed. Whereas, excessive organic matter can lead to organic residues, which may bring excessive residual chemical oxygen demand (COD) in the effluent, resulting in the requirement for further treatment of water (Ju et al. 2008; Mieseler et al. 2013). Thus, the appropriate molar ratio of an electron donor to perchlorate is important. Among organic electron donors, acetate is the most suitable because of higher perchlorate removal rate and lower biomass production in the effluent, which not only reduces the secondary contamination but also reduces the maintenance cost. Obviously, the inorganic electron donors such as hydrogen ($H_2$), zero-valent iron ($Fe^0$), elemental sulfur ($S^0$), and thiosulfate ($S_2O_3^{2-}$) are the good alternative, especially in drinking water treatment (Zhang et al. 2002; Nerenberg and Rittmann 2004; Shrout and Parkin 2006). Compared to acetate (2064 mg $L^{-1}$ $day^{-1}$), the perchlorate removal rate using $H_2$ as the electron donor reached to 7638.53 mg $L^{-1}$ $day^{-1}$, but $S^0$ only achieved 672 mg $L^{-1}$ $day^{-1}$. However, the utilization of inorganic

substance not only avoids the secondary organic contamination but also has decreased sludge production, which all can decrease the operation cost (Park and Yoo 2009; Mieseler et al. 2013). From Table 1, it can be clearly found that $S^0$ as the electron donor induces the lower biomass yield (2.47–11.4 mg-VSS mg-perchlorate$^{-1}$).

## Organic electron donors

### Acetate

Acetate is the most commonly used in bioreduction of perchlorate by PRB (Giblin et al. 2000; Gingras and Batista 2002; Ahn et al. 2009). Acetate can serve as both carbon source and electron donor during the perchlorate reduction (Zhu et al. 2016b). Patel et al. (2008) achieved the complete reduction of perchlorate from synthetic ion-exchanged brines in granular activated carbon (GAC)-based fluidized bed reactors (FBR) fed with acetate. Some studies indicated that acetate had better performance in perchlorate reduction (London et al. 2011; Lian et al. 2017). Lian et al. (2017) compared the acetate, succinate saccharose, and glucose on perchlorate bioreduction and bioelectricity generation in microbial fuel cell (MFC). Due to the simpler molecular structure, acetate could be

easily utilized by microorganisms, which made it a more suitable electron donor (Xu et al. 2015b). *Azospira* sp. KJ., a heterotrophic PRB, achieved the maximum perchlorate reduction rate of 13.2 mg-perchlorate $L^{-1}$ $h^{-1}$ with acetate as the electron donor (Xu et al. 2015b). The process of using acetate to reduce perchlorate is shown in Fig. 2, and the equation can be described as following (Ucar et al. 2016a):

$$CH_3COOH + ClO_4^- \rightarrow 2CO_2 + Cl^- + 2H_2O \quad (1)$$
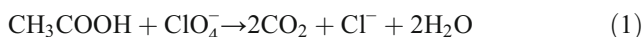
Perchlorate reduction followed first-order degradation kinetics when acetate served as the electron donor (Patel et al. 2008). The ratio of acetate to perchlorate is the key factor affecting the rate and efficiency of perchlorate reduction. Zhu et al. (2016a) reported that only a small amount of perchlorate was reduced without acetate, and as increased of the amount of acetate, the reduction extent and rate were improved. Shrout and Parkin (2006) investigated the bacterial perchlorate degradation in a mixed culture bioreactor and 100% perchlorate removal was achieved between 10 and 30 h at 1.2 mg-acetate mg-perchlorate$^{-1}$. The value was obviously lower than the results (2 and 1.94 mg-acetate mg-perchlorate$^{-1}$) reported by Zhu et al. (2016a) and Kim and Logan (2001). In order to achieve complete reduction of perchlorate, an excess of acetate was usually provided because it could alleviate the inhibition of perchlorate reduction led by the co-contaminant nitrate in water (Choi and Silverstein 2008; Zhu et al. 2016b). Contrary to the previous researches, Guan et al. (2015) thought that acetate could inhibit the growth of PRB. Simultaneously, they reported that nitrate could attenuate the inhibition and promoted the growth of PRB, further accelerating the degradation rate of perchlorate (Guan et al. 2015). In addition, excessive supply of acetate during biological perchlorate reduction may lead to the incomplete oxidation of acetate. The residual acetate and fermentation metabolites in the effluent contributed significantly to secondary organic pollution, which is actually a major shortcoming in

practical application (Liamleam and Annachhatre 2007; Mieseler et al. 2013).

## Ethanol

Ethanol has been utilized for dentrification, biological sulfate reduction, and biological perchlorate reduction as an effective organic electron donor (Liamleam and Annachhatre 2007). Ravnjak et al. (2013) found that the degradation efficiency of nitrate was higher than 99% using ethanol as electron donor in a two-stage anoxic/oxic biofilm membrane bioreactor. Ethanol also could be used to remove anionic contaminant in ion exchange membrane bioreactor (IEMB) (Matos et al. 2006). PRB *Dechloromonas* and denitrifiers, e.g., *Thauera*, *Azoarcus*, and *Paracoccus*, could proliferate in IEMB with the simultaneously removal of nitrate and perchlorate using ethanol (Ricardo et al. 2012). With the participation of microorganisms, the ethanol degradation process is as follows:
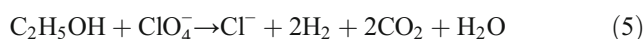
Acetogenesis:

$$C_2H_5OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2 \quad (2)$$

Methanogenesis:

$$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^- \quad (3)$$

$$4H_2 + HCO_3^-H^+ + 3H^+ \rightarrow CH_4 + H_2O \quad (4)$$

So the theoretical stoichiometry of the perchlorate reduction is as follows:

$$C_2H_5OH + ClO_4^- \rightarrow Cl^- + 2H_2 + 2CO_2 + H_2O \quad (5)$$

The concentration of ethanol in the biological treatment system must be controlled. Low concentration of ethanol could limit perchlorate and nitrate reduction (Matos et al. 2006). Under limiting ethanol supply, reduction of perchlorate declined from 33.8 ± 3.0 to 8.3 ± 0.8 mg $L^{-1}$ and the reduction rate of nitrate was almost unaffected (from 29.3 ± 0.7 to 27.6 ± 1.5 mg $L^{-1}$ day$^{-1}$) (Ricardo et al. 2012). Although part of ethanol also can be

