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*Published in:*  
Bioresource Technology

*Link to article, DOI:*  
[10.1016/j.biortech.2023.128916](https://doi.org/10.1016/j.biortech.2023.128916)

*Publication date:*  
2023

*Document Version*  
Peer reviewed version

[Link back to DTU Orbit](#)

*Citation (APA):*  
Feng, H., Yang, W., Zhang, Y., Ding, Y., Chen, L., Kang, Y., Huang, H., & Chen, R. (2023). Electroactive microorganism-assisted remediation of groundwater contamination: Advances and challenges. *Bioresource Technology*, 377, Article 128916. <https://doi.org/10.1016/j.biortech.2023.128916>

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## **Electroactive microorganism-assisted remediation of groundwater contamination: Advances and challenges**

Huajun Feng<sup>a</sup>, Wanyue Yang<sup>a</sup>, Yifeng Zhang<sup>b</sup>, Yangcheng Ding<sup>a</sup>, Long Chen<sup>a</sup>, Ying Kang<sup>c</sup>, Huan Huang<sup>c</sup>, Ruya Chen<sup>a\*</sup>

<sup>a</sup>. School of Environmental Science and Engineering, Zhejiang Gongshang University, Hangzhou 310018, Zhejiang, China

<sup>b</sup>. Department of Environmental Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark

<sup>c</sup>. Zhejiang Ecological Environmental Monitoring Center, 117 Xueyuan Road, Hangzhou 310012, Zhejiang, China

\*Corresponding author:

E-mail: [chenruya2021@163.com](mailto:chenruya2021@163.com) (Ruya Chen)

Journal Pre-proofs

**Abstract:** Groundwater contamination has become increasingly prominent; therefore, the development of efficient remediation technology is crucial for improving groundwater quality. Bioremediation is cost-effective and environmentally friendly, while coexisting ion stress can affect microbial processes, and the heterogeneous character of groundwater medium can induce bioavailability limitations and electron donor/acceptor imbalances. Electroactive microorganisms (EAMs) are advantageous in contaminated groundwater because of their unique bidirectional electron transfer mechanism, which allows them to use solid electrodes as electron donors/acceptors. However, the relatively low-conductivity groundwater environment is unfavorable for electron transfer, which becomes a bottleneck problem that limits the remediation efficiency of EAMs. Therefore, this study reviews the recent advances and challenges of EAMs applied in the groundwater environment with complex coexisting ions, heterogeneity, and low conductivity and proposes corresponding future directions.

**Keywords:** Groundwater; Electroactive microorganisms; Coexisting ion stress; Heterogeneity; Low conductivity

## 1. Introduction

There is 97% of the freshwater resources in groundwater (Li et al., 2021), and approximately 2.5 billion people use groundwater as their main source of drinking water (Li & Liu, 2022). Drinking contaminated groundwater can have serious effects on human health (Karunanidhi et al., 2022), while only 13.6% of the groundwater meets the quality standards in China (Mep, 2020). A prior challenge that needs to be addressed immediately, which is achieving efficient and stable groundwater remediation.

At present, groundwater pollutants mainly consist of heavy metals, inorganic non-metallic ions, and organic pollutants that are persistent, hidden, and complex, making effective treatment difficult (Cecconet et al., 2020). Most pollutant transformations in groundwater environments are slow due to a lack of suitable electron donors or acceptors; therefore, a suitable driving force is ultimately required to drive their biotic or abiotic reductions or oxidations, respectively (Wang et al., 2020). To accelerate pollutant transformation via natural processes, two major categories of technologies can be used

individually or in tandem: physicochemical technologies, and bioremediation (Daghio et al., 2017). Bioremediation is more economical and environmentally friendly than conventional treatment processes (e.g. activated carbon adsorption, chemical oxidation etc.), which have multiple problems such as high operating costs and significant secondary pollution (Sharma, 2020). Moreover, the interference of other coexisting pollutants and the generation of toxic by-products, heterogeneous distribution of groundwater substrates affecting electron donor/acceptor availability, and the lack of contact between pollutants and microorganisms have further restricted applications of those technologies (Azubuiké et al., 2016). Therefore, alternative technologies with low cost, low chemical consumption, and high controllability should be developed.

Electroactive microorganisms (EAMs), a group of microorganisms that can interact directly with electrodes via extracellular electron transfer (EET), are widespread in groundwater. Based on EAMs, the bioelectrochemical system (BES) combines the selectivity, sustainability, and environmental friendliness of microbial metabolism with the excellent controllability of electrochemistry, making it safer and more efficient to use immobilized microorganism and supply electron donors/acceptors (Feng et al., 2022a; Li & Yu, 2015). EAMs have been applied successfully for contaminated groundwater remediation (Ceconet et al., 2018), however, their applicability is limited by factors such as low conductivity. Most existing reviews focus on the removal of single contaminants by EAMs and a summary of BES configurations that exert the EET capacity of EAMs (Li & Yu, 2015; Pous et al., 2018).

Therefore, this review summarizes the limitations of microbial remediation in groundwater with coexisting ions and heterogeneous environmental conditions, as well as the superiority of EAMs, discusses the challenges of EAMs applied to groundwater with low conductivity, and an outlook on future research directions is provided.

## **2. Remediation performance of EAMs under coexisting ion stress**

Although focusing on a single contaminant can help study the removal mechanism of each contaminant, it is inconsistent with the current situation of multiple contaminants coexisting in actual groundwater. Interactions between different contaminants can occur, including conflicting redox conditions and triggering of cell damage. Recent studies on coexisting groundwater contamination have focused on both heavy metal ions and oxygenated anion stress. Table 1 summarizes the current research findings related to the effects of coexisting ion stress on groundwater contamination bioremediation. It is demonstrated that coexisting ion stress has complex effects, and even contradictory inhibitory or promotive effects can occur in different environmental systems.

## 2.1. Inhibition of pollutant degradation

Inhibition of groundwater microbial remediation by coexisting ions is a common biotoxicological phenomenon in a compound contaminated environment. It typically occurs via two pathways, as shown in Fig.1. One is that because there aren't enough electron donors in the groundwater environment, contaminants are forced to compete with one another for electron donors, which leads to inhibition (Xie et al., 2014). The other is that the toxicity of coexisting ions can cause damage to microorganisms associated with contaminant degradation, leading to decreased cellular activity (Qian et al., 2022).

### 2.1.1 Electron donor competition

Several studies have shown that most of the coexisting ion inhibition formed by competition for electron occurs in the presence of  $\text{NO}_3^-$  (Sun et al., 2022). The basic premise for this inhibition is the lack of electron donors in the groundwater environment. For example, when the system contained sufficient acetate as an electron donor and bioremediation was used to remove chlorine-containing contaminants from groundwater, *Geobacter lovleyi* sp. nov. strain SZ and the *Dehalococcoides mccartyi*-strain FL2 showed a low hydrogen threshold, and dechlorination was uninhibited by  $\text{NO}_3^-$  (He et al., 2005; Sung et al., 2006). However, when electron donors are lacking, the sulfate presence negatively affects rate of reductive dichlorination (Lai et al., 2015).-Cao et al. further demonstrated that the bioreduction processes of chlorophenols and nitrates were mutually inhibited, which was mitigated by adding a high concentration of a carbon source (glucose) (Cao et al., 2017). Similarly, Xie et al. found that perchlorate reduction was completely inhibited in the presence of 2.1 mM  $\text{NO}_3^-$  and significant perchlorate reduction can only be observed when the nitrate is completely removed (Xie et al., 2014) because the redox potential of denitrification is more conducive for the reaction to occur (Löffler et al., 1999). In general, coexisting ion competition for electron donors followed a thermodynamically determined order, with the higher redox potential being more easily reduced (Löffler et al., 1999). However, Wang et al. found that when perchlorate coexists with nitrate, the rate of perchlorate reduction to chloride (redox potential of 0.87 at neutral pH) is lower than nitrate reduction to nitrogen (redox potential of 0.75 at neutral pH) (Wang et al., 2021a). Lv et al. further found that the priority of  $\text{NO}_3^-$  in competition with  $\text{ClO}_4^-$  may be caused by the lower energy needed by narG and pcrA for proton and electron transfers in nitrate reduction, compared to perchlorate reduction (Lv et al., 2020). Therefore, enzyme specificity plays a major role in the competition for electron donors.

In actual groundwater bioremediation projects, it is necessary to inject high-concentration electron donors to alleviate the competition process between the

coexisting ions (Weatherill et al., 2019). However, it will increase the risk of secondary groundwater contamination, and side reactions such as methanogenic and acidic fermentation can occur, reducing the efficiency of electron utilization, thus increasing remediation costs and causing other problems. EAMs can use more effective electrons (e.g., solid electrodes) as electron donors to selectively enhance the microbial reduction process in groundwater environments (Lin et al., 2021), such as reductive dechlorination and denitrification (Tang et al., 2022). Some studies also found the weak electrical stimulation can alter the micro-ecological niches or functions of EAMs via changing the eco-environmental factors (e.g., ORPs, ion migration rate) to enhance bioactivity, accelerate biological reduction of stress factors (e.g.  $\text{NO}_3^-$ ) and shorten the inhibition time, thus slowing down the inhibition effect (Chen et al., 2022a; Tang et al., 2023). For example, Zhang et al. found that TCE was completely removed within 32 h under high concentration of nitrate (100 mg/L), and the dechlorination activity was well maintained. (Zhang et al., 2022) In addition, compared to dosing soluble chemicals as electron donors, solid-state electron donor is more economical and environmentally friendly (Lin et al., 2022). For example, Zhu et al. found that using ore as an additional electron donor increased nitrate removal efficiency (Zhu et al., 2019). The applied current or potential can be changed to continually monitor and regulate electron supply. This approach could potentially minimize competing reactions (Aulenta et al., 2011), and Nguyen et al. further found that higher hydrogen production at a cathode potential of -700 mV in the presence of sulfate might be one of the reasons why inhibition of the nitrate reduction rate by sulfate ions could be overcome ultimately (Nguyen et al., 2016a). Similarly, hydraulic retention time (HRT) also affects the stress effect between coexisting ions. Dell'Armi et al. found that the side reactions represented by  $\text{SO}_4^{2-}$  and nitrate reduction were significantly controlled, and the reduction dechlorination coulomb efficiency of perchloroethylene reached the maximum when the HRT was 1.8 d (Dell'Armi et al., 2021). Most of the methods to mitigate inhibition discussed above are based on stimulating EAMs to accelerate the efficient removal of one kind of pollutant through via changes in external conditions, thus shortening the inhibition time. And certain EAM strains can simultaneously remove coexisting ions without inhibition. For example, An et al. found that *Stenotrophomonas maltophilia* W26 could simultaneously remove  $\text{NO}_3^-$  and Cr(VI) under aerobic conditions, and as the  $\text{NO}_3^-$  concentration increased from 100 mg/L to 700 mg/L, the ability of the cells to remove Cr(VI) gradually increased, with the final removal rate increasing by 80.8% (An et al., 2021). From the perspective of the reduction mechanism,  $\text{NO}_3^-$  and Cr(VI) reduction occurs in the periplasm with a quinone or cytochrome c as electron donors, and in the cytoplasm using NAD(P)H as an electron donor, respectively (Yu et al., 2016). Different electron donors reduce the electron competition between the two reduction pathways (Thatoi et al., 2014). This may be one reason for the disinhibition of the EAMs. In addition, a recent study—used  $\text{S}_0$  as an electron donor to couple BES with a sulfur autotrophic denitrification system, effectively

reducing the competitive effect of  $\text{NO}_3^-$  on reductive dechlorination (Chen et al., 2022b; Chen et al., 2022c), opening up an attractive avenue for effective groundwater remediation based on nitrate contamination. However, when the sulfur autotrophic denitrification system is applied to the removal of  $\text{NO}_3^-$  from groundwater, the concentration of Fe(II) needs to be controlled. It is because some studies have shown that when the Fe(II) concentration is too high, it decreases the functional gene abundance, and when oxygen is present, Fe(II) can be converted to ferric hydroxide, causing a decrease in pH and inhibiting bacterial activity (Pang & Wang, 2021). In summary, many of the current methods for lifting the inhibition of coexisting ions are mostly for the coexistence of a few pollutants, but in actual groundwater, there are always multiple ions coexisting, and more in-depth studies are needed.

