



Research review paper

Bioelectrochemical system platform for sustainable environmental remediation and energy generation



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ABSTRACT

The increasing awareness of the energy–environment nexus is compelling the development of technologies that reduce environmental impacts during energy production as well as energy consumption during environmental remediation. Countries spend billions in pollution cleanup projects, and new technologies with low energy and chemical consumption are needed for sustainable remediation practice. This perspective review provides a comprehensive summary on the mechanisms of the new bioelectrochemical system (BES) platform technology for efficient and low cost remediation, including petroleum hydrocarbons, chlorinated solvents, perchlorate, azo dyes, and metals, and it also discusses the potential new uses of BES approach for some emerging contaminants remediation, such as CO₂ in air and nutrients and micropollutants in water. The unique feature of BES for environmental remediation is the use of electrodes as non-exhaustible electron acceptors, or even donors, for contaminant degradation, which requires minimum energy or chemicals but instead produces sustainable energy for monitoring and other onsite uses. BES provides both oxidation (anode) and reduction (cathode) reactions that integrate microbial–electro–chemical removal mechanisms, so complex contaminants with different characteristics can be removed. We believe the BES platform carries great potential for sustainable remediation and hope this perspective provides background and insights for future research and development.

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Contents

1. Introduction	318
2. The unique advantages of BESs for environmental remediation	318
3. Current developments of BESs in environmental remediation	318
3.1. Hydrocarbons and derivatives	318
3.2. Chlorinated organic compounds	322
3.3. Perchlorate	322
3.4. Azo dyes	323
3.5. Metals	323
4. Potential developments of BESs in environmental remediation	327
4.1. Carbon dioxide	327
4.2. Nutrients	327
4.3. Micropollutants	329
5. Main factors influencing BES remediation performance	330
5.1. Contaminated matrix physical and chemical conditions	330
5.2. Functional microorganisms and community	330
5.3. BES reactor configurations	331
5.4. Co-generation of energy products	332
5.5. Scale-up considerations for real-world applications	332
Acknowledgments	332
References	332

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1. Introduction

The widespread chemical contamination of the environment is a serious problem across the world, as it severely threatens human health and damages vulnerable ecosystems. Countries are investing heavily to remediate different contaminants in surface and groundwater, soil and sediment, as well as in the atmosphere. For example, during the past decade, the United States Environmental Protection Agency (EPA) had allocated \$243 million US dollars per year for highly contaminated Superfund site cleanup, and it is estimated that \$335–681 million US dollars per year will be needed for future cleanup (<http://www.publicintegrity.org/2011/02/22/2121/epa-superfund-cleanup-costs-outstrip-funding>). The Chinese national plan for prevention and control of groundwater pollution (2011–2020) is investing approximately \$5.8 billion US dollars till 2020 to investigate the groundwater pollution, and the initial market size was estimated to be around \$16 billion US dollars (Council, 2011; Yin et al., 2011). Despite the huge investment and active practice, the cleanup of different sites contaminated by various pollutants remains a very challenging task. Challenges exist primarily because each site is unique, most of the current technologies require large amounts of energy and chemical supply, and the remediation practice could last years to decades. Compared with physical excavation or chemical oxidation/reduction, which are generally energy and chemical intensive, bioremediation is considered cost-effective and environmentally friendly. However, the performance of bioremediation is primarily governed by the interplay between the abundance of electron donor and electron acceptor, as well as carbon sources for the functional microorganisms, and common challenges for bioremediation include lack of contact between the contaminants and amendments due to the heterogeneous matrix, the limitation of the electron donor/acceptor availability and slow kinetics.

This review aims to introduce a new energy positive bioremediation process called bioelectrochemical systems (BESs) for enhanced and accelerated remediation. The BES is an emerging platform technology also known as microbial electrochemical systems, or MXCs. Traditional BES reactors consist of an anode, a cathode and an optional separator. Electron donor type of substrates can be oxidized by microorganisms in the anode chamber to generate electron flow (current) to the cathode, where in the cathode chamber, the electrons can be used for direct electricity production (microbial fuel cells, MFCs), or used to reduce electron acceptor type of chemicals and produce less toxic or value-added products (microbial electrolysis cells, MECs, or microbial electrosynthesis, MES) (Cheng et al., 2009; Logan and Rabaey, 2012; Logan et al., 2008; Lovley, 2011; Wang and Ren, 2013). Many functional microbial groups are involved in different degradation and respiration processes, and electrochemically active bacteria (EAB) are those directly interact with the electrodes for extracellular electron transfer. While there have been multiple reviews discussed the developments of using BESs for wastewater treatment, chemical synthesis, and other applications, no review or perspective has been provided for BES based environmental remediation, mainly because it is in relatively early stage, but also due to its complexity and diversity of this application (Lovley, 2006; Rabaey and Rozendal, 2010; Schröder, 2012; Sleutels et al., 2012). In the past decade, many studies have reported that BES can be an effective approach for removing environmental pollutants, such as hydrocarbons and derivatives, chlorinated organic compounds, perchlorate, azo dyes and heavy metals. One of the first BES remediation studies was uranium recovery from contaminated subsurface with electrodes serving as the electron donor (Gregory and Lovley, 2005). This review aims to provide a comprehensive summary and discussion of the current status of this research area. Moreover, we identified several emerging contaminants that can also be removed by BES method, including CO₂ in air and nutrients and micropollutants in water.

2. The unique advantages of BESs for environmental remediation

The unique feature of BESs for environmental remediation is the use of electrodes as non-exhaustible electron acceptors, or even donors, for contaminant degradation, requiring very little to zero external energy or external chemical amendments, while a small amount of energy is generated for onsite uses. This is a huge advantage compared with traditional physical, chemical, or even biological remediation methods, because they either consume large amount of energy (such as soil vapor extraction, bioventing, or biosparging), or they need external chemical addition (such as chemical oxidation or bioremediation). By reducing or eliminating the energy and chemical costs, BESs can have lower operational costs, which can be beneficial considering general remediation processes could last several years to decades. The produced electrical current from BES not only can serve as a real-time bioremediation indicator but also can power wireless sensors for remote online monitoring. The energy generated can be harvested with the voltage boosted to required levels for usage, such as 3.3 V for most environmental wireless sensors (Wang et al., 2015b). Unlike other processes that only provide one redox condition, BESs provide both oxidation (anode) and reduction (cathode) reactions that integrate microbial–electrochemical removal mechanisms, so complex contaminants with different characteristics can be removed. Due to the driving force from cathode reactions, many studies have demonstrated that using BES as a remediation technology can accelerate remediation process and shorten remediation time (Huang et al., 2011; X. Wang et al., 2012). Additionally, the configuration of BESs for remediation can be very flexible, from a simple graphite rod snorkel to multiple-chambered containers, making it easily integrable with existing remediation infrastructures, such as monitoring wells or piezometers.

In this perspective article, we summarized the main remediation mechanisms that have been investigated in the BES platform, and more importantly, we discussed the potential new use of BES approach for some emerging contaminants remediation, such as CO₂ in air and nutrients and micropollutants in water. While the overall principle of BES remediation is to use the redox gradient between the electrodes and the contaminants, there have been several different mechanisms applied so far, as shown in Fig. 1: (1) reduced contaminants, such as petroleum hydrocarbon and biofuels, can be used as electron donors and anaerobically oxidized using the anode; (2) oxidized contaminants, such as metal ions, azo dyes, perchlorate, and chlorinated solvents, etc. can be used as electron acceptors and anaerobically reduced using the cathode; (3) through competing with the anode or cathode as the electron acceptor or donor, some chemicals can be removed in the anode chamber (i.e., nitrate) or cathode chamber (i.e., ammonia), respectively; (4) for trace organic pollutants or metals, electrode sorption can play an important role in conversion and removal; and (5) for real remediation practices, because of the presence of a variety of contaminants on one site, a combination of the above mechanisms may occur, which may also involve other removal mechanisms, such as photochemical reactions. Tables 1–8 summarize the literature published so far on BES remediation of different environmental contaminants, and the main degradation pathways of different types of contaminants at the electrodes are shown in Fig. 2.