**Fig. 2** The process of perchlorate (per)chlorate/nitrate reduction. Adapted with permission from Xu et al. (2015b), Copyright 2015, Elsevier
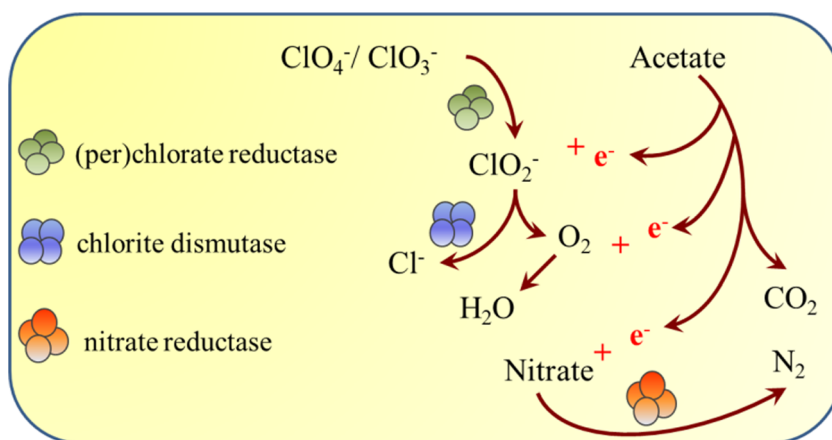
consumed by heterotrophic organisms, excessive ethanol may cause residual COD in the effluent (Velizarov et al. 2000). IEMB technology solves the problem of organic residual because of the low diffusion coefficient of ethanol ($1.8 \times 10^{-8}$ $cm^2$ $s^{-1}$) in the membrane (Fonseca et al. 2000). The biofilm on the membrane surface can decrease the ethanol concentration on the membrane surface, which ensures the sufficient utilization of ethanol by organisms. Ricardo et al. (2012) found that the biomass growth yield ($Y_p$) was 3.64 mg-VSS mg-perchlorate$^{-1}$ using ethanol as electron donor, which deviated strongly from the stoichiometric ratio of perchlorate/ethanol. The estimation value was 1.53 g g$^{-1}$ while the obtained experimental value was 0.042 g g$^{-1}$. They attributed the overestimated $Y_p$ to the ethanol consumed by other organisms, e.g., fermentative bacteria to produce acetic acid.

## Carbohydrate-based electron donor

Carbohydrate-based electron donors (CBEDs) such as molasses, glucose, high fructose corn syrup, and cellobiose are effective electron donors that are susceptibly degradable under anaerobic conditions. The CBED has been approved by the National Sanitation Foundation (NSF) International for drinking water treatment (Upadhyaya et al. 2015). CBED has been used as a substitute for acetic acid to reduce perchlorate from drinking water in fixed bed reactors (FXBRs) and fluidized bed reactors (FLBRs) (Upadhyaya et al. 2015). As Upadhyaya et al. (2015) reported, it needed longer empty bed contact time (EBCT) and higher influent CBED COD to attain water quality comparable to that of acetic acid. In addition, the biomass yield using CBED was higher, which required more frequent maintenance.

Molasses, a sugar production by-product, is one of the most cost-effective CBED because of its low price and easy availability. The major components in molasses are the polysaccharides with long carbon chains. Therefore, similar to other CBEDs, molasses must be better fermented to lactate by microorganisms such as *Lactobacilli* in order to increase its bioavailability before it is used as the electron donor (Maree et al. 1991). In addition, there are plenty of non-biodegradable caramelized products in molasses, which can accumulate in the sludge (Annachhatre and Suktrakoolvait 2001). The accumulation of non-biodegradable caramelized product reduced the activity of biomass and impacted the COD removal, leading to excessive residual COD in outflow (Liamleam and Annachhatre 2007). Another major defect of using molasses is that there are the high volatile fatty acid (VFA) contents in the reactor due to the fermentation of molasses. The acidification induced by VFAs accumulation negatively affects the growth of both methanogens and PRB. But the problem can be solved well by the addition of NaOH or NaHCO$_3$.

## Glycerol

Glycerol is a non-expensive by-product of the growing biodiesel production industry, so it is cheap and easily available (Yazdani and Gonzalez 2007). When it was used as an electron donor in IEMB, bioreduction efficiency of perchlorate exceeded 99% with inlet perchlorate concentration as high as 250 mg L$^{-1}$ (Fox et al. 2016). The benefit of glycerol as the electron donor is its much lower diffusion rate ($6.9 \times 10^{-9}$ ($\pm 4.7 \times 10^{-10}$) $cm^2$ $s^{-1}$) to penetrate the membrane, which is 60% lower than the ethanol (Velizarov et al. 2000). So the organic carbon concentration in effluent was kept lower level, averaging 1.82 ($\pm$ 0.70) mg-C L$^{-1}$ and always less than 3 mg-C L$^{-1}$ (Fox et al. 2016). In order to further avoid the cross-contamination led by organic carbon, the supply of carbon source (e.g., glycerol, ethanol) can be controlled according to the stoichiometric demand for complete perchlorate degradation.

Glycerol is a complex organic that is difficult to be utilized directly by PRB. So biological reduction of perchlorate with glycerol as the electron donor is a two-stage process, in which glycerol is firstly fermented in the suspension of IEMB, and then PRB in the biofilm attached on the membrane use these fermentation products to achieve the bioreduction of perchlorate (Fox et al. 2016). The population analysis showed that a glycerol fermenter, *Klebsiella oxytoca*, was the dominant bacteria in the suspension phase, while the typical PRB, *Azospirillum* sp. were the foremost strain in the biofilm (Fox et al. 2016).

The reduction reaction of perchlorate utilized glycerol is as follows:

$$4C_3H_8O_3 + 7ClO_4^- \rightarrow 16H_2O + 12CO_2 + 7Cl^- \tag{6}$$
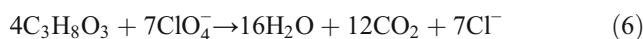
## Methane

Recently, simple gaseous organics methane (CH$_4$) has received extensive attention as a carbon source and electron donor for biological perchlorate reduction (Beal et al. 2009; Ettwig et al. 2010; Ettwig et al. 2016). Firstly, the price of CH$_4$ is relatively low and it can be obtained from anaerobic digesters (Zhang et al. 2016; Wang et al. 2017a, b). Meanwhile, different with that of high water solubility for common organic carbon sources such as acetate and ethanol, CH$_4$ is poorly soluble in water, which avoids the secondary organic contamination, especially when treating perchlorate-containing groundwater (Lv et al. 2018). So CH$_4$ is an ideal organic carbon source. Although its availability to PRB is limited by the low solubility, membrane biofilm reactor (MBfR) can solve the issue by achieving high gas transmission rate, which has been successfully applied to biological wastewater treatment with gaseous H$_2$ and CH$_4$ as the electron donors (Nerenberg and Rittmann 2004; Martin and Nerenberg

2012). $CH_4$ can be directly used by denitrifiers, PRB, methylotrophs, and methanotrophs (Chen et al. 2016; Xie et al. 2018). When perchlorate serves as the electron acceptor, the reaction is thermodynamically feasible (Luo et al. 2015; Xie et al. 2018):

$$CH_4 + ClO_4^- \rightarrow CO_2 + Cl^- + 2H_2O \qquad (7)$$
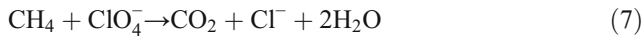
As was mentioned above, the pathway of biological perchlorate reduction involves a step to produce $O_2$, which is necessary for the $CH_4$ oxidation (Bender et al. 2005; Luo et al. 2015; Chen et al. 2016). But Miller et al. (2014) demonstrated that aerobic methanotrophs could not utilize the $O_2$ produced through perchlorate bioreduction. Actually, there was no report that $CH_4$ could reduce perchlorate until Luo et al. (2015) demonstrated that the bioreduction of perchlorate using $CH_4$ is feasible.