### 2.1.2 Pollutant toxicity

The sources of toxic pollutants are diverse and ubiquitous in groundwater environment. Unlike organic pollutants, heavy metals are not converted to simpler forms by chemical or biological methods. They can only be transformed into less toxic substances, such as Hg(II) to  $\text{Hg}^0$ , As(III) to As(V), and Cr(VI) to Cr(III) (Priyadarshane & Das, 2021). At the macroscopic level, when ions coexist, the presence of heavy metal ions reduces the diversity of microorganisms, selectively enriching one type of microorganism and thus reducing the degradation of another pollutant (Pang & Wang, 2023). Microbial activity is highly dependent on the concentration of the pollutant according to Schulz's law, which states low concentration stimulation, medium concentration inhibition, high concentration killing (Rosner et al., 2021). Most studies have shown that the biodegradation rate of coexisting contaminants decreases with increasing metal concentrations (Oriomah et al., 2015). Studies such as those by Oriomah et al. are representative, which showed that *Achromobacter xylosoxidans* was tolerant to both Cu(II) and used motor oil. However, the degradation capacity of *A. xylosoxidans* for used engine oil decreased from 40% to 5% as the mass concentration of Cu(II) increased to 200 mg/L (Oriomah et al., 2015). The inhibition mechanism is manifested in the damage or inhibition of cell viability. In a contaminated environment where heavy metals exist, microorganisms can rely on substances such as metabolic enzymes and organic acids to reduce complex heavy metals intracellularly and extracellularly (Feng et al., 2022b). These actions occupy the normal metabolic pathways of cells and disturb the original contaminant metabolic pathways (Biswas et al., 2015; Wan et al., 2021). As found by Wan et al. Tetrabromobisphenol A (TBBPA) may regulate the metabolic flux of glucose by inhibiting the Embden-Meyerhof-Parnas (EMP) and pentose phosphate (PP) pathways and stimulating the glyoxylate bypass to decrease the generation of NADH in *P. denitrificans*. This finally led to the inhibitory effect of TBBPA on denitrification (Wan et al., 2019). Thus, the complexity of the inhibitory effects of heavy metals on co-occurring contaminants is reflected in their



effects on cellular metabolism, which—inhibits the bioavailability of the remaining contaminants in turn. In addition to their own toxicological effects, heavy metals can affect the metabolic pathways of contaminants by inhibiting their degrading enzymatic systems (Ballard & Towarnicki, 2020). Liu et al. found that catechol 2,3-dioxygenase of *Bacillus malacitensis* was induced in the presence of Pb(II) at 100–300 mg/L, which stimulated the production of oxygen radicals, resulting in a change in the spatial conformation of the enzyme protein and masking of the catalytically active site (Liu et al., 2015).

Unlike non-electroactive microorganisms, EAMs have more complex metabolic pathways, which may be inhibited in various ways, including inhibition of biofilm development and cytochrome c secretion in the outer membranes (Amanze et al., 2022; Li et al., 2020). However, EAMs have a superior ability to tolerate and absorb heavy metals compared to other microorganisms. Taking *S. oneidensis* as an example, on the one hand, the intracellular heavy metals (e.g., Cr(VI)) can be re-excluded outwards by the efflux system to reduce toxicity (Gang et al., 2019). On the other hand, it increases the strength of the cell membrane to prevent heavy metals (e.g., U(VI)) from entering the cell and up-regulates the genes (e.g., *pspBC*) encoding proteins associated with membrane stress (Bencheikh-Latmani et al., 2005). In addition, EAMs can recover performance after the removal of high concentrations of heavy metal ions and produce tolerant strains, providing new insights into the treatment of heavy metal-containing organic wastewater (Saran et al., 2022; Zhang et al., 2018). Therefore, to mitigate the inhibitory effect of heavy metals on coexisting ions, it is necessary to ensure that the microorganisms are tolerant to heavy metals due to the cell viability directly affecting the rate of contaminant removal. In the case of the coexistence of heavy metals and organic matter, the reduction performance of EAMs to coexisting ions can be improved by exposing detoxifying EAMs to moderate concentrations of heavy metals under suitable operating conditions (Chaudhary et al., 2022). For example, Lai et al. found that the inhibition of reductive dechlorination by Cr(VI) was significantly weaker after the domestication of microorganisms than that of undomesticated microorganisms. The hypothesis that microorganisms can effectively adapt to coexisting contamination scenarios was confirmed by long-term continuous flow tests (Lai et al., 2021).

In addition, EAMs can transfer electrons to the extracellular space through their unique EET pathway. At the same time, toxic pollutants with strong electrophilicity can be used as the final electron acceptors in the process of extracellular respiration due to their good ability to accept electrons (Zheng et al., 2020). It can be achieved by the addition of mediators that can accelerate the EET, thereby significantly weakening the toxic effect on microorganisms and enhancing the bioremediation process. For example, Qian et al. found iron sulfide nanoparticles (FeS NPs) could act as effective electron shuttle to drive the electron to flow towards the extracellular Cr(VI) reduction,

which significantly accelerates electron transfer and greatly weakens the inhibition effect on  $\text{SO}_4^{2-}$  (Qian et al., 2022). What is more, it might construct another alternative electron pumping shortcut besides the conventional EET pathway via the respiration chain, to relieve the limitation of steric hindrance on the diffusion of macromolecular electron receptors, and has a great detoxification effect on microorganisms.

Similarly, anthraquinone-2, 6-disulfate (AQDS), as a common analogue of humus substances, has been shown to effectively mediate the extracellular bioreduction of a range of heavy metals (Orsetti et al., 2013). Wang et al. increased the bioaccumulation rate of Cu(II) and Se(VI) by 14.7 times by adding AQDS. Compared with control without AQDS, microbial activity was higher and intracellular ROS level was lower (Wang et al., 2022). In addition to extracellular reduction, AQDS also raises the redox potential of the heme center of OmcA in MR-1 and accelerates electron efflux.

## 2.2. Promotion of pollutant degradation

The promoting effect of coexisting ions in the groundwater environment is illustrated in Fig.2. Recent studies have found that the presence of certain concentrations of pollutants may also facilitate the removal of co-existing ions. According to current research, the reasons for this facilitation can be divided into two main categories: 1) coexisting contaminants themselves act as electron donor/acceptor pairs with each other, and 2) altering the relevant cellular structures and facilitating electron transfer.

### 2.2.1. Reciprocal electron donor/acceptor pairs

Reciprocal electron donor/acceptor pairs generally occur between oxygenated anions and reduced pollutants. Pollutants subjected to oxidative biodegradation can often be stimulated to promote pollutant co-removal by providing other limiting electron acceptors (e.g, nitrate, sulfate) to the naturally occurring microbial community. Nguyen et al. verified that electrons generated in the anodic anaerobic oxidation of As(III) are effectively recycled for cathodic denitrification (Nguyen et al., 2016b). Ceballos et al. treated synthetic groundwater with a BES and found that *Achromobacter agilis* could simultaneously achieve 519  $\text{g}/(\text{m}^3 \cdot \text{d})$   $\text{N-NO}_3^-$  ( $\text{NO}_3^- \rightarrow \text{N}_2$ ) and 90  $\text{g}/(\text{m}^3 \cdot \text{d})$  As(III) conversion ( $\text{As(III)} \rightarrow \text{As(V)}$ ) (Ceballos-Escalera et al., 2021). The reason for this may be that in the presence of nitrate, it acts as a dissolved electron acceptor to promote the oxidation of arsenite, which can provide more catabolic energy for microbial growth and activity compared to solid electron acceptors (electrodes).

Similarly, when sulfate is present, sulfate-reducing bacteria (SRB) can act as biocatalysts for EET. When heavy metals and  $\text{SO}_4^{2-}$  coexist, sulfuric acid can be reduced to sulfide using sulfate as the terminal electron acceptor. The remaining sulfide becomes hydrogen sulfide or combines with heavy metal ions to form a precipitate (Muyzer &

Stams, 2008). For example, Arulmani et al. used SRB strains BY7 and SR10 to achieve sulfate reduction rates of  $93.2 \pm 2.6$  and  $998.4 \pm 1.6$  g/(m<sup>3</sup>·d) and Sb removal efficiencies of 88.2% and 96.3%, respectively, and the total removal rate of Sb ~~removal rate~~ depended on the sulfide concentration produced by the sulfate reduction reaction (Arulmani et al., 2021). In addition, electron donors/acceptors can be generated indirectly through redox reactions, resulting in electron donor/acceptor pairs that promote the degradation of coexisting pollutants. For example, when petroleum hydrocarbons (PH) and chlorinated aliphatic hydrocarbons (CAHs) coexist, a BES can anodize the microbe-driven pH to produce H<sub>2</sub>, which in turn acts as an electron donor to maintain the reductive dechlorination of CAHs at the cathode, facilitating the co-degradation of pollutants (Cruz Viggì et al., 2022).

### 2.2.2. Facilitate electron transfer

Heavy metals promote the degradation of coexisting ions. Individual heavy metals in the appropriate concentration range have a low cytotoxic effect on cells and may also positively contribute to pollutant degradation by EAMs through mechanisms such as modulation of cell membrane adsorption or secretion of antioxidant enzymes (Hu et al., 2022; Yang et al., 2022b). Cu(II) is an important component of antioxidant enzymes such as catalase and superoxide dismutase and is also an integral part of the electron transport process in the cellular oxidative respiration system; thus, the presence of Cu(II) enhances cellular tolerance to coexisting pollutants and electron transfer efficiency, thus improving the reduction of coexisting ions (Xu et al., 2015). In addition, it was demonstrated that the presence of Cu(II) accelerated the EET of *Shewanella oneidensis* MR-1 (MR-1) by promoting the production of electron shuttle mediators (riboflavin) (Xu et al., 2016). Similarly, the Cr(VI) reduction efficiency of MR-1 was remarkably enhanced by 83.7% under 20 mg/L Cu NPs exposure. Cu NPs improved the electron migration capacity of MR-1 by enhancing flavin mononucleotide secretion (Chen et al., 2022d). In addition, Cu(II) itself can act directly as an electron shuttle to promote EET, resulting in 1.49 times greater removal of Cr(VI) compared to the absence of Cu(II). Further analysis showed that the presence of Cu(II) reduced the overpotential and diffusion resistance of the system (Li & Zhou, 2019b). Similarly, Fe(III) as an electron shuttle mediator via an indirect electron mediation by the Fe(III)/Fe(II) couple enhance the reduction of Cr(VI) (Wang et al., 2017). Ca(II) had some positive effects (Fitzgerald et al., 2012). For example, Volland found that exogenous Ca(II) can improve cell tolerance by reducing the toxicity of heavy metals like Cd(II), Cr(VI), and Pb(II) to cells (Volland et al., 2014).

In addition to trace heavy metals that can promote EET rates, organic contaminants with dielectric constant ( $\epsilon$ ) values below 2.61 in contaminated groundwater (benzene, toluene, carbon tetrachloride and tetrachloroethylene) also promoted EET (Liu et al.,

2021). For example, Liu et al. verified that aromatic benzenes promote EET by inducing increased cell membrane permeability and increasing the secretion and release of flavin mononucleotides as electron shuttling or cofactors (Liu et al., 2019), which promoted the reduction of Fe(III) by MR-1 but had no effect on the number of cells or the morphology of MR-1. In contrast to the principle of anaerobic degradation of benzene by *Geobacter* with Fe(III) oxide as the sole electron acceptor (Zhang et al., 2012), there was no decrease in benzene concentration in this study. Liu et al. subsequently verified that  $\epsilon$  with a negative correlation trend with reduction intensity. Lower  $\epsilon$  values resulted in stronger deprotonation of phosphorus-related groups on the cell surface and induced a more negative surface charge on MR-1. The lower membrane zeta potential enhanced the membrane permeability and stimulated more electron shuttle release and faster Fe(III) reduction (Liu et al., 2021). In contrast, EAM-mediated Fe(III) reduction is prevalent in groundwater environments and can also affect the transport and transformation of other environmental contaminants, as Fe(III) is an important electron acceptor in aquifers. Microbial secretion can assist in reducing various extracellular electron acceptors with significant implications for future research.

A common problem with the above studies is that coexisting ions show consistent facilitation in the appropriate concentration range, and general EAM is inhibited with high concentrations of coexisting ions. However, there are also cases where high concentrations of coexisting ions can promote cell activity and indirectly promote the degradation of coexisting pollutants, which will vary depending on the EAMs (Ceballos-Escalera et al., 2021). In conclusion, research on the application of EAMs in composite pollution is still in its initial stages, and the response mechanisms of EAMs in the presence of different coexisting ions remain unknown. As a result of the different resistance mechanisms of EAMs in response to complex pollution toxicity, groundwater remediation is complicated, and the preferred strategy for the future development of EAMs technology is to exploit and enhance the positive effects of weakening and counteracting their stress.

In real groundwater, the goal was not only to remove the targeted pollutants, but also to decrease the overall toxicity caused by the targeted chemicals and the potential intermediates (Liu et al., 2023). Thus, this is also a form of interaction of coexisting ions. The bidirectional electron transfer properties of EAMs allow organics to use electrodes as electron donors and acceptors for reductive oxidative degradation, resulting in sequential reductive oxidation (Yang et al., 2022a). Zhuang et al. reported that, in the presence of magnetite, electrons from the metabolic oxidation of benzoate by anthozoic bacteria were transferred via electrical conduction to *Desulfovibrio sp.* for the reduction of sulfate, and magnetite-stimulated direct interspecies electron transfer (DIET) in *Geobacter sulfurreducens* (which oxidizes acetate but cannot use sulfate) and *Desulfovibrio sp.* (which reduces sulfate but cannot use acetate) (Zhuang et al., 2019). In

addition to bidirectional electron-transferring EAMs, there is also a biofilm with bidirectional electron transfer obtained by polarity reversal, which is generally first enriched with electrogenic microorganisms under anodic conditions to form a bioanode, and then domesticated by periodically switching electrode potentials and changing culture substrates (Pous et al., 2016). In contrast, secretions produced by EAMs can promote the enrichment of other microorganisms on the electrode, such as the *pilA* protein produced by *G. sulfurreducens*, which promotes the attachment of EAMs to the electrode (Richter et al., 2012). In addition, *Geobacter* maintains intracellular redox homeostasis by releasing and binding riboflavin, which also accelerates the growth of EAMs (Okamoto et al., 2014). Thus, the DIET process of EAMs can be facilitated and the electrochemical performance of the biocathode can be improved by an order of magnitude. Furthermore, excess electrons can be stored in the redox proteins of EAMs (e.g. polyhemoglobin C-type cytochromes) under electron acceptor-limited conditions and release these electrons as transient currents in addition to steady-state currents upon repolarization (Wang et al., 2021b).