3. Current developments of BESs in environmental remediation

3.1. Hydrocarbons and derivatives

Hydrocarbons are organic compounds composed of carbon and hydrogen, and when hydrogen atoms are replaced by other functional groups, the derived hydrocarbons are called hydrocarbon derivatives. As the primary energy source for current civilizations, petroleum hydrocarbon contamination in soil and groundwater is a widespread environmental problem. Major hydrocarbon compounds that pose health and environmental concerns include BTEX (benzene, toluene, ethylbenzene,

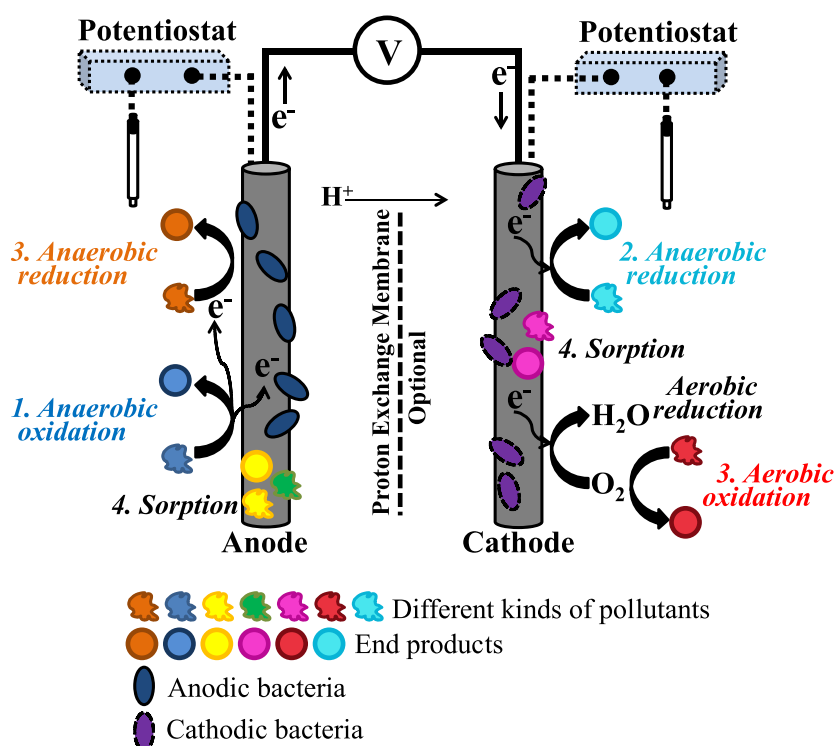


Fig. 1. Main remediation mechanisms using the BES platform: (1) anaerobic oxidation at the anode; (2) anaerobic reduction at the cathode; (3) competing with electrodes as electron acceptor or donor, such as anaerobic reduction at the anode and aerobic oxidation at the cathode; (4) sorption on the electrodes, and (5) combined mechanisms.

and xylenes), PAHs (polycyclic aromatic hydrocarbons), etc., and total petroleum hydrocarbon (TPH) has been used to characterize the overall hydrocarbon concentration. Bioremediation techniques such as biosparging, biostimulation, and bioaugmentation have been shown effective and environmentally friendly compared to physical and chemical remedies, but the survival of the injected microbial strains competing with native dominant ones, the poor contact or spreading of amendments (microbes or electron donor) with the target contaminants, the low kinetics and requirement of external electron acceptor supply still are limiting factors of application (Das and Chandran, 2011; Tyagi et al., 2011).

Several studies demonstrated that bioelectrochemical systems or microbial fuel cells can solve problems of scarcity of electron donor/acceptor or create the right environment to significantly stimulate and enhance hydrocarbon degradation accompanied by energy production, because the electrode may serve as a non-exhaustible electron acceptor for hydrocarbon oxidation, which eliminates the necessity of aeration but sustains an aerobic-like metabolic pathway on the cathode (Lu et al., 2014a,b; X. Wang et al., 2012). Table 1 summarizes the BES studies on using different hydrocarbon pollutants including crude oil (X. Wang et al., 2012), refinery wastewater (Morris and Jin, 2008), petroleum sludge (Chandrasekhar and Mohan, 2012; Mohan and Chandrasekhar, 2011), aromatic compounds (Rakoczy et al., 2013; Wu et al., 2013; Zhang et al., 2010), and diesel (Morris et al., 2009b), and all studies showed that the electrode approach could increase hydrocarbon degradation rate by multiple times without using any external energy or chemicals. For example, Wang et al. found that the removal of TPH within 1 cm of the anode in the closed-circuit mode was enhanced by 120% compared to that in the open-circuit mode in a U-tube MFC (X. Wang et al., 2012), and the specific contents of n-alkanes from C8 to C40 were analyzed for the first time. The same group later on improved hydrocarbon bioremediation through the application of multilayer anodes and electrode arrangement optimization (Li et al., 2014; Zhang et al., 2014). Recent findings by Lu et al. (Fig. 3A) demonstrated that accompanied with a current output up to 86 mA/m², TPH removal rate almost

doubled in soils close to the anode (63.5–78.7%) than that in the open circuit positive controls (37.6–43.4%) (Lu et al., 2014a). Studies also showed that TPH degradation rate was increased by nearly 12 folds in a contaminated sediment (Morris and Jin, 2012), and similar approach can be applied to other contaminated water bodies, such as shallow lagoon, ponds, marshes, and groundwater aquifers as well (Huang et al., 2011; Li and Yu, 2015; Yuan et al., 2010).

In addition to mixed hydrocarbon contaminants, pure chemicals have also been tested in lab scale studies. One study showed that when phenol and glucose–phenol mixture were both used as substrates in the anode of two-chamber MFCs, the maximum power densities were 9.1 W/m³ and 28.3 W/m³, respectively. More interestingly, double voltage peaks appeared when glucose–phenol mixture was used, which also led to phenol degradation by 20% at the first voltage peak and 90% at the second voltage peak, respectively (Luo et al., 2009). The degradation of phenol was found to be positively correlated with the removal of chemical oxygen demand (COD) in waterlogged soils (Huang et al., 2011). When two furan derivatives and eight phenolic compounds were tested in single-chamber air-cathode MFCs, only 5-hydroxymethyl furfural (5-HMF) could be used as the sole substrate, while all other compounds had to be mixed with glucose (Catal et al., 2008). Another group, however, demonstrated that furfural was able to be used by microorganisms in MFCs and support power generation (Luo et al., 2010, 2011). While generally it is difficult to analyze the degradation products of mixed compounds, by using a poised electrode (+300 mV vs. Ag/AgCl) as the electron acceptor, studies showed that final products can be tracked, and aromatic hydrocarbon-contaminated sediment, toluene, benzene and naphthalene were all degraded to the final product CO₂ (Zhang et al., 2010).

Other studies employed different removal mechanisms, taking advantage of the full spectrum of the redox reaction and power generation, though most BES studies stimulated hydrocarbons degradation by using such pollutants as electron donors. Nitrobenzene (NB) could be reduced to less toxic aniline by an abiotic cathode of MFC with electrons supplied from the anode (J. Li et al., 2010). The removal rate of NB

Table 1
Bioelectrochemical system platform for remediation of hydrocarbons and their derivatives.

Pollutants (media)	Treatment	Inoculum	Poised potential ^a	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Petroleum (soil, groundwater, sediment)	Anodic	Petroleum contaminated soils		0.2628 ± 0.0009 g TNAs/kg soil	79%	66%		2.7	X. Wang et al. (2012)
	Anodic	Petroleum contaminated soils		0.0017 ± 0.0001 g TPAHs/kg soil	42%	30%			
	Anodic	Petroleum contaminated soils		25.7 g TPH/kg soil	8.3%, 12.5%	6.4%		0.324	Zhang et al. (2014)
	Anodic	Petroleum contaminated soils		25.7 g TPH/kg soil				0.324	Li et al. (2014)
	Anodic	Diesel and engine oil contaminated soil		11.46 ± 0.60 g/kg soil	47.5–78.7%	37.5–44.5%		3	Lu et al. (2014a)
	Anodic	Soil from a diesel fuel storage tank impacted area		12.25 ± 0.36 g TPH/kg soil	82.1–89.7%	67.9%		50	Lu et al. (2014b)
	Anodic	Contaminated groundwater						0.01–246.5	Morris and Jin (2008)
	Anodic	Real field petroleum based oil sludge		413 ± 2 g TPH/kg sludge	41.08%	20.72%		0.5	Mohan and Chandrasekhar (2011)
	Anodic	Real field petroleum sludge from an oil refinery		413 ± 2 g TPH/kg sludge	11–35%			0.5	Chandrasekhar and Mohan (2012)
	Anodic	Diesel contaminated groundwater		0.3 g/L	82%	31%		0.9	Morris et al. (2009b)
Phenol (wastewater)	Anodic	Contaminated sediment		16 g/kg	24%	2%		0.05	Morris and Jin (2012)
	Anodic	Mixed aerobic and anaerobic sludge		0.4 g phenol/L, 1 g phenol/L + 0.5 g glucose/L	95.5 ± 1.7%, >95%	88.3 ± 3.9%		0.88, 0.116	Luo et al. (2009)
	Anodic	Waterlogged soil		0.08 g/L	90.1%	12.3%/27.6%		1.57	Huang et al. (2011)
	Sorption			0.1 g/L	159.8 g/kg	112.8 g/kg		0.1	Yang et al. (2013a)
	Sorption			0.02–0.3 g/L	235 g/kg	150.4 g/kg		0.1	Yang et al. (2013b)
Benzoate (wastewater)	Anodic	<i>Geobacter metallireducens</i>	+0.3 V (vs. Ag/AgCl)	0.14 g/L				0.94	Zhang et al. (2010)
Toluene (sediment)	Anodic	<i>Geobacter metallireducens</i> , hydrocarbon-contaminated sediments	+0.3 V (vs. Ag/AgCl)	0.1 g/L, 0.0009 g/L	~100%	14–76.9%	CO ₂	0.94	Zhang et al. (2010)
Naphthalene (sediment)	Anodic	Hydrocarbon-contaminated sediments		0.0128 g/L	~100%	13.6–54.5%		0.94	
Benzene (sediment, groundwater, wastewater)	Anodic			0.0007 g/L	~100%	54.5–63.6%		0.94	
	Anodic	Benzene- and sulfide-contaminated groundwater		0.0117–0.0195 g/L	18–80%		CO ₂ , bacterial fatty acids	1	Rakoczy et al. (2013)
	Anodic	The bacteria from the oil cracking wastewater treatment plant cultured with BTEX		0.01087 g/L, 0.02174 g/L	100%		CO ₂	1.6	Wu et al. (2013)
Furan derivatives and phenolic compounds (wastewater)	Anodic	Wastewater		0.032 g/L 5-HMF, 0.023 g/L syringaldehyde, 0.019 g/L vanillin, 0.0185 g/L trans-cinnamic acid, 0.02425 g/L trans-4-hydroxy-3-methoxy-cinnamic acid, 0.0205 g/L 4-hydroxy-cinnamic acid, 0.028 g/L 3,5-dimethoxy-4-hydroxy-cinnamic acids (without glucose or with 1.2 g glucose/L)				0.012	Catal et al. (2008)
Furfural (wastewater)	Anodic	A mixture of aerobic and anaerobic sludge or microorganisms taken from the anode chamber		0.01–0.19 g/L (0.2–1 g glucose/L) or 0.64 g/L as a sole fuel	100%			0.036	Luo et al. (2010)
Nitrobenzene (NB) (wastewater)	Anodic	A mixture of aerobic and anaerobic sludge		0.3 g/L	100 ± 0.1%	100 ± 0.0%		0.2	Luo et al. (2011)
	Anodic	A mixture of aerobic and anaerobic sludge		0.05, 0.15, 0.25 g/L, 1 g glucose/L	100%			0.054	J. Li et al. (2010)
	Cathodic			0.25 g/L	98%			0.054	J. Li et al. (2010)
	Cathodic		Add no power or 20 mA	0.185 g/L	0.16 ± 0.005 g/L/d, 1.05 ± 0.004 g/L/d	0.005–0.238 g/L/d	Aniline	0.672	Mu et al. (2009b)
	Cathodic	Nitrobenzene reducing consortium enriched from a activated sludge	0.5 V, 0.15 V	0.06 g/L (0.5 g glucose/L or 0.84 g/L NaHCO ₃)	98.70 ± 0.87%, 98.93 ± 0.77%	73.75 ± 3.2%, 71.6%	Aniline	0.17	A. Wang et al. (2011)