It is well-known that there are two categories of $CH_4$ oxidation: anaerobic and aerobic $CH_4$ oxidation (Xie et al. 2018), which are usually coupled to denitrification. Anaerobic $CH_4$ oxidation coupled to denitrification (ANMO-D) usually involves two distinct bacterial groups: archaea and denitrifying bacteria (Ettwig et al. 2008; Ettwig et al. 2009; Hu et al. 2009). Archaea can generate $H_2$ by reverse methanogenesis to reduce nitrate to nitrite ($NO_2^-$) themselves. Denitrifiers such as NC10 further reduce the nitrite using $CH_4$ via an "intra-aerobic" pathway (Ettwig et al. 2009). Aerobic methane oxidation coupled to denitrification (AMO-D) is carried out by the effects of methane oxidizers (methanotrophs) and denitrifiers in combination (Eisentraeger et al. 2001; Knowles 2005; Knittel and Boetius 2009). Methanotrophs oxidize $CH_4$ in the presence of $O_2$ and produce acetate and other soluble organic matters. Then the denitrifiers use these organics as electron donors to reduce nitrate (Eisentraeger et al. 2001; Knowles 2005; Knittel and Boetius 2009).

Considering the similar structure to nitrate, it is logical that the key PRB can reduce the perchlorate using a chlorite dismutase in a manner similar to nitric oxide (NO) disproportionation in denitrification (Ettwig et al. 2010). Therefore, Luo et al. (2015) pointed out that there were two possible mechanisms for the degradation of perchlorate with $CH_4$: (1) anaerobic methane oxidation coupled to perchlorate reduction (ANMO-PR) and (2) micro-aerobic methane oxidation coupled to perchlorate reduction (mAMO-PR) and illustrated the mechanisms in Fig. 3. According to the influence of dissolved oxygen (DO) and $CH_4$/$NO_3^-$ mole ratio on perchlorate reduction, Chen et al. (2016) found that ANMO-PR played important role for the biological perchlorate reduction in the MBfR fed with $CH_4$. Bacteria domination in the perchlorate-reducing biofilm, and the increasing proportion of the particulate methane mono-oxygenase (pMMO) in respiratory gene copies all supported that the $CH_4$-oxidizing biofilm likely respired perchlorate combined with the mono-oxygenation of $CH_4$ using the $O_2$ intracellularly generating from $ClO_2^-$ dismutation, whose manner is similar to nitrate disproportionation in denitrification (Bender et al. 2005; Luo

et al. 2015; Chen et al. 2016). Rikken et al. (1996) discovered that $O_2$ was released extracellularly during complete perchlorate degradation. Luo et al. (2015) speculated that the reduction of perchlorate coupling oxidation of $CH_4$ may be realized by a mixture of PRB and methanotrophs using pMMO and perchlorate reductase (pcrA) separately. Miller et al. (2014) confirmed that the methanotrophs used extracellular $O_2$ come from $ClO_2^-$ disproportion by PRB Dechloromonas agitate CKB to oxidize $CH_4$ aerobically. However, $O_2$ is also a competitive electron acceptor of perchlorate and is superior to perchlorate by PRB acceptance. Therefore, the actual DO concentrations in the MBfR system should be far below theoretical demand. Luo et al. (2015) named this hypothesized mechanism as mAMO-PR, and the mechanism is demonstrated in Fig. 3b.

## Inorganic electron donors

### Hydrogen

Hydrogen ($H_2$) has been used for perchlorate biological treatment in many researches (Zhao et al. 2011; Wang et al. 2014; Chen et al. 2017). According to Ontiveros-Valencia et al. (2013), the removal of perchlorate could reach 98% with inlet perchlorate concentration at 10 mg $L^{-1}$ in a $H_2$-based MBfR. MBfR is one of the most widely used reactors when the electron donor is gaseous, because it can achieve near 100% gas utilization efficiency for high gas transmission rate, further ensuring high nitrate and perchlorate removal rates (Tang et al. 2012; Tang et al. 2013; Zhao et al. 2013a). $H_2$ as the electron donor in heterotrophic perchlorate reduction has a number of advantages, including (1) $H_2$ has low solubility, so it is easy to be stripped from water; (2) $H_2$ is non-poisonous; (3) hydrogenotrophic bacteria utilizing inorganic carbon sources ($CO_2$, $HCO_3^-$) grow slowly, thus producing less metabolic sludge, and the metabolites are mainly $H_2O$ (Zhao et al. 2013b); and (4) $H_2$ as the electron donor does not require additional organic substances, avoiding excessive COD residue in the effluent (Nerenberg et al. 2002; Sahu et al. 2009). However, the price of $H_2$ is expensive to limits its extensive use. Meanwhile, the explosive risk of $H_2$ in transportation, storage, and utilization also is the issue.

In the bio-reduced perchlorate membrane reactor, almost no microorganisms can grow, except for a few anaerobic bacteria, under the conditions where only $H_2$ was used as energy (Liamleam and Annachhatre 2007). Wan et al. (2016) found that the Thauera genus dominated in the mixed culture, which could simultaneously remove nitrate and perchlorate utilizing $H_2$. And Dechloromonas was in the ascendant during perchlorate reduction in a $H_2$-based MBfR (Zhao et al. 2011). Thrash et al. (2007) found a novel PRB, strain VDY, which could use $H_2$ readily as an electron donor to respire perchlorate. However, the typical PRB Dechloromonas and Azospira species could not utilize $H_2$ in the BER; they used the electrons

Fig. 3 a, b Mechanisms of the degradation of perchlorate with the CH$_4$ as the electron donor. Adapted with permission from Luo et al. (2015), Copyright 2015, American Chemical Society
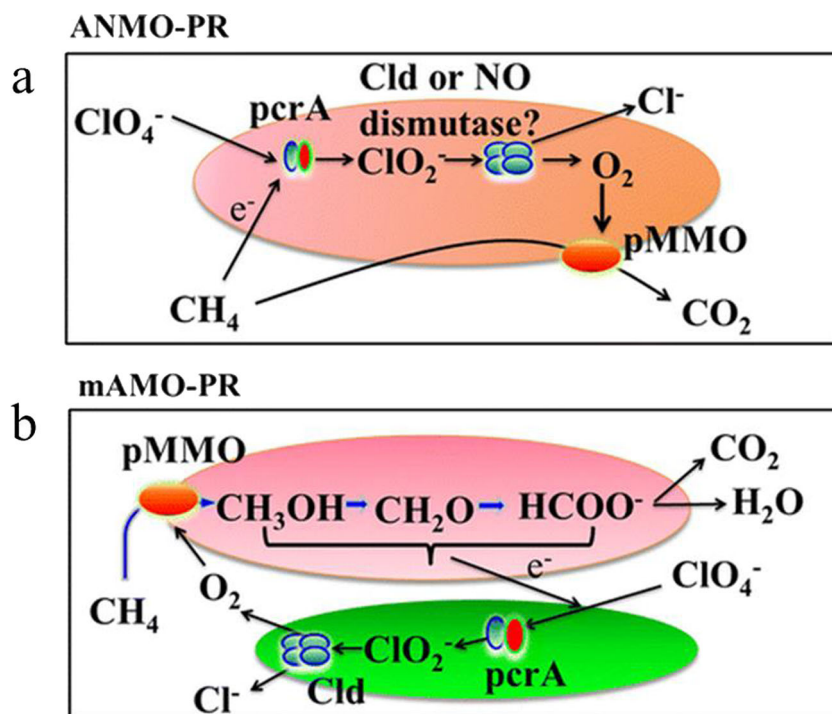