In addition to the interactions between coexisting ions summarized above, the influence of the degradation intermediates from one target compound (e.g., nitrate from NP or phenol from CP) on the degradation of another target, are worth further consideration.

### **3. The role of EAMs in heterogeneous groundwater media**

#### **3.1. Adverse effects of heterogeneity groundwater media on microbial remediation**

Groundwater consists of sand and gravel, often overlying or embedded in fine-grained sediments rich in clay and organic matter, thus forming a multi-scale, heterogeneous network of aquifers (Engel et al., 2021). The heterogeneity of groundwater makes contact between microbes and contaminants difficult, which creates various local electron donor/acceptor zones that give rise to chemical heterogeneity (e.g. downward gradient chemical concentration differences between solution and solid phase, soluble and insoluble nutrients), limited by the scarcity of bioavailability of metabolic electron donors/acceptors and nutrients (Murphy et al., 1997).

The pore-scale diffusion limitation is of little concern in bioremediation. In groundwater, where microorganisms are primarily attached to soil particles or are located in the sediment (Griebler & Lueders, 2009), and diffusion becomes the dominant mode of substrate transport to cells at the pore scale. The heterogeneity of groundwater affects the diffusive transport of electron acceptors/donors to cells (Hesse et al., 2010); microorganisms consume substrates faster than they can be supplied, and the availability of biodegradation is limited. As diffusion to the cell occurs at the micron scale, this can lead to steep diffusion gradients at the solution-cell interface, thereby reducing cell

surface concentrations and reaction rates (Meckenstock et al., 2015). Alternatively, multiple hydrophobic organic compounds are typically bound to soil particles in the core of the contamination plume or even present as separate phases in the subsurface (light or dense non-aqueous phase liquids), which means that the removal rates are mainly controlled by slow dissolution kinetics, and it is difficult for microorganisms to contact them. This bioavailability limitation can be overcome by injecting electron donors/acceptors, microorganisms, or solubility enhancers into the plume; however, the injection of excessive amounts of material can create an accumulation of unwanted side reactions. Therefore, additional costs and environmental concerns have prevented its widespread use.

Another major limitation is the low availability of electron donors and acceptors in the contaminant plume. Groundwater is often located in the soil pore spaces and rock fractures in an inadequately mixed state (Lai et al., 2015). In aquifers contaminated with hydrocarbons (as electron donors), dissolved electron acceptors (e.g. oxygen, nitrate, and sulfate) in the core of the contaminant plume are limited, thus limiting contaminant oxidation. Insufficient mixing within the aquifer allows electron acceptors to be replenished only at the physical boundaries of the contaminated plume (Li & Yu, 2015). This spatial limitation of biodegradation has a significant impact on groundwater remediation efficacy. Similarly, for certain electron-accepting contaminants such as dechlorinated organisms, the low bioavailability of electron donors becomes a major limiting factor, resulting in a low per-bacterial electron transfer efficiency and slow dechlorination and detoxification rates (Shen et al., 2015).

Therefore, there are two reasons why contaminants can form a continuous plume in natural groundwater matrices that are challenging to microbially remediate: 1) the combination of microorganisms, contaminants, and soil particles/sediments makes it difficult for contaminants to come into contact with microbes, resulting in bioavailability limitations, and 2) the spatial heterogeneity of groundwater results in inadequate electron donor/acceptor mixing, making it difficult to transfer electrons and meet optimal biological degradation conditions.

### **3.2. Advantages of EAMs in addressing spatial heterogeneity**

Recent studies have found that EAMs polarization electrodes can be inserted directly through the contaminated substrate in the contaminant plume center to provide electron donors (reducing nitrates, heavy metals, and chlorinated hydrocarbons) or as electron sinks (aromatic hydrocarbons and dissolved heavy metals) (Thapa et al., 2022), allowing direct contact between the contaminant and the microorganism and reducing bioavailability limitations (Paquete et al., 2022). For example, certain dechlorinating respiratory bacteria can use solid-state electrodes as electron donors for reductive

dechlorination respiration with representative microorganism such as *Geobacter* (Strycharz et al., 2008), *Anaeromyxobacter dehalogenans* (Strycharz et al., 2010), and *Dehalococcoides* (Jiang et al., 2022). This phenomenon provides new options for removing electron-accepting contaminants (nitrobenzene, and azo compounds.) from groundwater. Zhang et al. found that *Geobacter* could oxidize benzene, toluene, and naphthalene to CO<sub>2</sub> using graphite electrodes as electron acceptors (Zhang et al., 2010), which confirmed that EAMs became more competitive in the field of contaminated groundwater remediation.

In contrast, inadequate electron donor/acceptor mixing can also be used to establish electron transfer channels between spatially distant electron donor/acceptor pairs using techniques related to EAMs. First, the biological conditions for pollutant degradation are achieved macroscopically and directly by setting the distance between the cathode and anode; however, the increase in electrode distance can also affect the pollutant degradation performance. Recently, the microbial electrochemical snorkel (MES) has emerged as a new type of BES that consists of the direct coupling of a microbial anode to a cathode with a simple structure and a single wire rod spanning two regions with different chemical compositions, which is of great research value (Hoareau et al., 2019). MES provides a preferential pathway for electrons to move from the highly reduced region to the oxidized region, creating a flow of electrons at centimeter-scale distances (Fig.3A). Currently, MES is primarily applied for the degradation of pollutants half-buried in anoxic sediments and half-exposed in oxygenated overlying water, based on the principle that an electrode segment buried within the sediment acts as an anode, accepting electrons from pollutant oxidation. The electrons flow through the vent pipe to the section exposed to the aerobic environment (cathode), reducing oxygen to form water (Aulenta et al., 2021). And EAMs can respire and grow using MES as an alternate electron transfer pathway for oxygen reduction, allowing MES to mitigate methane release in subsurface environment in addition to stimulating organic substrate removal. The higher potential of MES causes EAMs (*Shewanella decolorationis* S12) to have electrochemical activities (Yang et al., 2013).

Similarly, EAMs capable of generating and regulating currents over centimeter-scale distances (7  $\mu\text{s}/\text{cm}$ ), known as cable bacteria, exist in marine sediments (Malvankar et al., 2015; Pfeffer et al., 2012). It allows the direct electrical coupling of microbial processes between electron donors and acceptors across a diffusion gradient via long-distance electron transport (LDET) and creates unique ecological niches in contaminated isolated aquifers (Fig.3B). Recent studies have found that cable bacteria are also present in hydrocarbon-contaminated aquifers, where they provide a means for the direct recycling of sulfate by electron transfer over 1–2 cm distance (Müller et al., 2016). Recycling of sulfate by LDET at the plume fringes might overcome the spatial separation of electron donors and acceptors to a certain extent (Pilloni et al., 2011). Most

reported bacteria capable of LDET so far have been Gram-negative. Recently, Yang et al. showed that a Gram-positive bacterium, *Lysinibacillus varians* GY32, is also capable of LDET, which can form centimetre-range conductive cellular networks (Yang et al., 2021). Theoretically, cable bacteria can function as long as the spatial variation of the redox gradient does not exceed the filament length. However, LDET via cable bacteria is mainly enriched at the 1–2 cm scale at the sediment-water interface, which can limit its application in practice. Thus, designing an LDET with an extended effective range is an important goal. Inspired by MES, the LDET can be mediated by conductive particles (Fig.3C). For example, it was found that the addition of pyrite increased the conductivity of deposits >1 cm by  $7 \pm 0.15 \mu\text{s}/\text{cm}$  to  $70 \mu\text{s}/\text{cm}$  (Malvankar et al., 2015). This high conductivity makes centimeter-scale LDETs possible. In addition, engineering processes can create LDETs by artificially injecting conductive materials into the soil or sediment (Yuan et al., 2021). For example, Cai et al. added highly conductive biochar to ameliorate the soil degradation of PCP, extending the 4 cm electron transfer in the absence of biochar to 20 cm (Cai et al., 2020). This type of LDET can achieve intrinsic contaminant removal by scattering conductive materials into a BES. In addition, one study showed that using a hybrid LDET process of MES with cable bacteria for hydrocarbon degradation further enhanced alkane degradation by 46% (Marzocchi et al., 2020). This may be because MES ensures the population activity of the cable bacteria in terms of lifetime and impact volume.

Another way to expand the radius of influence of the electrode through the flow of the electron transfer mediator, indirect electron transfer (MET), can also be involved in LDET as a complementary modality (Fig.3D). MET has a smaller size and higher diffusion of redox mediator molecules compared to the whole cell, enhancing their ability to interact with the solid electron receptor available surface area for interfacial capacity, thus greatly improving EET efficiency. In the absence of an electron transfer mediator, electron transfer occurs only across distances of less than a few nanometres (Kumar et al., 2017). For example, *S. oneidensis* has the ability to exploit extracellularly formed metallic FeS for long-distance EET (Kondo et al., 2015). Most EAMs can synthesize their redox mediators and secrete them extracellularly to mediate electron transfer; for example, *Shewanella* can synthesize flavin-like molecules (Von Canstein et al., 2008) and *Pseudomonas* can synthesize phenazines (Guan et al., 2019). In addition, non-bacterial synthetic artificial redox mediators have been studied to enhance the electron transfer rate of EAMs in microbial fuel cells, commonly quinones (Chen et al., 2015), metal ions (Li & Zhou, 2019a) and nanomaterials (Vishwanathan et al., 2016). Another natural substance (humic acid) was used as an electron shuttle. To solve the electron donor/acceptor imbalance via MET, dissolved humic substances are generally considered to have good solubility and diffusivity, which facilitate their participation in EET processes. However, most humic substances present in soils and sediments are in a granular rather than a dissolved state (Cervantes et al., 2001). Studies on the ability of



microorganisms to reduce solid humic substances and their ability to mediate EET are relatively scarce.

Therefore, bioavailability limitations and electron donor/acceptor imbalances due to spatial heterogeneity are common bottlenecks in the application of bioremediation for groundwater treatment, which can be effectively addressed by the unique EET of EAMs. Direct insertion into the contaminant matrix can reduce the bioavailability limitations. The electron donor/acceptor imbalance is addressed by directly coupling the anode and cathode between the oxidation and reduction zones to form an electron flow at the macroscopic level, and by extending the electrode influence distance through the LDET and MET of EAMs to achieve electron transfer. However, several key issues must be addressed before LDET can be applied to solve actual environmental problems. For example, the LDET mechanism is not yet fully understood, and there has been no research to prove whether cable bacteria to degrade pollutants. In addition, whether LDET can be scaled up to larger scales (i. e, decimeters or even meters) for in situ bioremediation by combining cable bacteria with conductive materials or MES should be further explored.

#### **4. Challenges of EAMs for low conductivity groundwater**

To reduce the influence of conductivity on the experiment, most current studies on EAMs for groundwater remediation with ionic strengths higher than 2500  $\mu\text{S}/\text{cm}$  (Wang et al., 2021a). However, the actual conductivity of groundwater is frequently  $<1000$   $\mu\text{S}/\text{cm}$  (Puig et al., 2012). The low conductivity of the solutions can lead to lower electron transfer efficiency and higher internal resistance, which in turn affects the overall degradation effect. For example, Puig et al. found that when the ionic strength of the solution decreased from 4078  $\mu\text{S}/\text{cm}$  to 1021  $\mu\text{S}/\text{cm}$ , the overpotential associated with ion transmission increased by 80%, the power density decreased from 400 to 100  $\text{mW}/\text{m}^2$  and the nitrate removal rate decreased from 0.105 to 0.076  $\text{mM-N}/\text{h}$  (Puig et al., 2012). It indicates that the conductivity of the solution significantly affected the power production and pollution removal efficiency of the system. This irreversible energy loss in the system under low conductivity conditions consists of the following: 1) increased resistance related to ion transfer between electrodes; 2) increased resistance of the bilayer diffusion boundary layer; 3) reduced proton transport efficiency in the biofilm; 4) membrane resistance due to the pH gradient between compartments (Puig et al., 2012).

A typical solution is to add electrolytes such as NaCl (Pous et al., 2015),—and  $\text{NaHCO}_3$  (Tong & He, 2013) to the groundwater environment. An increase in substrate salinity enhances ion transport and correspondingly improves the electron transfer power performance of EAMs. Recent studies have shown that the addition of NaCl to the anode electrolyte reduces the charge transfer resistance, which facilitates direct electron

transfer from the EAMs to the electrode (Kumar et al., 2020). However, there are still some theoretical and practical issues to be addressed. 1) The addition of liquid electrolytes to groundwater will be ineffective because of groundwater dilution, and higher electrolyte concentrations can increase remediation costs and create secondary pollution. 2) High salinity caused by polyelectrolytes may affect the activity of EAMs. 3) Some electrolytes, such as  $\text{SO}_4^{2-}$ , can compete with the anode for electrons resulting in electron loss (Zhao et al., 2022).