^a Numbers without “+” or “–” mean extra voltage is only added across the electrodes.

Table 2
Bioelectrochemical system platform for remediation of chlorinated organic compounds.

Pollutants (media)	Treatment	Inoculum	Poised potential ^a	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Tetrachloroethene (PCE) (groundwater)	Cathodic	<i>Geobacter lovleyi</i>	−0.3 V (vs. SHE)	0.0664 g/L	0.0042 g/d	0	cis-DCE	0.5	Strycharz et al. (2008)
	Cathodic	Mixed anaerobic and aerobic cultures	9–20 V	0.004 g/L, 0.007 g/L	0.0038 g/d		cis-DCE, VC, ethene	0.38	
Trichloroethene (TCE) (groundwater)	Cathodic	Dechlorinating species, homoacetogenic bacteria and methanogens	0.4 or 0.5 mA	0.0065–0.001 g/L			cis-DCE, VC, ethene	0.38	Lohner et al. (2011)
	Cathodic	An anaerobic TCE dechlorinating culture	−0.5 V, −0.8 V (vs. SHE)				cis-DCE, VC, ethene, ethane	0.3	Aulenta et al. (2007)
	Cathodic	An anaerobic TCE dechlorinating culture	−0.45 V (vs. SHE)	0.005 g/L, 0.01 g/L	255 ± 19 µeq/d	0	cis-DCE, VC, ethene	0.25	Aulenta et al. (2008)
	Cathodic	Mixed culture	−0.45 V (vs. SHE)	0.008 g	8.4 µeq/L		cis-DCE, VC, ethene	0.3	Aulenta et al. (2009)
	Cathodic	<i>Geobacter lovleyi</i>	−0.45 V (vs. SHE)	0.008 g	11.2 µeq/L		cis-DCE	0.3	Aulenta et al. (2009)
	Cathodic	Mixed culture enriched from brackish sediments by feeding TCE and H ₂	−0.25 V (vs. SHE)	0.008 g/L, 0.016 g/L	180 ± 23 µeq/L/d		cis-DCE	0.25	Aulenta et al. (2010)
	Cathodic	A TCE-to-ethene dechlorinating culture	−0.25–−0.75 V (vs. SHE)				cis-DCE, VC, ethene	1.77	Aulenta et al. (2011)
cis-Dichloroethene (cis-DCE) (groundwater)	Anodic	Aerobic vinyl chloride degrading mixed culture	0.4 or 0.5 mA				CO ₂ , H ₂ O, Cl	0.38	Lohner et al. (2011)
Vinyl chloride (VC) (groundwater)	Anodic	Mixed anaerobic and aerobic cultures	9–20 V	0.022 g/L, 0.014 g/L	0.0045 g/d			0.38	Lohner and Tiehm (2009)
Ethene (groundwater)	Anodic	Aerobic VC degrading mixed culture	0.4 or 0.5 mA				CO ₂ , H ₂ O, Cl	0.38	Lohner et al. (2011)
4-Chlorophenol (4-CP) (groundwater)	Anodic	Aerobic VC degrading mixed culture	0.4 or 0.5 mA				CO ₂ , H ₂ O	0.38	Lohner et al. (2011)
1,2-Dichloroethane (1,2-DCA) (groundwater)	Cathodic	Anaerobic sludge and photosynthetic bacteria	0.5 V	0.1 g/L	81.8 ± 2.9%	25.9 ± 4.4%, 2.7 ± 1.9%, 45.3 ± 3.7%	Phenol	0.16	Kong et al. (2014)
1,2-Dichloroethane (1,2-DCA) (groundwater)	Anodic	An anodophilic consortium enriched with acetate		0.099 g/L	>99%	75%	Ethene glycol, acetate, CO ₂	0.088	Pham et al. (2009)
	Anodic	A natural consortium from a 1,2-DCA contaminated site			>99%	<1%		0.088	

^a Numbers without “+” or “−” mean extra voltage is only added across the electrodes.

was $1.29 \pm 0.04 \text{ mol/m}^3/\text{d}$ and then increased to $8.57 \pm 0.03 \text{ mol/m}^3/\text{d}$ when extra power was supplied (Mu et al., 2009b). Microbially catalyzed cathode with supplemental power later on showed even higher removal rate (A. Wang et al., 2011). A MFC-sorption system was constructed by using the electrical potential generated across an MFC anode and cathode to physically drive phenol migration and removal by activated carbon fiber adsorption (Yang et al., 2013a,b).

Using BESs for hydrocarbon remediation is among the processes that are closest toward commercialization, and several pilot and field studies have been reported in the past few years. One simple configuration is a so-called “electrochemical snorkel”, where a single conductive rod spans the anaerobic and aerobic zones and functions as both an anode and cathode, though it cannot produce any electricity (Erable et al., 2011). For most in situ field applications, configurations of the BES vary on depths, matrix types, and other physical/chemical parameters. A recent study installed two column-type BES modules into a 50-L pilot scale reactor packed with diesel-contaminated soils, and results showed that 82.1–89.7% of the TPH was degraded after 120 days, which was an up to 241% increase of biodegradation compared to the control. The maximum current output was $70.4 \pm 0.2 \text{ mA/m}^2$, and the maximum radius of influence (ROI) could be more than 90 cm or exceed 300 cm should a non-degradation baseline be used (Lu et al., 2014b). Jin et al. reported field installations using a column design, because such configuration can be easily integrated with existing groundwater monitoring wells or piezometers, and the electric current can power sensors and be correlated with contaminant degradation profiles (Jin et al., 2013).

3.2. Chlorinated organic compounds

Chlorinated organic compounds such as perchloroethene (PCE) and trichloroethene (TCE) are widely used as solvents and degreasing agents. These toxic and carcinogenic compounds are among the most spread contaminants in soil and groundwater. The in situ remediation of PCE and TCE involves providing external electron donors to stimulate microbial dechlorination, in which PCE is sequentially reduced to TCE, *cis*-dichloroethene (*cis*-DCE), vinyl chloride (VC) and ethene/ethane. It has been reported that the BES cathode can serve as a permanent and stable electron donor for reductive dechlorination, while the anode can oxidize lower chlorinated organic compounds for further degradation. Table 2 summarizes the findings of BES remediation of chlorinated solvents. For example, a process named bio-electrochemically assisted reductive dechlorination (BEARD) suggested that a negatively polarized solid-state electrode (i.e., -450 or -500 mV vs. SHE), in the presence of exogenous (i.e., methyl viologen) or self-produced redox mediators could serve as an electron donor for the reductive dechlorination of TCE to *cis*-DCE and lower amounts of VC and ethene by a mixed culture (Aulenta et al., 2007, 2009). Using a different redox mediator anthraquinone-2,6-disulfonate (AQDS) and pure culture *Geobacter lovleyi*, TCE was only reduced to *cis*-DCE without VC and ethene formations (Aulenta et al., 2009, 2010). *G. lovleyi* was also used to reduce PCE

to TCE with a poised electrode as the electron donor (Strycharz et al., 2008). H_2 evolution may occur together with TCE reduction when higher methyl viologen (MV) concentrations were used (Aulenta et al., 2008). One major challenge of dechlorination is incomplete reduction and detoxification process that ends up with more toxic VC product. Studies showed that operating the electrode at more reducing values could get more complete reduction to ethene, but very negative potentials resulted in low Coulombic efficiencies (Aulenta et al., 2011). In order to further mineralize the dechlorination metabolites, Lohner et al. conducted a sequential reductive and oxidative biodegradation of chloroethenes by a coupled bioelectro-process (Fig. 3B) (Lohner and Tiehm, 2009; Lohner et al., 2011). Similarly, Kong et al. developed a new approach for dechlorination and mineralization of 4-chlorophenol (4-CP) by firstly reducing 4-CP at the biocathode and then feeding the dechlorination product phenol to the anode chamber for mineralization. The efficiencies of dechlorination and mineralization at the biocathode and bioanode were as high as $78.8 \pm 4.9\%$ and $71.3 \pm 1.4\%$, respectively (Kong et al., 2014). Overall, bioelectrochemical dechlorination is still in feasibility study stage, and more microbial characterization and process development need to be conducted.