directly on the surface of electrode or indirectly via an electron shuttle (AQDS) for the perchlorate reduction (Achenbach et al. 2001; Coates et al. 2001a). The theoretical stoichiometry is as follows (Thrash et al. 2007):

$$4H_2 + ClO_4^- \rightarrow Cl^- + 4H_2O \tag{8}$$

Nitrate and perchlorate can be reduced simultaneously by the combined action of PRB and denitrifying bacteria in a H$_2$-based MBfR. Similar to PRB, sulfate-reducing bacteria (SRB) can also use H$_2$ to reduce sulfate in water. To some extent, there is a competition not only to the common electron donor (H$_2$) but also to the space in the biofilm among these three groups (Zhao et al. 2014; Zhao et al. 2013b). Therefore, the unnecessary reduction of sulfate should be restricted. The degradation of varies electron acceptors in H$_2$-based reactors is illustrated in Fig. 4. Hydrogenotrophic perchlorate reduction by PRB is listed as follows (Zhao et al. 2013b):

$$ClO_4^- + 0.11H^+ + 0.11NO_3^- + 0.53CO_2 + 5.48H_2 \rightarrow Cl^-$$
$$+ 5.15H_2O + 0.11C_5H_2O_2N \tag{9}$$
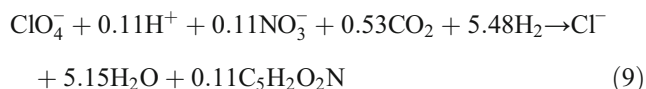
The perchlorate removal using H$_2$ as electron donor fitted zero-order kinetics model (Van Ginkel et al. 2008; Wang et al. 2014; Wan et al. 2016). And the availability of H$_2$ controlled the reduction kinetics when the system was not salt-inhibited (Butler et al. 2010). When H$_2$ was limiting, facultative denitrifying bacteria were superior to strict autotrophs, since organic products can be used as electron donors (Zhao et al.

2011). And the perchlorate reduction was suppressed by high nitrate loading (Zhao et al. 2013b). When the surface loading of nitrate was higher than $0.65 \pm 0.04$ g-N m$^{-2}$ day$^{-1}$, perchlorate removal was only $30 \pm 8\%$ in H$_2$-based MBfR. With the surface loading decreasing to $0.34 \pm 0.04$–$0.53 \pm 0.04$ g-N m$^{-2}$ day$^{-1}$, perchlorate in effluent was nondetectable. Meanwhile, reduction of nitrate to N$_2$ gas can produce the base and cause the increases of pH, which will exacerbate the precipitation of magnesium and calcium carbonates on the MBfR fibers. The precipitates influenced the H$_2$ flux to the biofilm and lead to a decline of denitrification and
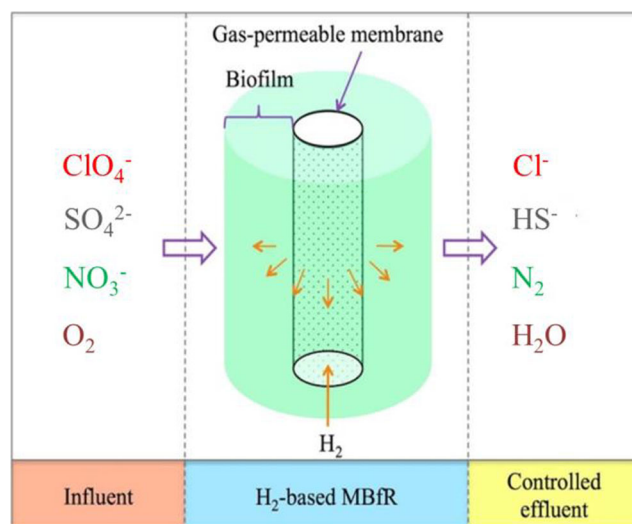


Fig. 4 Degradation of electron acceptors in H$_2$-based reactors. Adapted with permission from Chen et al. (2017), Copyright 2017, Elsevier

perchlorate reduction performance, but mild citric-acid washing can alleviate the states (Van Ginkel et al. 2011). Salinity is also an important factor because of the lower solubility of $H_2$ in high salinity solution (Sahu et al. 2009). The mass transfer coefficient of $H_2$ in brine is relatively low. Meanwhile, most of microorganisms are difficult to survive in high salinity environments. MBfRs solved this problem well and gave 30% nitrate and 42% perchlorate removal from synthetic IX brine (Sahu et al. 2009). Contaminated water and $H_2$ are introduced into different parts of the reactor: the shell side of the reactor and the cylindrical cavity of microporous hollow fiber membranes, respectively.

In practical application, $H_2$ can be externally supplied to the reactor or in situ generated. The external supply of $H_2$ has a fatal disadvantage that there are potential safety hazards because of the inherent explosive nature of $H_2$ (Thrash et al. 2007). Meanwhile, the expensive cost to produce the $H_2$ also limits its supply in bulk quantities. Some reports indicated that newly produced $H_2$ in situ had higher activity and could be more effectively utilized by bacteria than external supplied (Prosnansky et al. 2002). $H_2$ can be produced in situ through the cathode electrolysis of water (Butler et al. 2010). The highly negative operating potential of $-375$ mV versus Ag/AgCl and pH of 8.5 was sufficient to form $H_2$ at the surface of electrode, providing a soluble electron donor for PRB to reduce perchlorate. It was found that the maximum specific perchlorate reduction rate ($V_{max}$) reached to 17.46 mg g-$VSS^{-1}$ $h^{-1}$ (Wang et al. 2014), which is much than that fed with external $H_2$ (2.518 mg g-$VSS^{-1}$ $h^{-1}$ in Wan et al. (2016)). In addition, $H_2$ also is supplied through the corrosion of zero-valent iron (ZVI) (London et al. 2013). Yu et al. (2006) demonstrated that ZVI could play the role of electron donor providing $H_2$ in situ for the PRB *Dechloromonas* sp. to reduce perchlorate without external supply of $H_2$. The normalized maximum perchlorate utilization rate ($r_{max}$) reached to 9200 μg g-dry sludge$^{-1}$ $h^{-1}$. However, plenty of co-product hydroxide is formed accompanying with the $H_2$ production, and there is a requirement to control pH in order to neutralize the hydroxide.

## Zero-valent iron

As a strong reducing agent, ZVI has been used to treat pollutants via chemical reduction (Wu et al. 2013; Dong et al. 2017). Thermodynamically, perchlorate can be easily reduced by ZVI ($\Delta G° = -2495.9$ kJ $mol^{-1}$). However, the activation energy barrier between perchlorate and ZVI is so high that chemical process is too slow to repair in situ (Moore et al. 2003; Son et al. 2006; Yu et al. 2006). Recently, several studies have shown that ZVI served as the ultimate electron donor to enhance the perchlorate reduction by in situ supplying $H_2$ derived from the iron corrosion process (Son et al. 2006; Schaefer et al. 2007; Arthur et al. 2013). The batch addition

of ZVI achieves the continuous supply of $H_2$, which is obviously superior to the continuous supply of electron donors (organic matters, $H_2$ gas, etc.). Besides, iron is low cost, is safe to operate, and has no organic residuals in effluent (Son et al. 2006).