To ensure the effectiveness of EAMs in remediating groundwater contaminants, the overpotential of ion transport can also be mitigated by regulating the cathodic potential. For example, Guo et al. adjusted the cathodic potential to -200 mV vs. SHE, the reduction rates of nitrate and perchlorate increased by 53.74% and 38.04%, respectively (Guo et al., 2021). Thus, modulation of the cathodic potential can mitigate the overpotential associated with ion transport and improve the overall performance of EAMs in groundwater remediation. However, the structure and gene expression of the active biofilm community of EAMs may be significantly affected by different voltages, thus affecting the final product distribution (Van Doan et al., 2013). A potential that is too high or too low will lead to the generation of by-products that affect the final removal and have the disadvantage of high energy consumption.

One possible alternative is to reduce the internal resistance by changing the reactor configuration associated with EAMs; for example, single chamber reactors reduce the cathode and anode spacing by removing the ion exchange membrane, reducing the internal resistance of the device, and facilitating the mass transfer, which can further increase the electron transfer rate. Alternatively, the internal resistance can be reduced by modifying the electrode materials (Mier et al., 2021). For example, Sonawane et al. modified stainless steel electrodes by conductive polymer polyaniline and polypyrrole, which provided a large specific surface area for the growth of EAMs and provided a relatively large surface area for the reaction and interfacial electron transfer. Large electrochemically active surface area minimizes energy loss (Sonawane et al., 2018).

In addition, certain less-explored alternatives have been considered, direct application to pristine low-conductivity aqueous substrates using microfluidic reactors with very small inter-electrode distances or solid polymer electrolyte cells. For example, Rossi et al. constructed a continuous-flow MFC with electrodes separated only by a thin anion exchange membrane (100  $\mu\text{m}$ ), which reduced the solution resistance while facilitating the transport of hydroxide ions from the cathode to the anode (cathode-free). The internal resistance ( $R_{\text{INT}}=34\pm 1 \text{ m}\Omega \text{ m}^2$ ) was 83% lower than that of the cubic MFC electrode ( $202\pm 2 \text{ m}\Omega \text{ m}^2$ ) because the anion-exchange membrane and zero-gap electrode better improved the pH imbalance between the electrodes (Rossi et al., 2021). The modified “bioelectric well” used by Tucci et al. for the simultaneous removal of toluene

and sulfate from real groundwater (conductivity  $711\pm 17$   $\mu\text{s}/\text{cm}$ ) achieved an average toluene removal rate of  $31\pm 2$   $\text{mg}/(\text{L}\cdot\text{d})$ , which is the highest rate reported in the literature. This new BES uses concentric anode cathodes that are hydraulically connected to minimize ohmic losses by maintaining a close electrode spacing (Tucci et al., 2021). Tian et al. further found that when electrode spacing decreased, the internal electric field rather than ohmic internal resistance was the key factor to improve BES performance (Tian et al., 2023). A strong electric field accelerated phenol degradation by selectively enriching phenol degrading bacteria *Comamonas* and *Geobacter* in electroactive biofilm, and simultaneously stimulated *Geobacter* to secrete more cytochrome c in the outer membrane to promote EET (Tian et al., 2022). However, this study was conducted in a solution with high conductivity. When the conductivity decreases, the influence of ohmic internal resistance will increase. The mixed effect of electric field and ohmic internal resistance on EAMs needs further study.

Similarly, solid polymer electrolyte cells exhibit a sandwich structure, that is anode/polymer electrolyte/cathode, which also reduces the distance between electrodes to the micron scale, but ensuring proper current flux when used in low-conductivity media (Xiang et al., 2022). Several studies have reported that the choice of solid electrolytes as separators coupled with electrochemical techniques can achieve efficient removal of contaminants in groundwater, for example Oriol et al. that achieved 70–87% mineralization of imidacloprid in low-conductivity groundwater (Oriol et al., 2019). However, whether EAMs still have the same effect when used in the system remains to be explored.

## 5. Conclusions and outlook

The challenge of removing contaminants from groundwater environments has resulted in the development of several bioremediation technologies, particularly microbial electrochemical techniques, with EAMs at their core. Over the past 20 years, the field has developed sufficiently and pollutants with different chemical properties have been successfully treated using EAMs technologies. However, there are several issues that need further investigation.

1) When different ions coexist, heavy metals and oxygenated anions inhibit bioremediation due to pollutant toxicity and competition for the same limiting electron donor; while coexisting ions can also act as electron donor/acceptor pairs and accelerated electron transfer to promote degradation of pollutants by EAMs. However, the bioremediation of coexisting ions of EAMs is still in its initial stages, and the metabolic response mechanisms and regulatory principles of EAMs under different ions coexist conditions are unknown.

2) Heterogeneity of groundwater media can cause bioavailability limitations and

electron donor/acceptor imbalance, making groundwater contaminants persistent and difficult to degrade. The LDET and MET of EAMs can extend the electrode influence distance and establish electron transfer channels at a centimeter-scale distance for contaminant degradation. However, at present, the distance of LDET is limited to centimeters, and more resources are required to explore whether LDET can be extended to a larger scale.

3) The low conductivity of groundwater leads to an increase in the internal resistance of the BES, thereby reducing the effectiveness of EAMs in removing pollutants. Currently, the negative effects are mostly reduced by reactor configuration and shortening the electrode distance; however, the actual application of bioelectrochemical devices for EAMs is sparse in terms of configuration and single function, making it difficult to meet real application scenarios.

Therefore, EAMs require process optimization and upgrading in combination with a lot of engineering practice research to overcome technical bottlenecks such as environmental factors.

### **Declaration of competing interest**

The authors declare no competing financial interests or personal relationships that could influence the work reported in this paper.

### **Acknowledgements**

This work was supported by the National Natural Science Foundation of China (No. 51978615), the Natural Science Foundation of Zhejiang Province (No. LGG22E080014), the Zhejiang Provincial Ten Thousand Plan (No. 2021R52055) and Zhejiang Gongshang University graduate Research and Innovation Fund project, General Research Project of Zhejiang Provincial Education Department (Y202250208).

### **References**

- [1] Amanze, C., Zheng, X., Anaman, R., Wu, X., Fosua, B.A., Xiao, S., Xia, M., Ai, C., Yu, R., Wu, X. 2022. Effect of nickel (II) on the performance of anodic electroactive biofilms in bioelectrochemical systems. *Water Research*, **222**, 118889. <https://doi.org/10.1016/j.watres.2022.118889>.
- [2] An, Q., Deng, S.-m., Zhao, B., Li, Z., Xu, J., Song, J.-L. 2021. Simultaneous denitrification and hexavalent chromium removal by a newly isolated *Stenotrophomonas maltophilia* strain W26 under aerobic conditions. *Environmental Chemistry*, **18**(1), 20-30. <https://doi.org/10.1071/en20097>.

- [3] Arulmani, S.R.B., Dai, J., Li, H., Chen, Z., Zhang, H., Yan, J., Xiao, T., Sun, W. 2021. Efficient reduction of antimony by sulfate-reducer enriched bio-cathode with hydrogen production in a microbial electrolysis cell. *Science of The Total Environment*, **774**, 145733. <https://doi.org/10.1016/j.scitotenv.2021.145733>.
- [4] Aulenta, F., Palma, E., Marzocchi, U., Cruz Viggi, C., Rossetti, S., Scoma, A. 2021. Enhanced hydrocarbons biodegradation at deep-sea hydrostatic pressure with microbial electrochemical snorkels. *Catalysts*, **11**(2), 263. <https://doi.org/10.3390/catal11020263>.
- [5] Aulenta, F., Tocca, L., Verdini, R., Reale, P., Majone, M. 2011. Dechlorination of trichloroethene in a continuous-flow bioelectrochemical reactor: effect of cathode potential on rate, selectivity, and electron transfer mechanisms. *Environmental Science & Technology*, **45**(19), 8444-8451. <https://doi.org/10.1021/es202262y>.
- [6] Azubuiké, C.C., Chikere, C.B., Okpokwasili, G.C. 2016. Bioremediation techniques—classification based on site of application: principles, advantages, limitations and prospects. *World Journal of Microbiology and Biotechnology*, **32**(11), 1-18. <https://doi.org/10.1007/s11274-016-2137-x>.
- [7] Ballard, J.W.O., Towarnicki, S.G. 2020. Mitochondria, the gut microbiome and ROS. *Cell Signal*, **75**, 109737. <https://doi.org/10.1016/j.cellsig.2020.109737>.
- [8] Bencheikh-Latmani, R., Williams Sarah, M., Haucke, L., Criddle Craig, S., Wu, L., Zhou, J., Tebo Bradley, M. 2005. Global transcriptional profiling of *Shewanella oneidensis* MR-1 during Cr(VI) and U(VI) reduction. *Applied and Environmental Microbiology*, **71**(11), 7453-7460. <https://doi.org/10.1128/AEM.71.11.7453-7460.2005>.
- [9] Biswas, B., Sarkar, B., Mandal, A., Naidu, R. 2015. Heavy metal-immobilizing organoclay facilitates polycyclic aromatic hydrocarbon biodegradation in mixed-contaminated soil. *Journal of Hazardous Materials*, **298**, 129-137. <https://doi.org/10.1016/j.jhazmat.2015.05.009>.
- [10] Cai, X., Yuan, Y., Yu, L., Zhang, B., Li, J., Liu, T., Yu, Z., Zhou, S. 2020. Biochar enhances bioelectrochemical remediation of pentachlorophenol-contaminated soils via long-distance electron transfer. *Journal of Hazardous Materials*, **391**, 122213. <https://doi.org/10.1016/j.jhazmat.2020.122213>.
- [11] Cao, L., Sun, W., Zhang, Y., Feng, S., Dong, J., Zhang, Y., Rittmann, B.E. 2017. Competition for electrons between reductive dechlorination and denitrification. *Frontiers of Environmental Science & Engineering*, **11**(6), 1-10. <https://doi.org/10.1007/s11783-017-0959-x>.
- [12] Ceballos-Escalera, A., Pous, N., Chiluiza-Ramos, P., Korth, B., Harnisch, F., Bañeras, L., Balaguer, M.D., Puig, S. 2021. Electro-bioremediation of nitrate and arsenite polluted groundwater. *Water Research*, **190**, 116748. <https://doi.org/10.1016/j.watres.2020.116748>.

- [13] Ceconet, D., Callegari, A., Capodaglio, A.G. 2018. Bioelectrochemical systems for removal of selected metals and perchlorate from groundwater: A review. *Energies*, **11**(10), 2643. <https://doi.org/10.3390/en11102643>.
- [14] Ceconet, D., Sabba, F., Deveseri, M., Callegari, A., Capodaglio, A.G. 2020. In situ groundwater remediation with bioelectrochemical systems: a critical review and future perspectives. *Environment International*, **137**, 105550. <https://doi.org/10.1016/j.envint.2020.105550>.
- [15] Cervantes, F.J., Dijksma, W., Duong-Dac, T., Ivanova, A., Lettinga, G., Field, J.A. 2001. Anaerobic mineralization of toluene by enriched sediments with quinones and humus as terminal electron acceptors. *Applied and Environmental Microbiology*, **67**(10), 4471-4478. <https://doi.org/10.1128/aem.67.10.4471-4478.2001>.
- [16] Chaudhary, S., Yadav, S., Singh, R., Sadhotra, C., Patil, S.A. 2022. Extremophilic electroactive microorganisms: Promising biocatalysts for bioprocessing applications. *Bioresource Technology*, **347**, 126663. <https://doi.org/10.1016/j.biortech.2021.126663>.
- [17] Chen, B.-Y., Xu, B., Yueh, P.-L., Han, K., Qin, L.-J., Hsueh, C.-C. 2015. Deciphering electron-shuttling characteristics of thionine-based textile dyes in microbial fuel cells. *Journal of the Taiwan Institute of Chemical Engineers*, **51**, 63-70. <https://doi.org/10.1016/j.jtice.2014.12.031>.
- [18] Chen, F., Fan, B., Wang, C., Qian, J., Wang, B., Tang, X., Qin, Z., Chen, Y., Bin, L., Liu, W., Wang, A., Ye, Y., Wang, Y. 2022a. Weak electro-stimulation promotes microbial uranium removal: Efficacy and mechanisms. *Journal of Hazardous Materials*, **439**, 129622. <https://doi.org/10.1016/j.jhazmat.2022.129622>.
- [19] Chen, F., Li, Z., Ye, Y., Lv, M., Liang, B., Yuan, Y., Cheng, H.-Y., Liu, Y., He, Z., Wang, H., Wang, Y., Wang, A. 2022b. Coupled sulfur and electrode-driven autotrophic denitrification for significantly enhanced nitrate removal. *Water Research*, **220**, 118675. <https://doi.org/10.1016/j.watres.2022.118675>.
- [20] Chen, F., Ye, Y., Fan, B., Lv, M., Liang, B., Liu, W., Cheng, H.-Y., Chen, Y., Liu, Y., Wang, Y., Wang, A., Li, Z. 2022c. Simultaneous removal of tetrachloroethylene and nitrate with a novel sulfur-packed biocathode system: The synergy between bioelectrocatalytic dechlorination and sulfur autotrophic denitrification. *Chemical Engineering Journal*, **439**, 135793. <https://doi.org/10.1016/j.cej.2022.135793>.
- [21] Chen, L., Wu, Y., Shen, Q., Zheng, X., Chen, Y. 2022d. Enhancement of hexavalent chromium reduction by *Shewanella oneidensis* MR-1 in presence of copper nanoparticles via stimulating bacterial extracellular electron transfer and environmental adaptability. *Bioresource Technology*, **361**, 127686. <https://doi.org/10.1016/j.biortech.2022.127686>.
- [22] Choi, J.-H., Kim, I.H., Kim, Y.-K., Oh, B.-K. 2015. Effective bioremediation of Cadmium (II), nickel