3.3. Perchlorate

Perchlorate (ClO_4^-) is an imminent environmental threat during decades of release into soils and leaching into groundwater. Perchlorate is known to be linked to the inhibition of hormone production by thyroid gland and can cause damage to nervous systems. The extent of ClO_4^- release in the environment was not known until recent improvements in analytical methods that could detect ClO_4^- down to $4 \mu\text{g/L}$. As a result, numerous of ClO_4^- -contaminated sites have been identified throughout the U.S. and between 5–17 million people across 26 states are exposed to perchlorate in their drinking water (Bender et al., 2005). The high solubility and chemical stability makes perchlorate contamination difficult to remediate by conventional technologies (Logan, 2001). Microbial ClO_4^- reduction has been used by amendments of electron donors such as acetate, molasses, and other organic rich substrates, but such process is limited by the presence of nitrate, which is a preferred electron acceptor that consumes a large amount of chemicals (Tang et al., 2012a,b). Using an electrode as a non-exhaustible electron source to stimulate microbial perchlorate reduction has been studied. Studies showed that perchlorate-reducing bacteria could obtain electrons directly from the cathode or use electron shuttles as mediators to reduce perchlorate in the cathode chamber. Thrash et al. investigated *Dechloromonas* and *Azospira* species for perchlorate reduction with the assistance of electron shuttle AQDS (Table 3) (Thrash et al., 2007). Butler et al. used a denitrifying biocathode and obtained a maximum perchlorate removal rate of 24 mg/L/d and cathode conversion efficiency of 84% in lab scale experiments. They identified putative biocathode-utilizing perchlorate-reducing bacteria and confirmed that perchlorate reduction can be realized without additional electron mediators or applied electrode potentials (Butler et al., 2010). An earlier study also

Table 3
Bioelectrochemical system platform for remediation of perchlorate.

Pollutants (media)	Treatment	Inoculum	Poised potential	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Perchlorate (ClO_4^-) (groundwater)	Cathodic	Dissimilatory perchlorate reducing bacteria (DPRB)		0.09 g/L , 0.06 g/L/d	$\sim 100\%$	0			Thrash et al. (2007)
	Cathodic	An effluent from the biocathode of a denitrifying MFC, activated sludge, a chlorate-reducing enrichment from lake sediment, and a pure culture of <i>Dechloromonas</i> sp. PC1		$0.0001\text{--}0.02 \text{ g/L}$	$19\text{--}99\%$			0.8	Butler et al. (2010)

showed that perchlorate could be potentially removed by bacteria using low levels of H_2 produced at a poised cathode surface. Though using electrodes have many advantages over external chemical addition, including kinetic control, biofouling control, and low-cost, perchlorate research has not been active recently, so only a few feasibility studies have been reported so far (Thrash and Coates, 2008).

3.4. Azo dyes

Azo dyes are the most widely used synthetic dyes in textile, food, paper, leather, cosmetics, and pharmaceutical industries. Approximately 50% of the dyestuffs are discharged into water bodies that pose a great threat to natural environment and human health (Sudha et al., 2014). Azo dyes contain one or more azo groups ($-N=N-$), which are the most labile portions in the molecular structure that can be reduced and cleaved resulting in mutagenic or carcinogenic degradation products. Azo dyes are generally water-soluble, stable, and resistant to degradation, so their removal in traditional treatment systems is limited, but recent studies showed that many of the dyes, such as active brilliant red X-3B (ABRX3), congo red (CR), acid orange 7 (AO7), reactive blue 198 (RBU 198), acid black 172 (ABK 172), and methyl orange (MO), can be degraded in both anode chamber and cathode chamber of BES reactors (Chen et al., 2010; Liu et al., 2009; Mu et al., 2009a; Sun et al., 2009, 2012).

Co-metabolism has been demonstrated as the main removal mechanism for azo dye in the anaerobic anode chamber, or the anode side in the single-chamber BES or MFC. Under the anaerobic condition, the degradation of azo dyes happens in the presence of another compound (or carbon source) which is called the primary substrate (or co-substrate). Glucose is considered the optimal co-substrate in many studies, and other compounds, such as ethanol, acetate, pyruvate, molasses, rapeseed cake, corn-steep liquor, and confectionery wastewater (CW), have also been tested as possible co-substrate (Table 4) (Cao et al., 2010; Fernando et al., 2012; Sun et al., 2009). First, the primary substrate serves as the electron donor for EAB inhabited on the anode; then one portion of the electrons are transferred to the anode and then to the cathode for electricity production, while the other portion is used to reduce azo dyes. Therefore, the degradation of azo dyes in the anode chamber competes with the anode for electrons. Studies have found that larger anode surface area or membrane pore size could improve bacterial attachment and increase decolorization and power output (Hou et al., 2011b; Sun et al., 2012). The simultaneous addition of the co-substrate showed similar decolorization performance as compared to sequential addition, but it produced 75% higher power due to the acclimation of more efficient anodic communities (Hou et al., 2011a). Biocathode BES resulted in different anodic communities from traditional air-cathode and demonstrated higher decolorization rate (Hou et al., 2012), and a wetland-based cathode was found to improve the cathode potential with superior dye decolorization compared to non-planted or open-circuit controls (Fang et al., 2013).

Azo dyes can also be degraded in the BES cathode chamber by receiving electrons from the cathode electrode (Table 4). As shown in Fig. 3C, AO7 was removed at the cathode in a modified sleeve-type BES, with decolorization efficiency increased to more than 98% when the concentration of AO7 increased to 2.00 mM (Kong et al., 2013). Liu et al. ranked MO > Orange I > Orange II as azo-dye-feeding cathodes and concluded catholyte pH and dye structure are key factors affecting system performance (Liu et al., 2009). To enhance AO7 degradation rate, a poised cathode (-400 mV vs. SHE) was used and resulted in a decolorization rate as high as 13.18 ± 0.05 mol/m³/d (Mu et al., 2009a). Similar improvement could be achieved using photocatalytic rutile cathode, or by adding redox mediator thionine (Ding et al., 2010; Liu et al., 2011).

Fenton-like reactions could promote further azo dye degradation in BESs. Fe(II)-EDTA catalyzed persulfate catholyte provided a high oxidation potential for OG degradation (Niu et al., 2012) and FeVO₄ was

added in the catholyte to cleave the azo band and further mineralize the dye to CO₂ and H₂O (Luo et al., 2011). Other MFC-Fenton system was built with Fe³⁺ as the electron acceptor and its reduced product Fe²⁺ could promote the Fenton-like reaction to degrade amaranth (Fu et al., 2010). The enzyme, laccase, suspended in the catholyte was demonstrated to oxidize reactive blue 221 (RB221) for decolorization and reduce O₂ to H₂O for power generation (Bakhshian et al., 2011). In addition, because the azo bonds can be easily reduced in anaerobic condition while the aromatic amine products can be mineralized under aerobic condition, coupled anaerobic-aerobic processes such as sequential reactor plus microbial fuel cell system (A/O-MFC) or anode-cathode operation showed satisfactory removal of artificial azo dyes from wastewater (Kalathil et al., 2011; Z. Li et al., 2010).