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \tag{10}$$
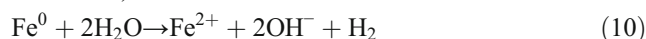
Generally, the perchlorate reduction by combined ZVI-PRB divides into three steps: (1) ZVI reduces $H^+$ to $H_2$ at the surface; (2) the diffusion path of $H_2$ is first to the bacteria attached to the iron surface, then to the bulk solution, and finally to bacteria suspended; and (3) PRB reduce perchlorate with $H_2$ as electron donor (Yu et al. 2006). Perchlorate is mainly reduced by PRB attached to the ZVI because the microorganisms mass attached to the ZVI was much larger than in the liquid (Yu et al. 2007). In addition, when there are energetic compounds coexisting with perchlorate, ZVI pretreatment could degrade these energetic compounds to eliminate their toxic inhibition to PRB, simultaneously, and these smaller molecules degraded products also served as the electron donors for enhanced bioremediation of perchlorate (Schaefer et al. 2007; Ahn et al. 2014).

Improved perchlorate reduction rate with ZVI as the electron donor should be ascribed to (1) the increasing iron surface activity and formation of $H_2$, (2) the strengthening mass transfer, and (3) the increasing cell density. However, the research of Yu et al. (2006) found that these factors all affected the biological reduction of perchlorate to some extent, but were not the key factor. Two factors that influence the success of this technology are cell density and pH. Bioreduction of perchlorate with ZVI as the electron donor is a complex process involving various functional microorganisms, including autotrophic and heterotrophic PRB, denitrifying bacteria, and homoacetogens. As the increase of initial cell density, the removal rate of perchlorate was enhanced, while amending the surface reactivity of ZVI by acid washing or sonication so as to accelerate the $H_2$ production had no effect on the acceleration of perchlorate reduction rate (Yu et al. 2006). Meanwhile, the presence of bacteria could accelerate the rate of iron corrosion (Yu et al. 2006). Besides, chloride and $O_2$, end-products of perchlorate bioreduction, would stimulate the corrosion of iron. Researches have shown that the optimum pH for PRB *Dechloromonas* sp. HZ is neutral 6.8, and little bioreduction of perchlorate happened at the initial pH 9 (Zhang et al. 2002; Yu et al. 2007). When the corrosion rate of iron is excessive, the pH will increase owing to the formation of $OH^-$, which is intolerant to the PRB. Meanwhile, higher pH can result in the formation of iron precipitates such as iron hydroxide to encapsulate bacteria (Shrout et al. 2005b; Son et al. 2006). This may make the capability of PRB to reduce perchlorate became worse (Andrews and Novak 2001; Huang et al. 2003; Yu et al. 2006; Yu et al. 2007). The activity of PRB was primarily affected by the initial pH of the
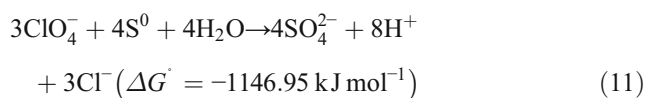
solution. As long as perchlorate bioreduction runs stably, microbial process was unaffected by pH (Yu et al. 2006). Therefore, pH control is crucial to maintain the stability of perchlorate bioreduction using ZVI as the electron donor. The most feasible inorganic phosphate-based buffer can effectively maintain the neutral pH, but it is inhibitive to the iron corrosion. Arthur et al. (2013) found Tris-EDTA (TE) was a cost-effective alternative.

## Elemental sulfur

Inorganic sulfur compounds, sulfite ($SO_3^{2-}$), tetrathionate ($S_4O_6^{2-}$), thiosulfate ($S_2O_3^{2-}$), elemental sulfur ($S^0$), and sulfide ($S^{2-}$), are wildly used as the inorganic electron donor in biological wastewater treatment. Among them, $S^0$ is more favored because it is easy to handle and due to its low cost and the high sulfur content among the reduced sulfur compounds (Ju et al. 2007; Ju et al. 2008; Ucar et al. 2016a). Furthermore, insoluble $S^0$ (solubility of 5 $\mu$g $L^{-1}$ at 20°C) can discharge electrons slowly as needed, showing its price and maintenance advantages (Ju et al. 2008).

The reaction of perchlorate with $S^0$ is a spontaneous exothermic reaction (Eq. (11)). As the perchlorate is reduced, the elemental sulfur is oxidized to sulfate (Ju et al. 2007; Ju et al. 2008):

$$3ClO_4^- + 4S^0 + 4H_2O \rightarrow 4SO_4^{2-} + 8H^+$$
$$+ 3Cl^- \left(\Delta G^{\cdot} = -1146.95\, kJ\, mol^{-1}\right) \qquad (11)$$

In Ju et al. (2008), a faster perchlorate reduction rate of 1.12 mM $day^{-1}$ was observed using $S^0$ as electron donor. *Sulfuricella*, *Sulfuritalea*, *Thiobacillus*, and *Sulfurimonas* are proven to be the effective DB/PRB using $S^0$ as electron donor (Wan et al. 2017). The maximum observed yield coefficient of microbial consortium with $S^0$ was 0.19 mg-dry weight (DW) mg-perchlorate$^{-1}$, which was less than that of heterotrophic perchlorate-reducing bacteria (0.34–0.36 mg-DW mg-perchlorate$^{-1}$) (Gao et al. (2015). This indicated that less excess biomass was produced during autotrophic perchlorate reduction process due to the lower microbial growth rate, which is more beneficial in practical applications.

Packing insoluble $S^0$ particles into the bioreactor provides a good way for long-term supply of electron donor. Ucar et al. (2016b) compared the performances of sulfur-based autotrophic and methanol-based heterotrophic perchlorate removal and the perchlorate reduction rates were 12 and 24 mg $L^{-1}$ $day^{-1}$, respectively. However, methanol in the effluent from heterotrophic reactor was up to around 20 mg $L^{-1}$. Therefore, although methanol-based perchlorate reduction is fast and effective, $S^0$ as an electron donor may be preferred due to elimination of effluent contamination by organic substrate. The removal of perchlorate in up-flow sulfur-packed reactors accorded with the half-order kinetic models (Wan

et al. 2017), indicating that reduction rate was mainly limited by the diffusion in biofilm. Koenig and Liu (2001) thought that the supply and concentration of soluble $S^0$ were not rate-limiting steps, because they were unable to control directly. If solid $S^0$ is sufficiently supplied, the contaminate removal may be limited by its dissolution rate. Ju et al. (2007) found that the effect of increasing $S^0$ concentrations on the kinetics of perchlorate reduction was related to particle size of $S^0$. 4 mM powder $S^0$ with particle size of 10–130 $\mu$m gave a rate of perchlorate reduction comparable to that of 200 mM granule $S^0$ with the major and minor oblate spheroid axis of 1.75 and 1 mm.