- (II), and chromium (VI) in a marine environment by using *Desulfovibrio desulfuricans*. *Biotechnology and Bioprocess Engineering*, **20**(5), 937-941. <https://doi.org/10.1007/s12257-015-0287-6>.
- [23] Cruz Viggi, C., Tucci, M., Resitano, M., Crognale, S., Di Franca, M.L., Rossetti, S., Aulenta, F. 2022. Coupling of bioelectrochemical toluene oxidation and trichloroethene reductive dechlorination for single-stage treatment of groundwater containing multiple contaminants. *Environmental Science and Ecotechnology*, **11**, 100171. <https://doi.org/10.1016/j.esec.2022.100171>.
- [24] Daghighi, M., Aulenta, F., Vaiopoulou, E., Franzetti, A., Arends, J.B.A., Sherry, A., Suárez-Suárez, A., Head, I.M., Bestetti, G., Rabaey, K. 2017. Electrobioremediation of oil spills. *Water Research*, **114**, 351-370. <https://doi.org/10.1016/j.watres.2017.02.030>.
- [25] Dai, Q., Zhang, S., Liu, H., Huang, J., Li, L. 2020. Sulfide-mediated azo dye degradation and microbial community analysis in a single-chamber air cathode microbial fuel cell. *Bioelectrochemistry*, **131**, 107349. <https://doi.org/10.1016/j.bioelechem.2019.107349>.
- [26] Dell'Armi, E., Zeppilli, M., De Santis, F., Petrangeli Papini, M., Majone, M. 2021. Control of Sulfate and Nitrate Reduction by Setting Hydraulic Retention Time and Applied Potential on a Membraneless Microbial Electrolysis Cell for Perchloroethylene Removal. *ACS Omega*, **6**(39), 25211-25218. <https://doi.org/10.1021/acsomega.1c03001>.
- [27] Engel, M., Boye, K., Noël, V., Babey, T., Bargar, J.R., Fendorf, S. 2021. Simulated aquifer heterogeneity leads to enhanced attenuation and multiple retention processes of zinc. *Environmental Science & Technology*, **55**(5), 2939-2948. <https://doi.org/10.1021/acs.est.0c06750>.
- [28] Feng, H.-J., Chen, L., Ding, Y.-C., Ma, X.-J., How, S.-W., Wu, D. 2022a. Mechanism on the microbial salt tolerance enhancement by electrical stimulation. *Bioelectrochemistry*, **147**, 108206. <https://doi.org/10.1016/j.bioelechem.2022.108206>.
- [29] Feng, H., Xu, L., Chen, R., Ma, X., Qiao, H., Zhao, N., Ding, Y., Wu, D. 2022b. Detoxification mechanisms of electroactive microorganisms under toxicity stress: A review. *Frontiers in Microbiology*, **13**. <https://doi.org/10.3389/fmicb.2022.1084530>.
- [30] Fitzgerald, L.A., Petersen, E.R., Gross, B.J., Soto, C.M., Ringeisen, B.R., El-Naggar, M.Y., Biffinger, J.C. 2012. Aggrandizing power output from *Shewanella oneidensis* MR-1 microbial fuel cells using calcium chloride. *Biosensors and Bioelectronics*, **31**(1), 492-498. <https://doi.org/10.1016/j.bios.2011.11.024>.
- [31] Gang, H., Xiao, C., Xiao, Y., Yan, W., Bai, R., Ding, R., Yang, Z., Zhao, F. 2019. Proteomic analysis of the reduction and resistance mechanisms of *Shewanella oneidensis* MR-1 under long-term hexavalent chromium stress. *Environment International*, **127**, 94-102. <https://doi.org/10.1016/j.envint.2019.03.016>.

- [32] Griebler, C., Lueders, T. 2009. Microbial biodiversity in groundwater ecosystems. *Freshwater Biology*, **54**(4), 649-677. <https://doi.org/10.1111/j.1365-2427.2008.02013.x>.
- [33] Guan, F., Yuan, X., Duan, J., Zhai, X., Hou, B. 2019. Phenazine enables the anaerobic respiration of *Pseudomonas aeruginosa* via electron transfer with a polarised graphite electrode. *International Biodeterioration & Biodegradation*, **137**, 8-13. <https://doi.org/10.1016/j.ibiod.2018.11.002>.
- [34] Guo, F., Luo, H., Shi, Z., Wu, Y., Liu, H. 2021. Substrate salinity: A critical factor regulating the performance of microbial fuel cells, a review. *Science of The Total Environment*, **763**, 143021. <https://doi.org/10.1016/j.scitotenv.2020.143021>.
- [35] He, J., Sung, Y., Krajmalnik-Brown, R., Ritalahti, K.M., Löffler, F.E. 2005. Isolation and characterization of *Dehalococcoides* sp. strain FL2, a trichloroethene (TCE)-and 1, 2-dichloroethene-respiring anaerobe. *Environmental Microbiology*, **7**(9), 1442-1450. <https://doi.org/10.1111/j.1462-2920.2005.00830.x>.
- [36] Heimann, A.C., Friis, A.K., Jakobsen, R. 2005. Effects of sulfate on anaerobic chloroethene degradation by an enriched culture under transient and steady-state hydrogen supply. *Water Research*, **39**(15), 3579-3586. <https://doi.org/10.1016/j.watres.2005.06.029>.
- [37] Hesse, F., Harms, H., Attinger, S., Thullner, M. 2010. Linear exchange model for the description of mass transfer limited bioavailability at the pore scale. *Environmental Science & Technology*, **44**(6), 2064-2071. <https://doi.org/10.1021/es902489q>.
- [38] Hoareau, M., Erable, B., Bergel, A. 2019. Microbial electrochemical snorkels (MESs): A budding technology for multiple applications. A mini review. *Electrochemistry Communications*, **104**, 106473. <https://doi.org/10.1016/j.elecom.2019.05.022>.
- [39] Hu, W., Yang, L., Shao, P., Shi, H., Chang, Z., Fang, D., Wei, Y., Feng, Y., Huang, Y., Yu, K., Luo, X. 2022. Proton self-enhanced hydroxyl-enriched cerium oxide for effective arsenic extraction from strongly acidic wastewater. *Environmental Science & Technology*, **56**(14), 10412-10422. <https://doi.org/10.1021/acs.est.2c02675>.
- [40] Huang, L., Zhou, P., Quan, X., Logan, B.E. 2018. Removal of binary Cr(VI) and Cd(II) from the catholyte of MFCs and determining their fate in EAB using fluorescence probes. *Bioelectrochemistry*, **122**, 61-68. <https://doi.org/10.1016/j.bioelechem.2018.02.010>.
- [41] Jiang, L., Yang, Y., Jin, H., Wang, H., Swift, C.M., Xie, Y., Schubert, T., Löffler, F.E., Yan, J. 2022. *Geobacter* sp. Strain IAE Dihaloeliminates 1, 1, 2-Trichloroethane and 1, 2-Dichloroethane. *Environmental Science & Technology*, **56**(6), 3430-3440. <https://doi.org/10.1021/acs.est.1c05952>.
- [42] Karunanidhi, D., Subramani, T., Srinivasamoorthy, K., Yang, Q. 2022. Environmental chemistry, toxicity and health risk assessment of groundwater: Environmental persistence and management



- strategies. *Environmental Research*, **214**, 113884. <https://doi.org/10.1016/j.envres.2022.113884>.
- [43] Kondo, K., Okamoto, A., Hashimoto, K., Nakamura, R. 2015. Sulfur-mediated electron shuttling sustains microbial Long-Distance Extracellular Electron Transfer with the aid of metallic iron sulfides. *Langmuir*, **31**(26), 7427-7434. <https://doi.org/10.1021/acs.langmuir.5b01033>.
- [44] Kumar, A., Hsu, L.H.-H., Kavanagh, P., Barrière, F., Lens, P.N.L., Lapinsonnière, L., Lienhard V, J.H., Schröder, U., Jiang, X., Leech, D. 2017. The ins and outs of microorganism–electrode electron transfer reactions. *Nature Reviews Chemistry*, **1**(3), 0024. <https://doi.org/10.1038/s41570-017-0024>.
- [45] Kumar, S.S., Kumar, V., Gnaneswar Gude, V., Malyan, S.K., Pugazhendhi, A. 2020. Alkalinity and salinity favor bioelectricity generation potential of Clostridium, Tetrathlobacter and Desulfovibrio consortium in Microbial Fuel Cells (MFC) treating sulfate-laden wastewater. *Bioresource Technology*, **306**, 123110. <https://doi.org/10.1016/j.biortech.2020.123110>.
- [46] Lai, A., Astolfi, M.L., Bertelli, V., Agostinelli, V.G., Zeppilli, M., Majone, M. 2021. Chromate fate and effect in bioelectrochemical systems for remediation of chlorinated solvents. *New Biotechnology*, **60**, 27-35. <https://doi.org/10.1016/j.nbt.2020.06.006>.
- [47] Lai, A., Verdini, R., Aulenta, F., Majone, M. 2015. Influence of nitrate and sulfate reduction in the bioelectrochemically assisted dechlorination of cis-DCE. *Chemosphere*, **125**, 147-154. <https://doi.org/>.
- [48] Li, H., Liu, Q. 2022. Reaction medium for Permeable reactive barrier remediation of groundwater polluted by heavy metals. *Frontiers in Environmental Science*, 1521. <https://doi.org/10.3389/fenvs.2022.968546>.
- [49] Li, M., Zhou, S. 2019a. Efficacy of Cu (II) as an electron-shuttle mediator for improved bioelectricity generation and Cr (VI) reduction in microbial fuel cells. *Bioresource Technology*, **273**, 122-129. <https://doi.org/10.1016/j.biortech.2018.10.074>.
- [50] Li, M., Zhou, S. 2019b. Efficacy of Cu(II) as an electron-shuttle mediator for improved bioelectricity generation and Cr(VI) reduction in microbial fuel cells. *Bioresource Technology*, **273**, 122-129. <https://doi.org/10.1016/j.biortech.2018.10.074>.
- [51] Li, P., Karunanidhi, D., Subramani, T., Srinivasamoorthy, K. 2021. Sources and consequences of groundwater contamination. *Archives of Environmental Contamination and Toxicology*, **80**(1), 1-10. <https://doi.org/10.1007/s00244-020-00805-z>.
- [52] Li, T., Chen, F., Zhou, Q., Wang, X., Liao, C., Zhou, L., Wan, L., An, J., Wan, Y., Li, N. 2020. Unignorable toxicity of formaldehyde on electroactive bacteria in bioelectrochemical systems. *Environmental Research*, **183**, 109143. <https://doi.org/10.1016/j.envres.2020.109143>.

- [53] Li, W.-W., Yu, H.-Q. 2015. Electro-assisted groundwater bioremediation: fundamentals, challenges and future perspectives. *Bioresource Technology*, **196**, 677-684. <https://doi.org/10.1016/j.biortech.2015.07.074>.
- [54] Lin, W., Feng, J., Hu, K., Qu, B., Song, S., He, K., Liu, C., Chen, Y., Hu, Y. 2022. Sulfidation forwarding high-strength Anammox process using nitrate as electron acceptor via thiosulfate-driven nitrate denitratation. *Bioresource Technology*, **344**, 126335. <https://doi.org/10.1016/j.biortech.2021.126335>.
- [55] Lin, X.-Q., Li, Z.-L., Nan, J., Su, J.-H., Liang, B., Li, C.-J., Wang, A.-J. 2021. Biodegradation and metabolism of tetrabromobisphenol A in microbial fuel cell: Behaviors, dynamic pathway and the molecular ecological mechanism. *Journal of Hazardous Materials*, **417**, 126104. <https://doi.org/10.1016/j.jhazmat.2021.126104>.
- [56] Liu, S.-H., Zeng, G.-M., Niu, Q.-Y., Gong, J.-L., Hu, X.-J., Lu, L.-H., Zhou, Y.-Y., Hu, X., Chen, M., Yan, M. 2015. Effect of Pb (II) on phenanthrene degradation by new isolated *Bacillus* sp. P1. *Rsc Advances*, **5**(69), 55812-55818. <https://doi.org/10.1039/c5ra04867b>.
- [57] Liu, S., Liu, H., Huang, Y., Ma, J., Wang, Z., Chen, R. 2021. Dielectric constants of organic pollutants determine their strength for enhancing microbial iron reduction. *Environmental Science and Pollution Research*, **28**(47), 67445-67455. <https://doi.org/10.1007/s11356-021-14060-9>.
- [58] Liu, S., Liu, H., Wang, Z., Cui, Y., Chen, R., Peng, Z., Yuan, S., Shi, L. 2019. Benzene promotes microbial Fe (III) reduction and flavins secretion. *Geochimica et Cosmochimica Acta*, **264**, 92-104. <https://doi.org/>.
- [59] Liu, Y., Li, X., Zhou, W., He, R., Zhang, Y., Zhao, N. 2023. Electrical stimulation accelerated phenanthrene biodegradation coupling with nitrate reduction in groundwater. *Separation and Purification Technology*, **309**, 123019. <https://doi.org/10.1016/j.seppur.2022.123019>.
- [60] Löffler, F.E., Tiedje, J.M., Sanford, R.A. 1999. Fraction of electrons consumed in electron acceptor reduction and hydrogen thresholds as indicators of halo-respiratory physiology. *Applied and Environmental Microbiology*, **65**(9), 4049-4056. <https://doi.org/10.1128/aem.65.9.4049-4056.1999>.
- [61] Luo, H., Hu, J., Qu, L., Liu, G., Zhang, R., Lu, Y., Qi, J., Hu, J., Zeng, C. 2019. Efficient reduction of nitrobenzene by sulfate-reducer enriched biocathode in microbial electrolysis cell. *Science of The Total Environment*, **674**, 336-343. <https://doi.org/10.1016/j.scitotenv.2019.04.206>.
- [62] Lv, P.-L., Shi, L.-D., Dong, Q.-Y., Rittmann, B., Zhao, H.-P. 2020. How nitrate affects perchlorate reduction in a methane-based biofilm batch reactor. *Water Research*, **171**, 115397. <https://doi.org/10.1016/j.watres.2019.115397>.
- [63] Malvankar, N.S., King, G.M., Lovley, D.R. 2015. Centimeter-long electron transport in marine