3.5. Metals

Metal contaminated water poses various health and environmental concerns, as most metals are not biodegradable but rather accumulate in living tissues, which cause diseases and disorders (Olojo and Awoniran, 2012; Raskin et al., 1994). Different from the compounds discussed above, metals in water cannot be mineralized to CO₂ and H₂O, and they can only be transformed to a different valence. Because many metals have high market values, an ideal treatment strategy is not disposal but accumulating and recovering metals during the treatment process. The overall strategy of metal conversion in BESs is the use of the cathode electrode as the electron donor to reduce oxidized metal ions, and the metal products will either deposit on the cathode surface or precipitate at the bottom of the reactor for recovery. We recently categorized bioelectrochemical metal conversion into 4 different mechanisms (Table 5) (Wang and Ren, 2014): when a metal has a redox potential that is higher than the BES or MFC anode potential, the metal ion can be reduced directly, because the reaction is spontaneous. Studies have demonstrated that many metals including Au(III), Ag(I), Cu(II), V(V), Cr(VI), Fe(III), and Hg(II) can be reduced using this method. For example, precious metals such as Au(III) or Ag(I) were reduced to Au⁰ or Ag⁰ at the cathode without using external power. Moreover, maximum power outputs of 6580 mW/m² and 4250 mW/m² were produced in the reactors, respectively (Choi and Cui, 2012; Choi and Hu, 2013; Tao et al., 2012). Depending on the concentrations of the reactants, pH conditions and the availability of oxygen, Cu(II) could be reduced to Cu⁰ or other products, including Cu₂O, CuCl, Cu₄(OH)₆SO₄, or CuSO₄·3Cu(OH)₂ (Fig. 3D) (Heijne et al., 2010; Tao et al., 2011a,b,c; Z. Wang et al., 2010). Cr(VI) could be reduced to Cr₂O₃, Cr³⁺, Cr(OH)₃ (An et al., 2014; Huang et al., 2010; Huang et al., 2011a; Li et al., 2008, 2009; Wang et al., 2008), and V(V) could be reduced to V(IV) and reoxidized as the deposits of Na₃VO₄ and V₂O₅ (Zhang et al., 2009, 2012, 2015). The cathodic reduction of Hg(II) in MFCs was complex due to mixed products, including Hg₂²⁺, Hg⁰, and Hg₂Cl₂ (Z. Wang et al., 2011). For metals with lower redox potentials, an external power supply can be used to force the electrons still travel from the anode to the abiotic cathode, which will be used as the electron donor for metal reduction. Such metals include Ni(II), Pb(II), Cd(II), and Zn(II), etc. The voltage applied is generally less than 2 V, lower than traditional electrochemical processes. For example, by applying an external voltage of 0.5–1.1 V, up to $67 \pm 5.3\%$ of Ni(II) was reduced from an initial concentration of 500 mg/L (Qin et al., 2012), while without external voltage no Ni could be reduced due to its low redox potential of -0.25 V (vs. NHE). Changing applied voltages stepwise could lead to sequential reduction of mixed metals in one catholyte, with a sequence of Cu(II), Pb(II), Cd(II) and Zn(II) (Modin et al., 2012), or with applying one voltage, metal ions were reduced in different removal rates (Luo et al., 2014). The third and fourth mechanisms are associated with microbial reduction of metal oxides on the cathode, with or without using an external potential. Tandukar et al. developed a biocathode using a mixture of denitrifying and anaerobic cultures and found Cr(VI) reduction occurred with the maximum rate of 0.46 mg Cr(VI)/g VSS/h and the corresponding power density was

Table 4
Bioelectrochemical system platform for remediation of azo dyes.

Pollutants (media)	Treatment	Inoculum	Poised potential	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Active brilliant red X-3B (ABRX3) (wastewater)	Anodic	A mixture of aerobic and anaerobic sludge		0.3–1.5 g/L (0.5 g COD glucose, acetate, sucrose, or confectionery wastewater/L)	77–100%	11.2%, 80.1%		1	Sun et al. (2009)
	Anodic	Anaerobic sludge		0.150 g/L (0.18 g COD glucose/L)	91.24%	85.85%, 75.38%		35.3	Fang et al. (2013)
Reactive blue 198 (RBu198) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			14.4%			0.2	Chen et al. (2010)
Acid black 172 (ABk172) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			0			0.2	Chen et al. (2010)
Reactive red 198 (RR198) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			98.8%			0.2	Chen et al. (2010)
Acid yellow 42 (AY42) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			0			0.2	Chen et al. (2010)
Reactive blue 171 (RBu171) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			79.4%			0.2	Chen et al. (2010)
Reactive black 5 (RBk5) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			97.2%			0.2	Chen et al. (2010)
Reactive blue 160 (RBu160) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			97.2%			0.2	Chen et al. (2010)
Reactive green 19 (RG19) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			89.2%			0.2	Chen et al. (2010)
Reactive red 141 (RR141) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			92.7%			0.2	Chen et al. (2010)
Reactive yellow (RY84) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			75.3%			0.2	Chen et al. (2010)
Direct black 22 (DBk22) (wastewater)	Anodic	<i>Proteus hauseri</i> ZMd44			0			0.2	Chen et al. (2010)
Orange I (wastewater)	Cathodic			0.0175 g/L	0.025–0.267 $\mu\text{mol}/\text{min}$		1-Amino-4-naphthol, Sulfanilic acid	0.15	Liu et al. (2009)
Orange II, aka Acid orange 7 (AO7) (wastewater)	Cathodic			0.0175 g/L	0.0139–0.142 $\mu\text{mol}/\text{min}$		1-Amino-2-naphthol, Sulfanilic acid	0.15	Liu et al. (2009)
	Cathodic			0.05 g/L	62 \pm 5.8–91%	8.2–9.5%, 42%	Sulfanilic acid, 1-amino-2-naphthol, phenol, benzaldehyde, naphthalene, CO ₂ and H ₂ O	0.2	Luo et al. (2011)
	Cathodic		–0.35– –0.55 V (vs. SHE)	0.067–0.245 g/L	34.6 \pm 1.8– 98.7 \pm 2.5%	5%	Sulfanilic acid, 1-amino-2-naphthol	6.73	Mu et al. (2009a)
	Anodic	<i>Shewanella oneidensis</i> , anaerobic digested sludge and a mixed inoculum of anaerobic sludge and <i>S. oneidensis</i>		0.035–0.35 g/L (0.3 g sodium acetate, rapeseed cake, molasses and corn-steep liquor/L)	>98%		Sulfanilic acid, 1-amino-2-naphthol	0.3	Fernando et al. (2012)

	Cathodic		0.049–0.7 g/L	>98%		Sulfanilic acid, 1-amino-2-naphthol	0.4	Kong et al. (2013)
Congo red (CR) (wastewater)	Anodic	A mixture of aerobic and anaerobic sludge	0.3 g/L (0.5 g COD glucose/L)	0.0016–0.0115 g/L/h			0.512	Sun et al. (2012)
	Anodic	A mixture of aerobic and anaerobic sludge	0.3 g/L (0.5 g COD glucose, ethanol or sodium acetate/L)	>98%	27.5%, 11.7%	Aromatic amines	1	Cao et al. (2010)
	Anodic	A mixture of aerobic and anaerobic sludge	0.3 g/L (0.5 g COD glucose/L)	~90%			0.512	Hou et al. (2011a)
	Anodic	A mixture of aerobic and anaerobic sludge	0.1–0.3 g/L (0.5 g COD glucose/L)	0.0017–0.0048 g/h/L			0.512	Hou et al. (2011b)
	Anodic	A mixture of aerobic and anaerobic sludge	0.3 g/L (0.5 g COD glucose/L)	96.4%			0.512, 0.8	Hou et al. (2012)
	Anodic	Anaerobic sludge	0.1–0.2 g/L (1 g glucose/L)	42.7–77%		Aromatic amines	0.44	Z. Li et al. (2010)
Methyl orange (MO) (wastewater)	Cathodic		0.016 g/L	0.016–0.298 μ mol/min		Sulfanilic acid, <i>N,N</i> -dimethyl- <i>p</i> -phenylenediamine	0.15	Liu et al. (2009)
	Cathodic		0.01–0.02 g/L	37.8–73.4%	17.8%	Hydrazine derivatives	1.25	Ding et al. (2010)
Orange G (wastewater)	Cathodic		0.16 g/L	>99%	0	<i>p</i> -aminobenzenesulfonate	0.25	Liu et al. (2011)
	Cathodic		0.045 g/L	6.8–98.2%	0		0.5	Niu et al. (2012)
Amaranth (A.G.) (wastewater)	Cathodic		0.025–0.075 g/L	82.5–100%			0.16	Fu et al. (2010)
Reactive blue 221 (RB221) (wastewater)	Cathodic	Laccase	0.0415–0.1125 g/L	63.3–86.6%			0.5	Bakhshian et al. (2011)
Dye wastewater (wastewater)	Anodic	Aerobic sludge and dye wastewater	488 Pt–Co units	73%	66%		0.5	Kalathil et al. (2011)
	Cathodic	Dye wastewater	488 Pt–Co units	77%	51%		0.5	Kalathil et al. (2011)
Remazol brilliant blue BB (wastewater)	Cathodic	Bakery's wastewater	0.04 g/L, 0.08 g/L	94 \pm 1%			0.012	Kumru et al. (2012)
Remazol turquoise blue (wastewater)	Cathodic	Bakery's wastewater	0.04 g/L, 0.08 g/L	53 \pm 5%			0.012	Kumru et al. (2012)
Remazol black RL (wastewater)	Cathodic	Bakery's wastewater	0.04 g/L, 0.08 g/L	78 \pm 11%			0.012	Kumru et al. (2012)
Reactive red 195 (wastewater)	Cathodic	Bakery's wastewater	0.04 g/L, 0.08 g/L	74 \pm 2%			0.012	Kumru et al. (2012)
Reactive yellow 145 (wastewater)	Cathodic	Bakery's wastewater	0.04 g/L, 0.08 g/L	92 \pm 2%			0.012	Kumru et al. (2012)

Table 5
Bioelectrochemical system platform for remediation of metals.