The main weakness of sulfur-based autotrophic perchlorate reduction is the formation of sulfates and acids (Guo et al. 2017). Except for as the by-products of perchlorate reduction, the sulfate mainly originates from $S^0$ disproportionation. $S^0$ is subject to disproportionation to $SO_4^{2-}$ and $S^2$, which is shown as Eq. (12) (Finster et al. 1998).

$$4S^0 + 4H_2O \rightarrow 3H_2S + SO_4^{2-} + 2H^+ \qquad (12)$$
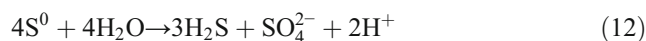
Although $S^{2-}$ had been used as an electron donor by certain isolates of PRB (Achenbach et al. 2001), e.g., *Dechloromonas agitata* sp. nov., 5 mM $S^{2-}$ appeared to cause toxicity for perchlorate bioreduction (Ju et al. 2007; Ju et al. 2008). Furthermore, the sulfate production from the $S^0$ disproportionation exceeded the theoretical sulfate production during the biological perchlorate reduction with $S^0$ as the electron donor, which is a potential drawback of this process (Boles et al. 2012; Gao et al. 2015; Wan et al. 2017). Previous research indicated that temperature, DO, and hydraulic retention time (HRT) had significant influence on $S^0$ disproportionation tendencies (Wan et al. 2019). Considering the balance of $S^0$ disproportionation and perchlorate reduction, higher temperature (27 ± 2 °C) and shorter HRT (0.75 h) was suitable to perchlorate removal by sulfur-packed bed reactor, in which over 99% perchlorate removal efficiency was achieved and sulfate in effluent was only 21.91 mg $L^{-1}$.

Ucar et al. (2016a) found that methanol supplementation could stimulate the mixed nutrient denitrification process, offering the advantages of higher perchlorate removal and lower effluent sulfate concentration. But this method also had the defect that the organic concentration was excessive in the effluent. In the sulfur-based reactor, most of $S^0$ disproportionation occurred close to the effluent where the oxanion (such as nitrate, perchlorate) decreased to low concentration (Wan et al. 2017). Zhang et al. (2018) used the step-feeding method to solve the unreasonable pollutants distribution in sulfur-based reactor, leading to high perchlorate reduction rate and low sulfate yield.

## Anthrahydroquinone

2,6-Anthrahydroquinone disulfonate (AH$_2$DS), as an effective electron donor, could selectively stimulate the perchlorate

bioremediation (Thrash et al. 2007; Van Trump and Coates 2009). Earlier studies showed that several organisms, including dissimilatory perchlorate-reducing bacteria (DPRB), could grow quickly with AH$_2$DS and nitrate as the electron donor and acceptor respectively (Coates et al. 2001a; Coates et al. 2001b). Cultures of *Azospira suillum*, *Geobacter*, *Dechloromonas agitate*, and *Dechloromonas aromatica* could reduce perchlorate while oxidizing the AH$_2$DS to 2,6-anthraquinone disulfonate (AQDS) (Thrash et al. 2007; Van Trump and Coates 2009).

Thrash et al. (2007) inoculated three representatives of environmentally dominant PRB *Azospira suillum*, *D. aromatica*, and *Dechloromonas agitata* in a bioelectrical reactor (BER) and found that the total concentration of anthraquinone remained constant during the experimental process, indicating an equal conversion between AH$_2$DS and AQDS. Simultaneously, no perchlorate reduction was observed fed with AQDS only. In contrast, if AH$_2$DS was provided, perchlorate was readily reduced by PRB *Dechloromonas agitata*. The same phenomena were observed in the study of Van Trump and Coates (2009). This demonstrated that AH$_2$DS is oxidized to AQDS while reducing perchlorate. The theoretical stoichiometry of the reaction is as follows (Zhu et al. 2019):

$$4C_{14}H_8O_8S_2^{2-}(AH_2DS)$$

$$+ ClO_4^- \rightarrow 4C_{14}H_6O_8S_2^{2-}(AQDS) + Cl^- + 4H_2O \qquad (13)$$
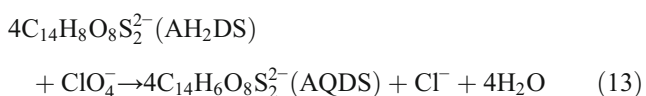
Van Trump and Coates (2009) demonstrated that PRB did not preferentially use acetate over AH$_2$DS as the electron donor. The oxidation rate of AH$_2$DS was not significantly influenced when acetate was added, whereas the mixture of acetate and AH$_2$DS provided additional electron-donating capacity and significantly enhanced the perchlorate reduction. 3.5 mM AH$_2$DS could result in an additional 1.5 mM perchlorate reduction over acetate-only treatment (Van Trump and Coates 2009).

There are many advantages using AH$_2$DS as electron donor. Firstly, the oxidation product of AQDS can be an electronic shuttle to accelerate electron transport efficiency and enhance perchlorate degradation in BER (Thrash et al. 2007). Secondly, AQDS, can be considered as a quinone-based redox mediators (QRM) because of its high redox buffering capacity, which could alleviate the inhibition of perchlorate reduction by long-term oxygen exposure and high concentration of nitrate (Zhu et al. 2019). In addition, the thermodynamic properties of hydroquinone make them only irritate a part of the underlying respiratory process. The midpoint reduction potential of AQDS/AH$_2$DS is about $-0.184$ V, which is suitable to inspire the perchlorate and nitrate reduction, but is too electropositive to the sulfate reduction or methanogenesis ($< -0.217$ V) (Van Trump and Coates 2009). The unique property of AH$_2$DS precludes undesirable

respiratory activities and prevents gross overgrowth of microbial biomass. While successful to improve perchlorate reduction in BER, the existence of AQDS has a drawback because it increases the expense and the requirements for further processing of residual AQDS in effluent (Thrash et al. 2007).

## Cathode

A new technology involving electrochemically stimulating bacterial reduction in a bioelectrical reactor (BER) had been applied in perchlorate treatment (Thrash et al. 2007; Shea et al. 2008; Jiang et al. 2017). Former studies suggested that PRB may utilize the cathode as electron donor for growth (Thrash et al. 2007). However, the electrode potential in their microbial fuel cell (MFC) was maintained at $-450$ mV, which was high enough to produce the H$_2$ on the surface of electrode for PRB to reduce perchlorate. With the assistance of an electron shuttle, anthraquinone-2,6-disulfonate (AQDS), an overestimated perchlorate removal rate of 17 mg L$^{-1}$ day$^{-1}$ (batch configuration) and 60 mg L$^{-1}$ day$^{-1}$ (continuous configuration) was gained respectively.