- sediments via conductive minerals. *The ISME Journal*, **9**(2), 527-531.  
<https://doi.org/10.1038/ismej.2014.131>.
- [64] Marzocchi, U., Palma, E., Rossetti, S., Aulenta, F., Scoma, A. 2020. Parallel artificial and biological electric circuits power petroleum decontamination: the case of snorkel and cable bacteria. *Water Research*, **173**, 115520. <https://doi.org/10.1016/j.watres.2020.115520>.
- [65] Meckenstock, R.U., Elsner, M., Griebler, C., Lueders, T., Stumpp, C., Aamand, J., Agathos, S.N., Albrechtsen, H.-J., Bastiaens, L., Bjerg, P.L. 2015. Biodegradation: updating the concepts of control for microbial cleanup in contaminated aquifers. *Environmental Science & Technology*, **49**(12), 7073-7081. <https://doi.org/10.1021/acs.est.5b00715>.
- [66] Mep. 2020. China's Ecological Environment Status Bulletin 2020, (Ed.) M.o.E.a.E.o.t.P.s.R.o. China. <https://www.mee.gov.cn/hjzl/sthjzk/zghjzkgb/202105/P020210526572756184785.pdf>, pp. 32.
- [67] Mier, A.A., Olvera-Vargas, H., Mejia-Lopez, M., Longoria, A., Vereas, L., Sebastian, P.J., Arias, D.M. 2021. A review of recent advances in electrode materials for emerging bioelectrochemical systems: From biofilm-bearing anodes to specialized cathodes. *Chemosphere*, **283**.  
<https://doi.org/10.1016/j.chemosphere.2021.131138>.
- [68] Miran, W., Nawaz, M., Jang, J., Lee, D.S. 2017. Chlorinated phenol treatment and in situ hydrogen peroxide production in a sulfate-reducing bacteria enriched bioelectrochemical system. *Water research*, **117**, 198-206. <https://doi.org/10.1016/j.watres.2017.04.008>.
- [69] Müller, H., Bosch, J., Griebler, C., Damgaard, L.R., Nielsen, L.P., Lueders, T., Meckenstock, R.U. 2016. Long-distance electron transfer by cable bacteria in aquifer sediments. *The ISME Journal*, **10**(8), 2010-2019. <https://doi.org/10.1038/ismej.2015.250>.
- [70] Murphy, E.M., Ginn, T.R., Chilakapati, A., Resch, C.T., Phillips, J.L., Wietsma, T.W., Spadoni, C.M. 1997. The influence of physical heterogeneity on microbial degradation and distribution in porous media. *Water Resources Research*, **33**(5), 1087-1103. <https://doi.org/10.1029/96wr03851>.
- [71] Muyzer, G., Stams, A.J. 2008. The ecology and biotechnology of sulphate-reducing bacteria. *Nature Reviews Microbiology*, **6**(6), 441-454. <https://doi.org/10.1038/nrmicro1892>.
- [72] Nguyen, V.K., Park, Y., Yang, H., Yu, J., Lee, T. 2016a. Effect of the cathode potential and sulfate ions on nitrate reduction in a microbial electrochemical denitrification system. *Journal of Industrial Microbiology and Biotechnology*, **43**(6), 783-793. <https://doi.org/10.1007/s10295-016-1762-6>.
- [73] Nguyen, V.K., Park, Y., Yu, J., Lee, T. 2016b. Simultaneous arsenite oxidation and nitrate reduction at the electrodes of bioelectrochemical systems. *Environmental Science and Pollution Research*, **23**(19), 19978-19988. <https://doi.org/10.1007/s11356-016-7225-9>.

- [74] Okamoto, A., Kalathil, S., Deng, X., Hashimoto, K., Nakamura, R., Neelson, K.H. 2014. Cell-secreted flavins bound to membrane cytochromes dictate electron transfer reactions to surfaces with diverse charge and pH. *Scientific Reports*, **4**(1), 1-8. <https://doi.org/10.1038/srep05628>.
- [75] Oriol, R., Clematis, D., Brillas, E., Cortina, J.L., Panizza, M., Sirés, I. 2019. Groundwater treatment using a solid polymer electrolyte cell with mesh electrodes. *ChemElectroChem*, **6**(4), 1235-1243. <https://doi.org/>.
- [76] Oriomah, C., Adelowo, O.O., Adekanmbi, A.O. 2015. Bacteria from spent engine-oil-contaminated soils possess dual tolerance to hydrocarbon and heavy metals, and degrade spent oil in the presence of copper, lead, zinc and combinations thereof. *Annals of microbiology*, **65**(1), 207-215. <https://doi.org/>.
- [77] Orsetti, S., Laskov, C., Haderlein, S.B. 2013. Electron transfer between iron minerals and quinones: Estimating the reduction potential of the Fe(II)-goethite surface from AQDS speciation. *Environmental Science & Technology*, **47**(24), 14161-14168. <https://doi.org/10.1021/es403658g>.
- [78] Pang, Y., Wang, J. 2023. Effect of ferric iron (Fe(III)) on heterotrophic solid-phase denitrification: Denitrification performance and metabolic pathway. *Bioresource Technology*, **369**, 128401. <https://doi.org/10.1016/j.biortech.2022.128401>.
- [79] Pang, Y., Wang, J. 2021. Inhibition of ferrous iron (Fe<sup>2+</sup>) to sulfur-driven autotrophic denitrification: Insight into microbial community and functional genes. *Bioresource Technology*, **342**, 125960. <https://doi.org/10.1016/j.biortech.2021.125960>.
- [80] Paquete, C.M., Rosenbaum, M.A., Bañeras, L., Rotaru, A.-E., Puig, S. 2022. Let's chat: Communication between electroactive microorganisms. *Bioresource Technology*, **347**, 126705. <https://doi.org/10.1016/j.biortech.2022.126705>.
- [81] Pfeffer, C., Larsen, S., Song, J., Dong, M., Besenbacher, F., Meyer, R.L., Kjeldsen, K.U., Schreiber, L., Gorby, Y.A., El-Naggar, M.Y. 2012. Filamentous bacteria transport electrons over centimetre distances. *Nature*, **491**(7423), 218-221. <https://doi.org/10.1038/nature11586>.
- [82] Pilloni, G., von Netzer, F., Engel, M., Lueders, T. 2011. Electron acceptor-dependent identification of key anaerobic toluene degraders at a tar-oil-contaminated aquifer by Pyro-SIP. *FEMS Microbiology Ecology*, **78**(1), 165-175. <https://doi.org/10.1111/j.1574-6941.2011.01083.x>.
- [83] Pous, N., Balaguer, M.D., Colprim, J., Puig, S. 2018. Opportunities for groundwater microbial electro-remediation. *Microbial Biotechnology*, **11**(1), 119-135. <https://doi.org/10.1111/1751-7915.12866>.
- [84] Pous, N., Carmona-Martínez, A.A., Vilajeliu-Pons, A., Fiset, E., Bañeras, L., Trably, E., Balaguer, M.D., Colprim, J., Bernet, N., Puig, S. 2016. Bidirectional microbial electron transfer: Switching an

- acetate oxidizing biofilm to nitrate reducing conditions. *Biosensors and Bioelectronics*, **75**, 352-358. <https://doi.org/10.1016/j.bios.2015.08.035>.
- [85] Pous, N., Puig, S., Balaguer, M.D., Colprim, J. 2015. Cathode potential and anode electron donor evaluation for a suitable treatment of nitrate-contaminated groundwater in bioelectrochemical systems. *Chemical Engineering Journal*, **263**, 151-159. <https://doi.org/10.1016/j.cej.2014.11.002>.
- [86] Priyadarshane, M., Das, S. 2021. Biosorption and removal of toxic heavy metals by metal tolerating bacteria for bioremediation of metal contamination: A comprehensive review. *Journal of Environmental Chemical Engineering*, **9**(1), 104686. <https://doi.org/10.1016/j.jece.2020.104686>.
- [87] Puig, S., Coma, M., Desloover, J., Boon, N., Colprim, J., Balaguer, M.D. 2012. Autotrophic denitrification in Microbial Fuel Cells treating low ionic strength waters. *Environmental Science & Technology*, **46**(4), 2309-2315. <https://doi.org/10.1021/es2030609>.
- [88] Qian, D., Liu, H., Hu, F., Song, S., Chen, Y. 2022. Extracellular electron transfer-dependent Cr(VI)/sulfate reduction mediated by iron sulfide nanoparticles. *Journal of Bioscience and Bioengineering*, **134**(2), 153-161. <https://doi.org/10.1016/j.jbiosc.2022.05.005>.
- [89] Richter, L.V., Sandler, S.J., Weis, R.M. 2012. Two isoforms of *Geobacter sulfurreducens* PilA have distinct roles in pilus biogenesis, cytochrome localization, extracellular electron transfer, and biofilm formation. *Journal of bacteriology*, **194**(10), 2551-2563. <https://doi.org/>.
- [90] Rosner, A., Armengaud, J., Ballarin, L., Barnay-Verdier, S., Cima, F., Coelho, A.V., Domart-Coulon, I., Drobne, D., Genevière, A.-M., Kokalj, A.J. 2021. Stem cells of aquatic invertebrates as an advanced tool for assessing ecotoxicological impacts. *Science of the Total Environment*, **771**, 144565. <https://doi.org/10.1016/j.scitotenv.2020.144565>.
- [91] Rossi, R., Baek, G., Saikaly, P.E., Logan, B.E. 2021. Continuous flow microbial flow cell with an anion exchange membrane for treating low conductivity and poorly buffered wastewater. *ACS Sustainable Chemistry & Engineering*, **9**(7), 2946-2954. <https://doi.org/10.1021/acssuschemeng.0c09144>.
- [92] Saran, C., Purchase, D., Saratale, G.D., Saratale, R.G., Romanholo Ferreira, L.F., Bilal, M., Iqbal, H.M.N., Hussain, C.M., Mulla, S.I., Bharagava, R.N. 2022. Microbial fuel cell: A green eco-friendly agent for tannery wastewater treatment and simultaneous bioelectricity/power generation. *Chemosphere*, **312**(Pt 1), 137072. <https://doi.org/10.1016/j.chemosphere.2022.137072>.
- [93] Sharma, I. 2020. Bioremediation techniques for polluted environment: concept, advantages, limitations, and prospects. in: *Trace Metals in the Environment-New Approaches and Recent Advances*, IntechOpen.
- [94] Shen, Y., Chapelle, F.H., Strom, E.W., Benner, R. 2015. Origins and bioavailability of dissolved