Pollutants (media)	Treatment	Inoculum	Poised potential ^a	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Au ³⁺ (wastewater)	Cathodic			0.1–2 g/L	99.89%		Au ⁰	0.144	Choi and Hu (2013)
Ag ⁺ (wastewater)	Cathodic			0.05–0.2 g/L	99.91 ± 0.00–98.26 ± 0.01%		Ag ⁰	0.224	Choi and Cui (2012)
Cu ²⁺ (wastewater)	Cathodic			0.108 g/L	95%		Ag ⁰	0.13	Tao et al. (2012)
	Cathodic			0.01–0.2 g/L	60.1–99.9%		Cu ⁰	0.274	Z. Wang et al. (2010)
	Cathodic			1 g/L	99.88%, 99.95%		Cu ⁰	0.033	Heijne et al. (2010)
	Cathodic			0–6.4 g/L	70%		Cu ⁰ , Cu ₂ O, Cu ₄ (OH) ₆ SO ₄	2	Tao et al. (2011a)
	Cathodic			0.05–2 g/L	>96%		Cu ⁰ , Cu ₂ O, CuSO ₄ ·3Cu(OH) ₂	2	Tao et al. (2011b)
	Cathodic			0.6 g/L, 2 g/L	92%, 48%		Cu ⁰ , Cu ₂ O, CuCl	16	Tao et al. (2011c)
	Cathodic			0.8 g/L	84.3%		Cu ⁰	0.18	Modin et al. (2012)
	Cathodic		1.0 V	0.32 g/L, 0.576 g/L	99.2 ± 0.1%		Cu ⁰	0.063	Luo et al. (2014)
	Cathodic			0.05–0.5 g/L	99.5%		Cr ₂ O ₃ , Cr ³⁺	0.44	Li et al. (2008)
	Cathodic			0.025–0.2 g/L	74.6–100%		Cr ³⁺	0.5	Wang et al. (2008)
Cr ⁶⁺ (wastewater)	Cathodic			0.026 g/L	97%		Cr ³⁺	0.5	Li et al. (2009)
	Cathodic	Cr(VI)-contaminated soil		0.0128–0.0392 g/L	2.0 ± 0.1–2.4 ± 0.2 g/kg VSS/h	2.6%, 8.4%	Cr ³⁺	0.5	Huang et al. (2010)
	Cathodic	A mixed bacterial culture using Cr(VI) as an electron acceptor		0.02–0.05 g/L	12.4–20.6 g/kg VSS/h	10%	Cr ³⁺ , Cr(OH) ₃	0.24	Huang et al. (2011b)
	Cathodic			0.25 g/L	75.4 ± 1.9%		Cr ³⁺	0.5	Zhang et al. (2012)
	Cathodic	A mixture of denitrifying and anaerobic cultures enriched in the presence of Cr(VI)		0.022–0.063 g/L	100%		Cr ³⁺ , Cr(OH) ₃	0.46	Tandukar et al. (2009)
	Cathodic	Primary clarifier effluent	–0.15 V, –0.3 V, –0.45 V, +0.2 V (vs. SHE)	0.02 g/L	0.0197 g/L/d		Cr ³⁺ , Cr(OH) ₃	0.128	Huang et al. (2011a)
	Cathodic			0.1–1 g/L	<75.1 ± 3.8%		Cr ₂ O ₃	0.441	An et al. (2014)
	Cathodic			0.5 g/L	25.3 ± 1.1%		VO ²⁺	0.5	Zhang et al. (2009)
	Cathodic			0.25 g/L, 0.5 g/L	67.9 ± 3.1%		VO ²⁺	0.5	Zhang et al. (2012)
	Anodic, Cathodic	Anaerobic granular sludge		0.075 g/L, 0.15 g/L	76.8 ± 2.9%		V ⁴⁺	0.5	Zhang et al. (2015)
Hg ²⁺ (wastewater)	Cathodic			0.025–0.1 g/L	89.5–99.3%		Hg ₂ ²⁺ , Hg, Hg ₂ Cl ₂	0.24	Z. Wang et al. (2011)
Ni ²⁺ (wastewater)	Cathodic		0.5–1.1 V	0.05–1 g/L	99 ± 0.6–33 ± 4.2%		Ni ⁰	0.028	Qin et al. (2012)
	Cathodic		1.0 V	0.295 g/L, 0.531 g/L	97 ± 1.3%		Ni ⁰	0.063	Luo et al. (2014)
Fe ²⁺ (wastewater)	Cathodic		1.0 V	0.504 g/L	97 ± 1.8%		Fe(OH) ₂	0.063	Luo et al. (2014)
Pb ²⁺ (wastewater)	Cathodic		0.34 V	0.4 g/L	47.5%		Pb ⁰	0.18	Modin et al. (2012)
Cd ²⁺ (wastewater)	Cathodic		0.51 V	0.8 g/L	62%		Cd ⁰	0.18	Modin et al. (2012)
	Cathodic			0.0224 g/L	90%		Cd ⁰		Abourached et al. (2014)
Zn ²⁺ (wastewater)	Cathodic		1.7 V	0.3 g/L	44.2%		Zn ⁰	0.18	Modin et al. (2012)
	Cathodic			0.026 g/L	97%		Zn ⁰	0.012	Abourached et al. (2014)
Se ⁴⁺ (wastewater)	Cathodic			0.4 g/L	93 ± 4%		Zn ²⁺	0.1	Fradler et al. (2014)
				0.05 g/L, 0.4 g/L	99%		Se ⁰	0.012	Catal et al. (2009)
As ⁵⁺ (wastewater)				0.0003 g/L	0.0000098 g/L		As ³⁺	0.125	Xue et al. (2013)

^a Numbers without “+” or “–” mean extra voltage is only added across the electrodes.

Table 6
Bioelectrochemical system platform for remediation of carbon dioxide.

Pollutants (media)	Treatment	Inoculum	Poised potential	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Carbon dioxide (CO ₂) (air)	Cathodic	The solution from an anode chamber of an existing two-chamber MEC reactor which produces methane	−0.7–−1.2 V (vs. Ag/AgCl)		~210 mmol/d/m ²		CH ₄	0.6	Cheng et al. (2009)
	Cathodic	Anaerobic sludge	−0.65–−0.9 V (vs. SHE)	Flush with N ₂ /CO ₂			CH ₄ , H ₂	0.54	Villano et al. (2010)
	Cathodic	<i>Sporomusa ovata</i>	−0.4 V (vs. SHE)	Flush with N ₂ /CO ₂			Acetate, 2-oxobutyrate	0.4	Nevin et al. (2010)
	Cathodic	<i>Sporomusa silvacetica</i> , <i>Sporomusa sphaeroides</i> , <i>Clostridium ljungdahlii</i> , <i>Clostridium acetivum</i> , <i>Moorella thermoacetica</i> , <i>Acetobacterium woodii</i>		Flush with N ₂ /CO ₂			Acetate, 2-oxobutyrate, formate	0.4	Nevin et al. (2011)
	Cathodic	Brewery waste	−0.59 V (vs. SHE)	Flush with 100% CO ₂			CH ₄ , acetate, H ₂	0.3	Marshall et al. (2012)
	Cathodic	Supernatant from a previous reactor	−0.59 V (vs. SHE)	Flush with 100% CO ₂			Acetate, H ₂	0.3	Marshall et al. (2013)
	Cathodic	<i>Chlorella vulgaris</i>		CO ₂ produced from anode oxidation	100%		Biomass, oxygen	0.44	X. Wang et al. (2010)

55 mW/m² (Tandukar et al., 2009). Setting the biocathode potential at −300 mV (vs. SHE), Huang et al. reported the improved startup time, Cr(VI) removal rate and power production compared to those without the set potential (Huang et al., 2011a). Several new approaches are recently reported for metal removal and recovery, including removing As(III) by an MFC-zero-valent iron hybrid system (Xue et al., 2013) and recovering Zn(II) by coupling an MFC with Supported Liquid Membrane (SLM) (Fradler et al., 2014). Detailed information in bioelectrochemical metal conversion could be found from a recent review (Wang and Ren, 2014).

The remediation and recovery of metals using the BES platform is a new and promising approach, but most studies are still limited to the laboratory scale, with the exception of only one pilot study reported (Tao et al., 2011c). The primary challenge is that two-chamber reactor could be more efficient and specific for metal reduction in the cathode and organic oxidation in the anode, but in reality both contaminants are present together and hard to separate. However, when single chamber reactor is used, the high metal concentration may inhibit microbial activities and hinder all biodegradation processes (Abourached et al., 2014; Catal et al., 2009). Other unresolved problems include low catholyte pH, which may result in H₂ evolution and the separation of metal products from the electrodes. Economic and possible life cycle analyses are also suggested before potential scale-ups and applications.

4. Potential developments of BESs in environmental remediation

4.1. Carbon dioxide

Carbon dioxide (CO₂) is a primary greenhouse gas emitted through human activities, and its concentration has increased by more than 40%, from 280 ppm to nearly 400 ppm since industrial revolution. Because CO₂ accumulation has been widely viewed as a main driver of climate change, much research and development work has been conducted to capture CO₂ and convert it to useful products. In this context, the BES platform can be developed to capture CO₂ via bioelectrochemical reduction or algal sequestration at the cathode and concurrently generating value-added chemicals or energy.