In fact, the electrons can directly transfer from the surface of cathode electrode to bacterial cell membrane by a physical contact between them. As shown in Fig. 5a, the outer membrane redox macromolecules, such as cytochromes can directly accept the electrons from the electrode, resulting in the reduction of terminal electron acceptors, for example perchlorate (Huang et al. 2011; Xie et al. 2014). Perchlorate reduction in a biocathode of MFC in the absence of exogenous electron shuttles was firstly reported by Shea et al. (2008). In dual-chamber MFC, a denitrifying biocathode was adapted to
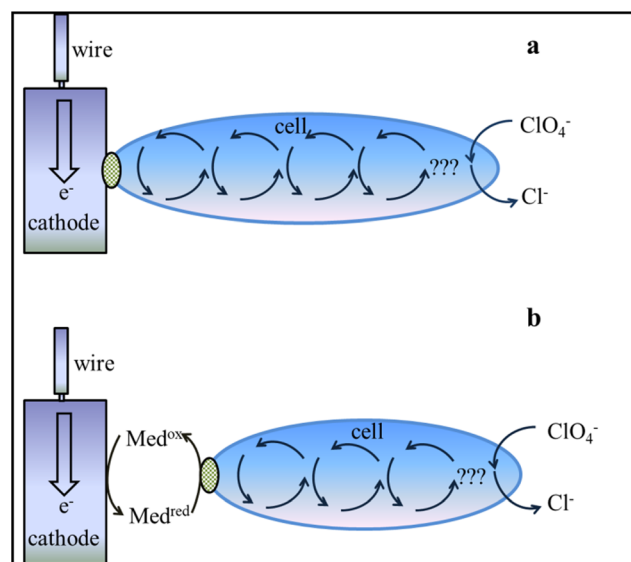
**Fig. 5** Mechanisms of electron transfer using cathode as electron donor for perchlorate bioreduction. Adapted with permission from Huang et al. (2011), Copyright 2011, Elsevier

perchlorate-reducing biocathode and PRB utilized the cathode as an electron donor with acetate oxidation in the anode compartment. However, the maximum perchlorate removal rate was only 12 mg-perchlorate $L^{-1}$ $day^{-1}$ since the soluble electron donor (acetate) in the medium was lacking. Butler et al. (2010) adopted a similar strategy to establish the perchlorate-reducing biocathode with a mixed culture. Curiously, *Dechloromonas* sp. PC1, a PRB, did not become an important member of the biocathode community after it was added. The observed maximum reduction rate of perchlorate reached to 24 mg $L^{-1}$ $day^{-1}$ without exogenous electron shuttles, but the perchlorate load increased slowly and reaching a 100% perchlorate feed needed 303 days. Mieseler et al. (2013) explored a new strategy to quickly set up stable biocathodic perchlorate reduction. They found that inoculation of cathodes with perchlorate-reducing preculture could shorten the startup time to only 21 days. The electrode properties can impact the microorganism attachment and the MFCs performance (Huang et al. 2011). Li et al. (2015) used a novel polyaniline (PANI)/

graphite biocathode for perchlorate reduction in a non-membrane microbial electrolysis cell. PANI with good electrocatalytic and porous structure properties was beneficial to film-forming and electron transfer. The perchlorate reduction rate of the biocathode is increased by more than 12% compared to the cathode without biofilm.

Except for direct electron transfer, some microbe could indirectly gain the electrons from electrode by the transportation of redox-active compounds (Fig. 5b). *Acinetobacter calcoaceticus*, a dominant bacteria in a mixed culture biocathode were found that they could utilize a self-excreted redox compound for extracellular electron transfer in microbially cathodic oxygen reduction (Freguia et al. 2008), which was similar to the function of pyrroloquinoline quinine, an electron shuttle between a soluble enzyme and an electrode (Laurinavicius et al. 2004). The reduction rate was mainly limited by the electron transfer between the bacteria and the anode in MFCs (Sun et al. 2013). Recently, artificial exogenous redox mediators, for example thionine (TH,

**Table 2** Perchlorate removal using biocathode of BES

| Electrodes material | $ClO_4^-$ removal rate (mg $L^{-1}$ $day^{-1}$) | Potential/ voltage applied | Power density | Current density | Ref. |
|---|---|---|---|---|---|
| Graphite | 17 (batch) 60 (continuous) | −450 mV | NA | NA | Thrash et al. (2007) |
| Graphite granules | 12 | NA | NA | NA[a] | Shea et al. (2008) |
| Graphite granules | 24 | NA | 0.3 mW $m^{-2}$ | 0.17 mA $m^{-2}$ | Butler et al. (2010) |
| Polyaniline modified graphite (cat.), graphite electrode (an.) | NA | −0.4 V vs. SCE | NA | NA | Li et al. (2015) |
| Pt-coated carbon cloth (cat.), carbon cloth (an.) | 600 | NA[b] | NA | NA | Lian et al. (2016) |
| Ti wire–carbon fiber brushes | 2 mg $m^{-2}$ $day^{-1}$ | NA | NA | NA. | Mieseler et al. (2013) |
| Carbon felts | NA[c] | NA | NA | 3.00 mA $m^{-3}$ | Jiang et al. (2017) |
| graphite granules | 16.07 | −0.50 V vs. SCE | NA | NA | Xie et al. (2014) |
| Granular graphite | NA | NA | 49.3 W $m^{-3}$ (MFC-1) 106.0 W $m^{-3}$ (MFC-2) | NA | Freguia et al. (2008) |
| Carbon paste electrodes modified with ferrocene derivatives | NA | 0.4 V | NA | NA | Laurinavicius et al. (2004) |

*SCE* saturated calomel electrode

[a] The average current at the reported maximum perchlorate removal was 0.28 mA

[b] The maximum voltage reported was 68 mV

[c] The maximum removal efficiency achieved 53.14% when the concentration was 0.40 mmol $L^{-1}$

$C_{14}H_{13}N_3O_2S$), potassium ferricyanide (FeCN, $K_3[Fe(CN)_6]$), methylene blue (MB, $C_{16}H_{18}ClN_3S$), neutral red (NR, $C_{15}H_{17}ClN_4$), anthraquinone-2,6-disulfonate (AQDS, $C_{14}H_6O_8S_2$), and resazurin (RZ, $C_{12}H_7NO_4$), are used to speed up the electron transfer from electron donor to acceptor (Lian et al. 2016), which may increase the reaction rates by one to several orders of magnitude (Dos Santos et al. 2005). Compared with a mediator-free MFC, MFCs added 3–9 μM resazurin exhibited 50.8–101.6% increases in perchlorate reduction rate, respectively (Lian et al. 2016). The catalyzing mechanism should attribute to the accelerated electron transfer from NADH toperchlorate reductase and the anode via NADH reductase, NADH-ubiquinone reductase, and methylnaphthoquinone led by resazurin. However, these artificial exogenous redox mediators are highly toxic compounds and lack long-term stability, which are unlikely to be approved in real bioremediation.

Application of bioelectrochemical systems (BES) in biological perchlorate reduction (Table 2) can provide virtually inexhaustible electron donor due to the possible use of anode and cathode (Pous et al. 2018), avoiding (or drastically lowering) the continuous addition of chemical agents (e.g., $H_2$, organic matter) as the electron donor or carbon source. Furthermore, the electrodes provide physical support for growth of microorganisms (Modin and Aulenta 2017).1

## Selection of electron donor

There are two basic principles can be considered when selecting an appropriate electron donor to reduce perchlorate biologically: (1) the capacity of electron donor to completely remove perchlorate while minimizing the existence of other contaminants in effluent and (2) the cost of electron donor per unit of perchlorate reduced to chloride.