- organic matter in groundwater. *Biogeochemistry*, **122**(1), 61-78. <https://doi.org/10.1007/s10533-014-0029-4>.
- [95] Sonawane, J.M., Ghosh, P.C., Adeloju, S.B. 2018. Electrokinetic behaviour of conducting polymer modified stainless steel anodes during the enrichment phase in microbial fuel cells. *Electrochimica Acta*, **287**, 96-105. <https://doi.org/10.1016/j.electacta.2018.07.077>.
- [96] Strycharz, S.M., Gannon, S.M., Boles, A.R., Franks, A.E., Nevin, K.P., Lovley, D.R. 2010. Reductive dechlorination of 2-chlorophenol by *Anaeromyxobacter dehalogenans* with an electrode serving as the electron donor. *Environmental Microbiology Reports*, **2**(2), 289-294. <https://doi.org/10.1111/j.1758-2229.2009.00118.x>.
- [97] Strycharz, S.M., Woodard, T.L., Johnson, J.P., Nevin, K.P., Sanford, R.A., Löffler, F.E., Lovley, D.R. 2008. Graphite electrode as a sole electron donor for reductive dechlorination of tetrachlorethene by *Geobacter lovleyi*. *Applied and Environmental Microbiology*, **74**(19), 5943-5947. <https://doi.org/10.1128/aem.00961-08>.
- [98] Sun, S., Hou, Y.-N., Wei, W., Sharif, H.M.A., Huang, C., Ni, B.-J., Li, H., Song, Y., Lu, C., Han, Y., Guo, J. 2022. Perturbation of clopyralid on bio-denitrification and nitrite accumulation: Long-term performance and biological mechanism. *Environmental Science and Ecotechnology*, **9**, 100144. <https://doi.org/10.1016/j.esc.2021.100144>.
- [99] Sung, Y., Fletcher, K.E., Ritalahti, K.M., Apkarian, R.P., Ramos-Hernández, N., Sanford, R.A., Mesbah, N.M., Löffler, F.E. 2006. *Geobacter lovleyi* sp. nov. strain SZ, a novel metal-reducing and tetrachloroethene-dechlorinating bacterium. *Applied and Environmental Microbiology*, **72**(4), 2775-2782. <https://doi.org/10.1128/aem.72.4.2775-2782.2006>.
- [100] Tang, Y., Li, T., Xu, Y., Ren, H., Huang, H. 2023. Effects of electrical stimulation on purification of secondary effluent containing chlorophenols by denitrification biofilter. *Environmental Research*, **216**, 114535. <https://doi.org/10.1016/j.envres.2022.114535>.
- [101] Tang, Y.Q., Chen, J.F., Xiao, Z.X., Liu, Z.M., Xu, L., Qin, Q.D., Wang, Y.Q., Xu, Y. 2022. Humic and biochar accelerated microbial reductive dechlorination of 2,4,6-trichlorophenol under weak electrical stimulation. *Journal of Hazardous Materials*, **439**. <https://doi.org/10.1016/j.jhazmat.2022.129671>.
- [102] Thapa, B.S., Kim, T., Pandit, S., Song, Y.E., Afsharian, Y.P., Rahimnejad, M., Kim, J.R., Oh, S.-E. 2022. Overview of electroactive microorganisms and electron transfer mechanisms in microbial electrochemistry. *Bioresource Technology*, **347**, 126579. <https://doi.org/10.1016/j.biortech.2021.126579>.
- [103] Thatoi, H., Das, S., Mishra, J., Rath, B.P., Das, N. 2014. Bacterial chromate reductase, a potential enzyme for bioremediation of hexavalent chromium: A review. *Journal of Environmental*

- Management*, **146**, 383-399. <https://doi.org/10.1016/j.jenvman.2014.07.014>.
- [104] Tian, L., Liao, C., Yan, X., Zhao, Q., Wang, Z., Li, T., Li, N., Wang, X. 2023. Endogenous electric field accelerates phenol degradation in bioelectrochemical systems with reduced electrode spacing. *Journal of Hazardous Materials*, **442**, 130043. <https://doi.org/10.1016/j.jhazmat.2022.130043>.
- [105] Tian, L., Yan, X., Wang, D., Du, Q., Wan, Y., Zhou, L., Li, T., Liao, C., Li, N., Wang, X. 2022. Two key *Geobacter* species of wastewater-enriched electroactive biofilm respond differently to electric field. *Water Research*, **213**, 118185. <https://doi.org/10.1016/j.watres.2022.118185>.
- [106] Tong, Y., He, Z. 2013. Nitrate removal from groundwater driven by electricity generation and heterotrophic denitrification in a bioelectrochemical system. *Journal of Hazardous Materials*, **262**, 614-619. <https://doi.org/10.1016/j.jhazmat.2013.09.008>.
- [107] Tucci, M., Carolina, C.V., Resitano, M., Matturro, B., Crognale, S., Pietrini, I., Rossetti, S., Harnisch, F., Aulenta, F. 2021. Simultaneous removal of hydrocarbons and sulfate from groundwater using a “bioelectric well”. *Electrochimica Acta*, **388**, 138636. <https://doi.org/10.1016/j.electacta.2021.138636>.
- [108] Van Doan, T., Lee, T.K., Shukla, S.K., Tiedje, J.M., Park, J. 2013. Increased nitrous oxide accumulation by bioelectrochemical denitrification under autotrophic conditions: Kinetics and expression of denitrification pathway genes. *Water Research*, **47**(19), 7087-7097. <https://doi.org/10.1016/j.watres.2013.08.041>.
- [109] Vishwanathan, A., Aiyer, K.S., Chunduri, L., Venkataramaniah, K., Siva Sankara Sai, S., Rao, G. 2016. Carbon quantum dots shuttle electrons to the anode of a microbial fuel cell. *3 Biotech*, **6**(2), 1-6. <https://doi.org/10.1007/s13205-016-0552-1>.
- [110] Volland, S., Bayer, E., Baumgartner, V., Andosch, A., Lütz, C., Sima, E., Lütz-Meindl, U. 2014. Rescue of heavy metal effects on cell physiology of the algal model system *Micrasterias* by divalent ions. *Journal of Plant Physiology*, **171**(2), 154-163. <https://doi.org/10.1016/j.jplph.2013.10.002>.
- [111] Von Canstein, H., Ogawa, J., Shimizu, S., Lloyd, J.R. 2008. Secretion of flavins by *Shewanella* species and their role in extracellular electron transfer. *Applied and Environmental Microbiology*, **74**(3), 615-623. <https://doi.org/10.1128/aem.01387-07>.
- [112] Wan, R., Li, X., Wang, L., Yang, G., Zheng, X., Zha, Y., Chen, Y., Meng, J. 2021. Ionic copper strengthens the toxicity of tetrabromobisphenol A (TBBPA) to denitrification by decreasing substrate transport and electron transfer. *Journal of Hazardous Materials*, **416**, 126203. <https://doi.org/10.1016/j.jhazmat.2021.126203>.

- [113] Wan, R., Wang, L., Chen, Y., Zheng, X., Chew, J., Huang, H. 2019. Tetrabromobisphenol A (TBBPA) inhibits denitrification via regulating carbon metabolism to decrease electron donation and bacterial population. *Water Research*, **162**, 190-199. <https://doi.org/10.1016/j.watres.2019.06.046>.
- [114] Wang, C., Dong, J., Hu, W., Li, Y. 2021a. Enhanced simultaneous removal of nitrate and perchlorate from groundwater by bioelectrochemical systems (BESs) with cathodic potential regulation. *Biochemical Engineering Journal*, **173**, 108068. <https://doi.org/10.1016/j.bej.2021.108068>.
- [115] Wang, Q., Huang, L., Pan, Y., Quan, X., Li Puma, G. 2017. Impact of Fe(III) as an effective electron-shuttle mediator for enhanced Cr(VI) reduction in microbial fuel cells: Reduction of diffusional resistances and cathode overpotentials. *Journal of Hazardous Materials*, **321**, 896-906. <https://doi.org/10.1016/j.jhazmat.2016.10.011>.
- [116] Wang, X.-M., Wang, L., Chen, L., Tian, L.-J., Zhu, T.-T., Wu, Q.-Z., Hu, Y.-R., Zheng, L.-R., Li, W.-W. 2022. AQDS activates extracellular synergistic biodegradation of copper and selenite via altering the coordination environment of outer-membrane proteins. *Environmental Science & Technology*, **56**(19), 13786-13797. <https://doi.org/10.1021/acs.est.2c04130>.
- [117] Wang, X., Aulenta, F., Puig, S., Esteve-Núñez, A., He, Y., Mu, Y., Rabaey, K. 2020. Microbial electrochemistry for bioremediation. *Environmental Science and Ecotechnology*, **1**, 100013. <https://doi.org/10.1016/j.ese.2020.100013>.
- [118] Wang, X., PrévotEAU, A., Rabaey, K. 2021b. Impact of periodic polarization on groundwater denitrification in Bioelectrochemical Systems. *Environmental Science & Technology*, **55**(22), 15371-15379. <https://doi.org/10.1021/acs.est.1c03586>.
- [119] Weatherill, J.J., Krause, S., Ullah, S., Cassidy, N.J., Levy, A., Drijfhout, F.P., Rivett, M.O. 2019. Revealing chlorinated ethene transformation hotspots in a nitrate-impacted hyporheic zone. *Water Research*, **161**, 222-231. <https://doi.org/10.1016/j.watres.2019.05.083>.
- [120] Xiang, Q., Cheng, W., Wen, S., Wu, B., Sun, J., Wang, S. 2022. Electro-peroxone with solid polymer electrolytes: A novel system for degradation of plasticizers in natural effluents. *Water Research*, **216**, 118302. <https://doi.org/10.1016/j.watres.2022.118302>.
- [121] Xie, D., Yu, H., Li, C., Ren, Y., Wei, C., Feng, C. 2014. Competitive microbial reduction of perchlorate and nitrate with a cathode directly serving as the electron donor. *Electrochimica Acta*, **133**, 217-223. <https://doi.org/10.1016/j.electacta.2014.04.016>.
- [122] Xu, W.-H., Jian, H., Liu, Y.-G., Zeng, G.-M., Li, X., Zhang, W. 2015. Bioreduction of chromate by an isolated *Bacillus anthracis* Cr-4 with soluble Cr (III) product. *Water, Air, & Soil Pollution*, **226**(3), 1-9. <https://doi.org/>.



- [123] Xu, Y.-S., Zheng, T., Yong, X.-Y., Zhai, D.-D., Si, R.-W., Li, B., Yu, Y.-Y., Yong, Y.-C. 2016. Trace heavy metal ions promoted extracellular electron transfer and power generation by *Shewanella* in microbial fuel cells. *Bioresource Technology*, **211**, 542-547.  
<https://doi.org/10.1016/j.biortech.2016.03.144>.
- [124] Yang, C.-E., Wu, C.-Y., Liu, Y.-C., Lan, E.I., Tsai, S.-L. 2019. Cometabolic degradation of toluene and TCE contaminated wastewater in a bench-scale sequencing batch reactor inoculated with immobilized *Pseudomonas putida* F1. *Journal of the Taiwan Institute of Chemical Engineers*, **104**, 168-176. <https://doi.org/10.1016/j.jtice.2019.09.003>.
- [125] Yang, K., Abu-Reesh, I.M., He, Z. 2022a. Enhancing the degradation of selected recalcitrant organic contaminants through integrated cathode and anode processes in microbial electrochemical systems: A frontier review. *Journal of Hazardous Materials Letters*, **3**, 100057.  
<https://doi.org/10.1016/j.hazl.2022.100057>.
- [126] Yang, L., Feng, Y., Wang, C., Fang, D., Yi, G., Gao, Z., Shao, P., Liu, C., Luo, X., Luo, S. 2022b. Closed-loop regeneration of battery-grade FePO<sub>4</sub> from lithium extraction slag of spent Li-ion batteries via phosphoric acid mixture selective leaching. *Chemical Engineering Journal*, **431**, 133232. <https://doi.org/10.1016/j.cej.2021.133232>.
- [127] Yang, Y., Guo, J., Sun, G., Xu, M. 2013. Characterizing the snorkeling respiration and growth of *Shewanella decolorationis* S12. *Bioresource Technology*, **128**, 472-478.  
<https://doi.org/10.1016/j.biortech.2012.10.103>.
- [128] Yang, Y., Wang, Z., Gan, C., Klausen, L.H., Bonn e, R., Kong, G., Luo, D., Meert, M., Zhu, C., Sun, G., Guo, J., Ma, Y., Bjerg, J.T., Manca, J., Xu, M., Nielsen, L.P., Dong, M. 2021. Long-distance electron transfer in a filamentous Gram-positive bacterium. *Nature Communications*, **12**(1), 1709.  
<https://doi.org/10.1038/s41467-021-21709-z>.
- [129] Yu, X., Jiang, Y., Huang, H., Shi, J., Wu, K., Zhang, P., Lv, J., Li, H., He, H., Liu, P., Li, X. 2016. Simultaneous aerobic denitrification and Cr(VI) reduction by *Pseudomonas brassicacearum* LZ-4 in wastewater. *Bioresource Technology*, **221**, 121-129.  
<https://doi.org/10.1016/j.biortech.2016.09.037>.
- [130] Yuan, Y., Zhou, L., Hou, R., Wang, Y., Zhou, S. 2021. Centimeter-long microbial electron transport for bioremediation applications. *Trends in Biotechnology*, **39**(2), 181-193.  
<https://doi.org/10.1016/j.tibtech.2020.06.011>.
- [131] Zhang, T., Bain, T.S., Nevin, K.P., Barlett, M.A., Lovley, D.R. 2012. Anaerobic benzene oxidation by *Geobacter* species. *Applied and Environmental Microbiology*, **78**(23), 8304-8310.  
<https://doi.org/10.1128/aem.02469-12>.
- [132] Zhang, T., Gannon, S.M., Nevin, K.P., Franks, A.E., Lovley, D.R. 2010. Stimulating the