The process of using electrons derived from the cathode to reduce CO₂ into methane or different organic compounds is called microbial electrosynthesis (MES) (Rabaey and Rozendal, 2010; Rabaey et al.,

2011; Villano et al., 2010). By using a poised cathode between −0.7 V to −1.0 V (Table 6), methane was produced from an MES reactor with abiotic anode and biocathode acclimated with *Methanobacterium palustre* (Cheng et al., 2009). Later studies found that multiple-carbon chemicals such as acetate or ethanol may also be produced using the similar concept. Nevin et al. found that when the cathode was acclimated by *Sporomusa ovata*, CO₂ could be reduced to acetate, 2-oxobutyrate, or formate by using the electrons from the electrode. By using a solar-powered potentiostat, they calculated that the captured solar energy was orders of magnitude more efficient than photosynthesis (Fig. 4A) (Nevin et al., 2010, 2011). Other studies showed that by using CO₂ as the only carbon source, acetate, methane, and hydrogen were formed by an autotrophic microbial community originated from brewery waste with a poised potential of −590 mV (vs. SHE) (Marshall et al., 2012, 2013). Different from MES, another process called microbial carbon capture cell (MCC) was developed by using algal cells to take in CO₂ at the cathode to produce biomass and O₂ (X. Wang et al., 2010). While using bioelectrochemical process to capture and convert CO₂ shows great potential, all of the studies so far have only demonstrated the feasibilities. Many scientific questions remain to be answered in terms of electrosynthesis mechanisms, kinetics, and products; logistical and economic feasibilities are also pressing challenges for larger scale production (Lovley and Nevin, 2011; Rabaey and Rozendal, 2010; Rabaey et al., 2011; Zhou et al., 2013).

4.2. Nutrients

Nitrogen and phosphorus in wastewater and contaminated ground-water cause eutrophication and other environmental and health concerns, and there has been a shift to recover these nutrient resources for farming rather than continue discharging them to already overloaded water bodies. Traditional nitrogen removal process includes aerobic nitrification followed by anoxic denitrification, with the first step requiring energy intensive aeration and the second one needing external organic substrates. As recently reviewed by Kelly and He, many different BES configurations and operations have been tested for partial or complete nitrogen removal, though most studies showed limited success (Kelly and He, 2014). Another review by Arredondo et al. provided economic and energy analysis to help researchers better design and operate BESs for ammonium recovery (Arredondo et al.,

Table 7
Bioelectrochemical system platform for remediation of nutrients.

Pollutants (media)	Treatment	Inoculum	Poised potential ^a	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
Ammonium (NH_4^+) (wastewater)	Cathodic		5–20 mA	1 g/L	94%, 79%		NH_3	0.18	Wu and Modin (2013)
	Cathodic	A mixed activated and digested sludge		0.028 g/L	96%		NO_3^-	0.8	Zhang and He (2012a)
	Cathodic	A mixed aerobic and anaerobic sludge		0.02–0.08 g/L	84–97%		NO_3^-	0.24	Zhang and He (2012b)
Nitrate (NO_3^-) (wastewater)	Cathodic	Mixed aerobic and anaerobic sludge and sediment	0–0.3 V	0.052–0.152 g/L/d	<0.146 g/L/d		N_2	1.3	Clauwaert et al. (2007)
	Cathodic	A mixed culture of denitrifying bacteria		0.518–0.66 g/L	2.3–4%		N_2 , NO_2^-	0.25	Lefebvre et al. (2008)
	Cathodic			0.595 g/L	0.0114 g NO_3^- /L/d	0.040 g NO_3^- /L/d	N_2	0.9	Morris et al. (2009a)
	Cathodic	Sludge	4.0 V	0.03 g/L	0.00044 ± 0.00008–0.00109 ± 0.00017 g/L/h	0.00008–0.00068 g/L/h	N_2 , NO_2^-	0.45	Feng et al. (2013)
	Cathodic	A mixed activated and digested sludge		0.025 g/L	66.7–89.6%		N_2	0.8	Zhang and He (2012a)
	Cathodic	A mixed aerobic and anaerobic sludge		0.05 g/L	50–90%		N_2	0.24	Zhang and He (2012b)
	Cathodic	Denitrifying sludge		0.055 ± 0.0002–0.0667 ± 0.0009 g/L	0.41 g/L/d		N_2	0.672	Virdis et al. (2008)
	Cathodic	A microbial consortium performing carbon and nitrogen removal	+0.1 V, 0 V, –0.1 V, –0.2 V (vs. SHE)	0.031 g/L	0.0036 ± 0.0004–0.006 ± 0.0003 g N/L/h		N_2 , N_2O	0.5	Virdis et al. (2009)
	Cathodic	A microbial consortium in the MFC performing carbon and nitrogen removal		0.407 g/L			N_2	0.672	Virdis et al. (2010)
	Anodic	Digested sludge	0 V, 0.5 V, 0.8 V, 1.0 V	0.0064, 0.0112, 0.0234, and 0.032 g/L	0.049 ± 0.004–0.268 ± 0.019 g NO_3^- -N/L/d	135.0 ± 3.9–158.5 ± 4.2 g NO_3^- -N/L/d	N_2	2	Tong and He (2013)
Nitrite (NO_2^-) (wastewater)	Migration		0 V or 0.8 V	21.4 ± 0.2, 50	55.6%, 60%	9.3%	NO_3^-	2	Tong and He (2014)
	Anodic			–	–		NO_3^-	0.46	Chen et al. (2014)
	Cathodic	An effluent from a parent MFC		0.0425 ± 0.0017 g/L	37 ± 5%		N_2 , NO_2^-	0.65	Puig et al. (2011)
Phosphate (wastewater)	Cathodic			0.015–0.97 g	<82%		Struvite	2.5	Fischer et al. (2011)
	Cathodic		0.75 V, 0.90 V, 1.05 V	0.38 g/L	20–40%	0	Struvite	0.028	Cusick and Logan (2012)

^a Numbers without “+” or “–” mean extra voltage is only added across the electrodes.

Table 8
Bioelectrochemical system platform for remediation of trace organic compounds.

Pollutants (media)	Treatment	Inoculum	Poised potential	Initial concentration	Removal efficiency		End-products	Reactor size (L)	Ref.
					Closed circuit	Control/open circuit			
26 TORCs (wastewater)	Anodic, cathodic, sorption	Anaerobic sludge		26 TORCs (500 ng/L), 1.24 g/L CH ₃ COONa	37.9–98.7%	3.8–98%		0.11, 0.24	Wang et al. (2015a)
10 TORCs (wastewater)	Anodic, sorption	Wastewater	−0.4 V (vs. Ag/AgCl)	10 TORCs (50 µg/L), 0.5 g/L CH ₃ COONa	14–100%	16–100%		0.028	Werner et al. (2015)

2015). One new mechanism of ammonia removal in BESs is to convert ammonium to volatile ammonia gas in high pH condition and then strip and recover ammonia in acid solution (Table 7) (Wu and Modin, 2013). Another way to remove nitrogen in BESs is similar to the conventional process, where ammonium is firstly oxidized by nitrifying bacteria either in a separated aerobic reactor or a single-chambered BES/MFC, and then the produced nitrate can be reduced using the cathode (Chen et al., 2014; Clauwaert et al., 2007; Feng et al., 2013; Lefebvre et al., 2008; Morris et al., 2009a; Zhang and He, 2012a,b). The biggest challenge of such simultaneous nitrification and denitrification (SND) process is dissolved oxygen, as it competes with nitrate for electrons. Several modified designs have been reported by using multiple chambers and sequential flows, but the systems were quite complex for scale-up (Virdis et al., 2008, 2010; Zhang and He, 2012a,b). Puig et al. found that both nitrate and nitrite can be used interchangeably as the electron acceptor for autotrophic denitrification at the cathode, but nitrite is oxidized via biological or electrochemical processes if oxygen is present (Puig et al., 2011). Nitrous oxide accumulation was found during the process, which is a potent greenhouse gas and could be a main electron loss that reduces Coulombic efficiency (Virdis et al., 2009). For treating nitrate present in groundwater, diluted nitrate could be firstly concentrated then removed through ion migration and denitrification (Tong and He, 2014), or by inserting a BES reactor into the contaminated aquifer and recirculating to achieve heterotrophic denitrification. External voltage was shown to improve nitrate removal by increasing the rate from 154.2 ± 24.4 to 208.2 ± 13.3 g NO₃[−]-N/m³/d (Fig. 4B) (Tong and He, 2013).

Conventional enhanced biological phosphorus removal (EBPR) is accomplished by polyphosphate-accumulating organisms (PAOs), which release phosphate in anaerobic phase and take in and store excess phosphate during the following aerobic stage. Phosphorus removal and recovery in BESs can be processed through electrochemical precipitation as struvite or magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O), which is a slow-release fertilizer. It was reported that phosphate was extracted by reducing iron phosphate (FePO₄) in the digested sewage sludge, and then the phosphate containing liquid

was stoichiometrically reacted with MgCl₂ and NH₄OH to precipitate struvite (Fischer et al., 2011). Struvite precipitation can be enhanced under a high pH condition (Cusick and Logan, 2012), or boosted by an external power supply. In an integrated photo-bioelectrochemical (IPB) system, phosphate could be removed in the cathode compartment by algal growth (Xiao et al., 2012).