The choice of electron donor is greatly influenced by thermodynamic and kinetic parameters because they influence the competition of PRB and other microbial, further affect the treatment efficiency and costs. $H_2$ (with $CO_2$) is a favored electron donor for various PRB. Meanwhile, suitable operating conditions should be controlled to minimize the competition between PRB and other microbial activities in order to make PRB be dominant. For example, sulfate reduction could be restricted through proper control over the $H_2$-based MBfR (Chen et al. 2017). And SRB decreased significantly under high acceptor loading and high $H_2$ pressure (Wan et al. 2016).

An excellent organic electron donor contributes to the growth and activity of the PRB. Compared with single organic substrate, multiple organic substrates had higher perchlorate degradation efficiency (Liamleam and Annachhatre 2007). For example, $AH_2DS$ did not significantly affect the oxidation of acetate, but the mixed medium of acetate/$AH_2DS$ brought additional electron-donating ability and markedly improved the reduction

of perchlorate (Van Trump and Coates 2009). Better reduction efficiencies of perchlorate were observed in the methanol/$S^0$-based mixotrophic reactor, simultaneously, and external carbon supplementation prevented the excessively high sulfate concentration in the effluent (Ucar et al. 2016a). Therefore, in order to obtain the optimal perchlorate reduction, it is necessary to use the mixture of multi-type electron donors.

The cost and availability of electron donor is the key factors in practical application and should also be considered. Table 3 shows the cost of some common electron donors in term of per ton of perchlorate removal. The performance of perchlorate bioreduction with acetate as the electron donor is better than molasses (Nerenberg et al. 2006; Lian et al. 2017), but the costs of acetate is higher than molasses. To start the treatment system, acetate may be necessary, and molasses can serve as the long-term electron donor (Perlmutter et al. 2001). It should be noted that complicated organic substrates such as hydrocarbons, glycerol, and molasses are difficult to be the completely utilized by microorganisms. Therefore, high-concentration COD in the effluent is inevitable, which requires subsequent process to residual organics. Meanwhile, complex organic substrates cannot be directly utilized by PRB and need extra pre-fermentation to convert into small molecules organic compounds. Therefore, complex organic electron donors should be avoided unless the above-mentioned issues can be solved well.

The inorganic electron donors ($H_2$, $S^0$, etc.) could completely reduce perchlorate and produce less metabolic sludge production. As a waste by-product of oil refining, the $S^0$ is cost-effective. But the excessive sulfate production is a potential drawback (Boles et al. 2012; Gao et al. 2015; Wan et al. 2017). Generally speaking, $H_2$ is a suitable electron donor, especially to treat high-concentration perchlorate. However, there are safety hazards in the storage and use of $H_2$, even electrolysis of $H_2$ with electrochemical and microbial coupling, or iron corrosion to produce $H_2$ can be utilized. Recently, the simplest organic matter $CH_4$ exhibits great potential to replace the $H_2$ as the electron donor and carbon source in the perchlorate bioreduction (Bender et al. 2005; Luo et al. 2015; Chen et al. 2016). Compared with $H_2$, $CH_4$ is cheaper, is a more extensive source, and has lower explosion risk.

## Conclusions and prospects

Biological reduction is considered to be a promising alternative due to its cost-effective way. In order to ensure complete removal of perchlorate, a sufficient amount of suitable electron donor is necessary. Acetate is a suitable electron donor because of its high perchlorate removal rate and low microbial residues. To some extent, organic electron donors are not an ideal choice unless further treatment is available to remove organic residues from

**Table 3** The electron donors cost per ton of perchlorate

| Electron donor | Mass ratio[a] (kg-electron donor kg-perchlorate$^{-1}$) | Price[b] (USD t-electron donor$^{-1}$) | Cost[c] (USD t-perchlorate$^{-1}$) |
|---|---|---|---|
| Acetate | 0.604 | 120–290 | 72–175 |
| Ethanol | 0.463 | 628–800 | 291–371 |
| Molasses | NA[d] | 100–218 | NA |
| Glycerol | 0.529 | 555–800 | 293–424 |
| Methane | 0.161 | 600–888 | 97–143 |
| Hydrogen with $CO_2$ | 0.080 (for $H_2$), 0.442 (for $CO_2$) | 2950–4915 (for $H_2$), 45 (for $CO_2$) | 257–416 |
| Element sulfur | 0.429 | 131–291 | 56–125 |
| Zero-valent iron | 2.252 | 438–512 | 986–1153 |

[a] The mass ratio of electron donor and perchlorate, calculated from molar mass and reaction equation

[b] The price per ton of electron donors (in USD), which is based on the Chinese price standard for industrial raw materials

[c] The electron donors cost per ton of perchlorate (in USD), which is equal to the mass ratio of the electron donor to the perchlorate multiplied by the unit price of the electron donor

[d] Mix ingredients

the effluent. Multiple organic electron donors have better performance of perchlorate reducing compared with a single organic electron donor. Relatively speaking, $H_2$ is a suitable inorganic electron donor, especially for the treatment of high-load perchlorate wastewater. When selecting the suitable electron donor, it needs to consider treatment costs, availability, reduction efficiency, and secondary pollution.

Despite its various advantages, biological treatment has its deficiency. When dealing with perchlorate-containing drinking water or groundwater, the unknown pathogens and the secondary contamination led by external electron donor should be concerned. To address the shortcoming of biodegradation, it needs to integrate one or more physicochemical and biological process. For example, integrating the ion exchange with a membrane bioreactor such as IEMB could address the problem of biomass accumulation and secondary contamination of effluent. In addition, appropriate reactors, such as FBR, should be designed to prevent the loss of organic matter, avoiding high COD residual in the effluent. And for gaseous electron donors such as $H_2$ or $CH_4$, hydrophobic microporous polyethylene fiber is suitable to increase gas utilization efficiency and improve the safe utilization of hazardous gas (Zhao et al. 2014; Luo et al. 2015). In situ electrochemical $H_2$ production or combined with anaerobic digestion to produce the $CH_4$ is also an ideal alternative, avoiding the storage of large amounts of $H_2$ or $CH_4$. Apart from these, a combination of organic and inorganic electron donors can be used to improve degradation efficiency.

Methanol is a common supplemental electron donor in wastewater treatment because of its availability and cost-effectiveness (Glombitza 2001; Weijma et al. 2003; Liamleam and Annachhatre 2007), but few studies have used it for perchlorate reduction. Therefore, methanol can also be considered as an electron donor for heterotrophic perchlorate reduction in future research. Furthermore, biological reduction has been proved to be an enzymatic reaction and the biocatalysts greatly affect the perchlorate reduction process. Some studies have shown that catalytic degradation of perchlorate is feasible (Chaturvedi and Dave 2013; Liu et al. 2013; Liu et al. 2015; Seraj et al. 2017). Ford et al. (2016) developed a bioinspired iron catalyst inspired by the active sites of (per)chlorate reductase enzymes and nitrate reductase. So it is an interesting idea that if it is possible to supplement enzymes instead of microorganisms to reduce perchlorate. Accordingly, the above recommendations must be further studied and applied in pilot-scale experiment.

## Compliance with ethical standards

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