- anaerobic degradation of aromatic hydrocarbons in contaminated sediments by providing an electrode as the electron acceptor. *Environmental microbiology*, **12**(4), 1011-1020. <https://doi.org/>
- [133] Zhang, X.-Y., Li, Z.-L., Chen, F., Wang, S.-P., Nan, J., Huang, C., Chen, X.-Q., Cao, D., Bai, C.-H., Wang, H.-C., Han, J.-L., Liang, B., Wang, A.-J. 2022. Influence of nitrate concentration on trichloroethylene reductive dechlorination in weak electric stimulation system. *Chemosphere*, **295**, 133935. <https://doi.org/10.1016/j.chemosphere.2022.133935>.
- [134] Zhang, Y., Li, G., Wen, J., Xu, Y., Sun, J., Ning, X.-a., Lu, X., Wang, Y., Yang, Z., Yuan, Y. 2018. Electrochemical and microbial community responses of electrochemically active biofilms to copper ions in bioelectrochemical systems. *Chemosphere*, **196**, 377-385. <https://doi.org/10.1016/j.chemosphere.2018.01.009>.
- [135] Zhao, F., Xin, J., Yuan, M., Wang, L., Wang, X. 2022. A critical review of existing mechanisms and strategies to enhance N<sub>2</sub> selectivity in groundwater nitrate reduction. *Water Research*, **209**, 117889. <https://doi.org/10.1016/j.watres.2021.117889>.
- [136] Zheng, T., Li, J., Ji, Y., Zhang, W., Fang, Y., Xin, F., Dong, W., Wei, P., Ma, J., Jiang, M. 2020. Progress and prospects of Bioelectrochemical Systems: electron transfer and its applications in the microbial metabolism. *Front Bioeng Biotechnol*, **8**, 10. <https://doi.org/10.3389/fbioe.2020.00010>.
- [137] Zhu, T.-t., Cheng, H.-y., Yang, L.-h., Su, S.-g., Wang, H.-c., Wang, S.-s., Wang, A.-j. 2019. Coupled sulfur and iron(II) carbonate-driven autotrophic denitrification for significantly enhanced nitrate removal. *Environmental Science & Technology*, **53**(3), 1545-1554. <https://doi.org/10.1021/acs.est.8b06865>.
- [138] Zhuang, L., Tang, Z., Ma, J., Yu, Z., Wang, Y., Tang, J. 2019. Enhanced anaerobic biodegradation of benzoate under sulfate-reducing conditions with conductive iron-oxides in sediment of Pearl River Estuary. *Frontiers in Microbiology*, **10**, 374. <https://doi.org/10.3389/fmicb.2019.00374>.

**Table 1**

Effect of coexisting ion stress on groundwater remediation.

Stresses	Stress factor	Substrate	Microorganism	Mechanism	Reference
	$\text{NO}_3^-$ , $\text{SO}_4^{2-}$	Cis-dichloroethylene (cis-DCE)	Inoculation with the indigenous consortium in the real groundwater	Electron donor competition	(Lai et al., 2015)
	$\text{NO}_3^-$	$\text{ClO}_4^-$	<i>Proteobacteria</i>	Electron donor competition	(Wang et al., 2021a)
	$\text{NO}_3^-$	$\text{ClO}_4^-$	Autotrophic denitrifiers	Electron donor competition	(Xie et al., 2014)
	$\text{SO}_4^{2-}$	Chlorinated ethenes	KB-1/TCE <sup>TM</sup> (related to <i>Dehalococcoides ethenogenes</i> )	Electron donor competition	(Heimann et al., 2005)
	Cr(VI)	$\text{SO}_4^{2-}$	SRB	Electron donor competition	(Qian et al., 2022)
Inhibition	$\text{SO}_4^{2-}$	$\text{NO}_3^-$	<i>Shinella spp.</i>	Electron donor competition	(Nguyen et al., 2016a)
	Fe(III)	$\text{NO}_3^-$	A community dominated by complete denitrifiers	Pollutant toxicity	(Pang & Wang, 2023)
	Cr(VI)	Trichloroethene (TCE)	<i>Dehalococcoides spp</i>	Pollutant toxicity	(Lai et al., 2021)
	Pb(II)	PAHs	<i>Bacillus malacitensis</i>	Pollutant toxicity	(Liu et al., 2015)
	Cd(II)	Cr(VI)	<i>Stenotrophomonas sp.</i> YS1, <i>Stenotrophomonas maltophilia</i> YS2, <i>Serratia marcescens</i> YS3, <i>Achromobacter xylosoxidans</i> YS8	Pollutant toxicity	(Huang et al., 2018)

Stresses	Stress factor	Substrate	Microorganism	Mechanism	Reference
	Se(VI)	Cu(II)	<i>S. oneidensis</i> MR-1	Facilitate electron transfer	(Wang et al., 2022)
	Fe(II)/Ni(II)	Toluene, TCE	<i>P. putida</i> F1	Facilitate electron transfer	(Yang et al., 2019)
	Cu(II)	Cr(VI)	Null	Facilitate electron transfer	(Li & Zhou, 2019b)
	Cu NPs	Cr(VI)	<i>S. oneidensis</i> MR-1	Facilitate electron transfer	(Chen et al., 2022d)
	Fe(III)	Cr(VI)	Null	Facilitate electron transfer	(Wang et al., 2017)
Promotion	SO <sub>4</sub> <sup>2-</sup>	NB	<i>Wolinella sp.</i>	Reciprocal electron donor/acceptor pairs	(Luo et al., 2019)
	SO <sub>4</sub> <sup>2-</sup>	4-CP	SRB	Reciprocal electron donor/acceptor pairs	(Miran et al., 2017)
	SO <sub>4</sub> <sup>2-</sup>	Cr(VI), Ni(II), Cd(II)	<i>D. desulfuricans</i>	Reciprocal electron donor/acceptor pairs	(Choi et al., 2015)
	Sulfide	Azo dye	<i>Proteobacteria</i>	Reciprocal electron donor/acceptor pairs	(Dai et al., 2020)
	NO <sub>3</sub> <sup>-</sup>	As(III)	<i>Sideroxydans lithotrophicus</i> , <i>Achromobacter agilis</i>	Reciprocal electron donor/acceptor pairs	(Ceballos-Escalera et al., 2021)

Note: Inhibition/Promotion: When multiple pollutants coexist, one pollutant will inhibit/promote the degradation of

another pollutant

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Figure :

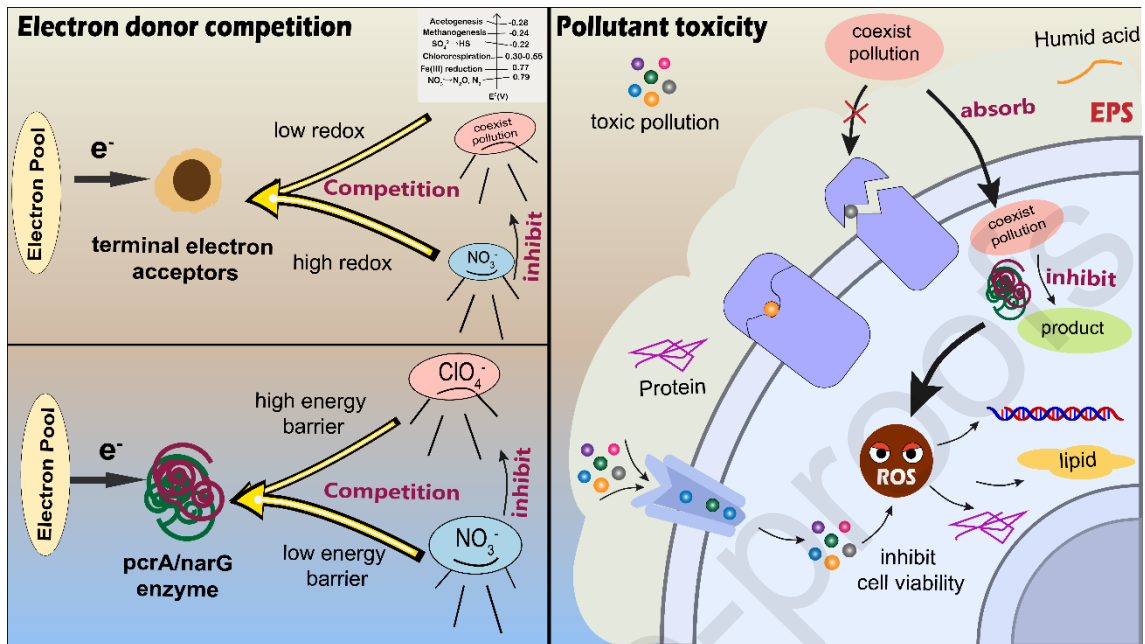
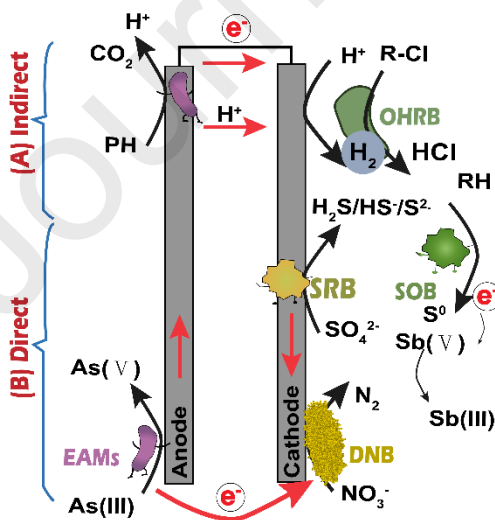


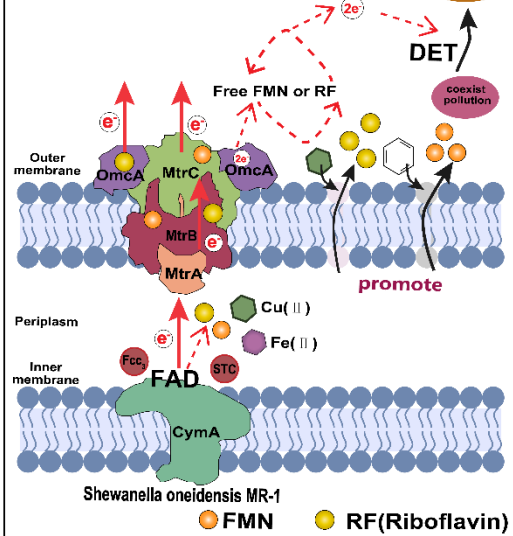
Fig.1. Diagram illustrating two inhibitory effects between coexisting ions.

Abbreviations: EPS, extracellular polymeric substances; ROS, reactive oxygen species.

**Reciprocal electron donor/acceptor pairs**

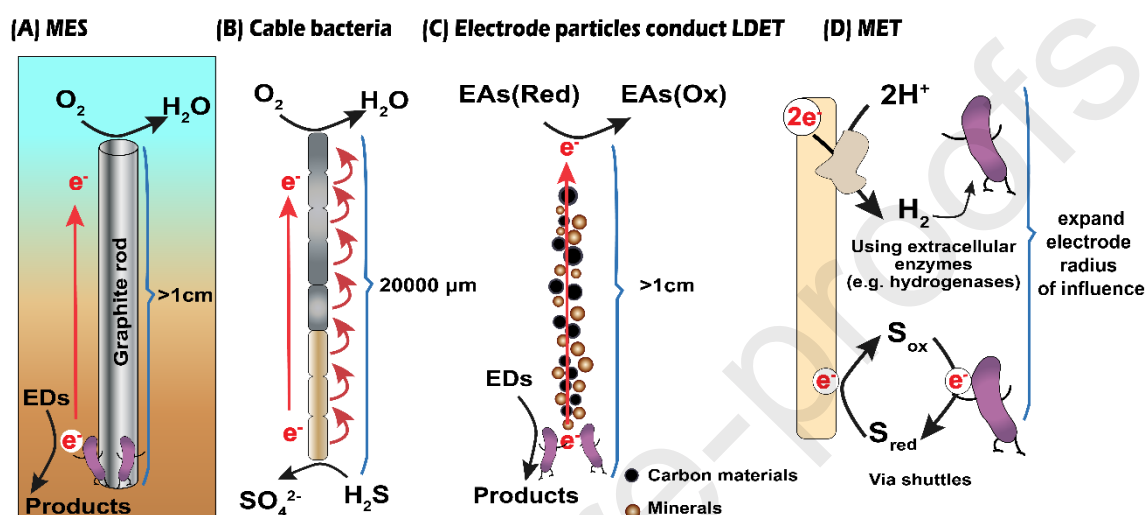


**Facilitate electron transfer**



**Fig.2.** Promoting effect between coexisting ions.

Abbreviations: ORHB, organohalide respiring bacteria; SRB, sulfate reducing bacteria; SOB, sulfur oxidizing bacteria; DNB, denitrifying bacteria; PH, petroleum hydrocarbons; FMN, flavin mononucleotide; RF, riboflavin; FAD, flavin adenine dinucleotide.

**Fig.3.** Schematic diagrams of the various LDET processes and MET.

(A) Electrode snorkels conduct LDET to link spatially separated redox reactions. (B) Cable bacteria conduct LDET via an electron-hopping model. (C) LDET is conducted by natural conductive minerals (e.g., pyrite) or artificial electroconductive materials (e.g., biochar). The electrons are generated by the microbial oxidation of electron donors (EDs), and remote electron acceptors [EAs (Ox)] receive the electrons to be reduced [EAs (red)]. (D) MET expand the radius of influence of the electrode through the flow of the electron transfer medium with the medium.

### Highlights

- EAMs can use coexisting ions to promote electron transfer to assist remediation.
- EAMs can mitigate the low bioavailability limits of bioremediation by complex EET.
- EAMs can solve the problem of electron donor/acceptor imbalance by LDET and MET.
- Micron electrode spacing reduces energy loss due to groundwater's low conductivity.

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