While there have been different strategies to partially or completely remove nitrogen or phosphate from contaminated water, so far none of the process has been considered viable and scalable, partially due to the complex removal mechanisms of these nutrients. Most studies so far focused on nutrient removal from wastewater, yet few study actually investigated nutrient removal in contaminated aquifers or groundwater to remediate eutrophication.

4.3. Micropollutants

Micropollutants generally refer to trace organic compounds (TORCs) that are present in wastewater at very low concentrations (µg/L and ng/L). Traditional treatment processes are not designed to remove such pollutants, but their releases to water bodies have significant negative impacts on ecosystems and public health. The occurrence of micropollutants in wastewater is relevant to human activities including personal care products, pharmaceuticals, disinfection byproducts, and pesticides, which results in diverse properties of micropollutants regarding to biodegradability, molecular weight, hydrophobicity and charge state. While expensive advanced oxidation and membrane processes have been used to remove TORCs from water, there have been few studies investigating the feasibility of using the bioelectrochemical approach. However, we consider BESs can potentially be an effective process for micropollutant removal, because it provides a unique environment, where both oxidation and reduction reactions and different microbial communities and functions that may potentially remove TORCs with various characteristics. The potential integrated microbial-electro-chemical removal mechanism may enhance the TORC removal as well. In a recent study, we tested 26 micropollutants with various physico-chemical properties in single-chamber and two-chamber

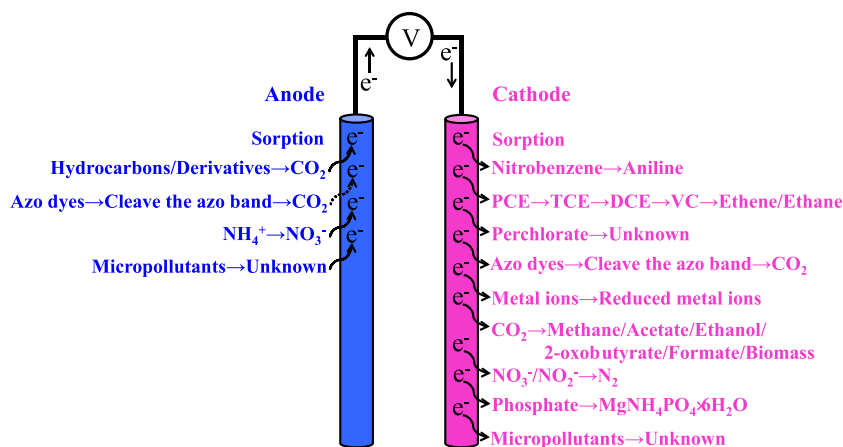


Fig. 2. Main degradation pathways of different types of contaminants at the electrodes in bioelectrochemical systems.

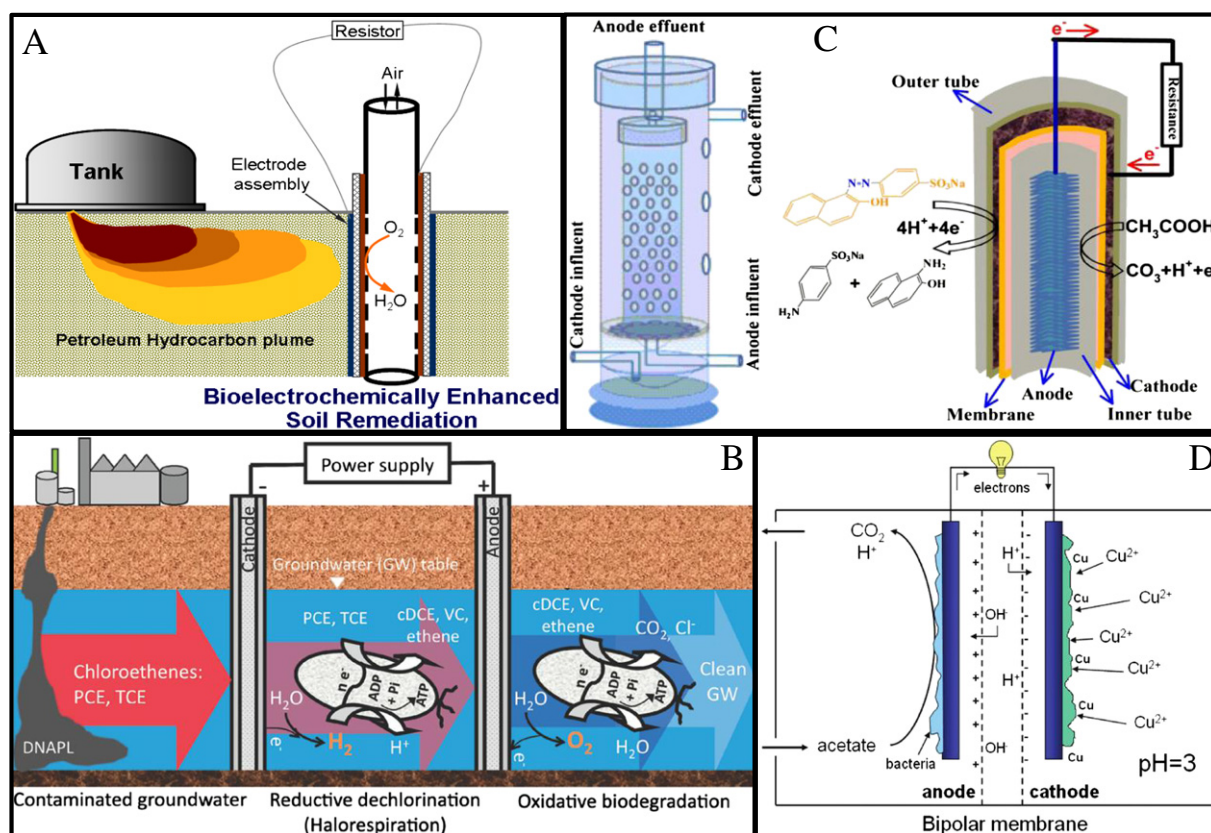


Fig. 3. Typical BES reactor configurations and applications in environmental remediation: (A) column design for hydrocarbon and derivative removal; (B) tubular design for chlorinated organic compound removal; (C) integrated azo dye degradation, and (D) BES metal removal. (Heijne et al., 2010; Kong et al., 2013; Lohner et al., 2011; Lu et al., 2014a).

MFCs. The results showed that low concentrations of micropollutants had no significant influence on power production. Both sorption (electrical and physical–chemical) and biodegradation are primary mechanisms for neutral TORC removal, and removal efficiencies were affected by the biodegradability probability and hydrophobicity properties of the compounds. Positively charged micropollutants were more easily removed than negatively charged micropollutants due to electrostatic interactions between the compounds and bacteria (Table 8 and Fig. 4C) (Wang et al., 2015a). Another study evaluated attenuation of 10 TORCs in both MFCs and MECs, and it was found that several TORCs were considerably attenuated due to sorption, and enhanced biotransformation was found for other TORCs (Werner et al., 2015). While these are only the beginning of exploring such feasibility, more studies are needed to investigate the removal mechanisms, functional bacterial communities, and system development.

5. Main factors influencing BES remediation performance

5.1. Contaminated matrix physical and chemical conditions

All bioremediation processes are influenced by the physical and chemical conditions of the contaminated matrix (e.g., soil, groundwater), especially for in situ bioremediation. The biodegradation rate and contact with a treatment are significantly affected by matrix pH, salinity, temperature, nutrient content, soil water content, and soil permeability (Atlas and Cerniglia, 1995; Leahy and Colwell, 1990). Specifically for BESs, the contaminated matrix typically requires water saturation for proton transfer from the anode to the cathode. Also, background nutrient content, especially N and P, would be required to be at levels that support anaerobic microbial activity. Soil remediation can be more challenging than groundwater remediation because soil types and textures significantly affect the permeability of oxygen and water and therefore

influence the mass transfer of ions and contaminants, leading to performance variations. Local climate can be another factor, as temperature fluctuation, moisture level, and seasonal changes can significantly affect microbial and electrochemical remediation process.

5.2. Functional microorganisms and community

Unlike the application of BESs for wastewater treatment, where common consortia of heterotrophs and EAB can be found almost everywhere, the microbial community for environmental remediation is generally quite specific, because specific groups of microbes are needed for the targeted contaminants, such as chlorinated solvents. As shown in Tables 1–8 and Fig. 1 and discussed above, many studies demonstrated that by using electrodes to provide or accept electrons can significantly facilitate the degradation of pollutants and produce energy, as compared with open circuit control or natural attenuation. This enhancement was hypothesized due to the accelerated electron transfer process by either a single species of bacteria that is capable of metabolizing both the contaminant and the electrode, or in most cases synergistic activities between the contaminant-catabolizing microorganisms and the electrochemically active bacteria on the electrode. For example, recent studies found that *Geobacter* spp. can form highly conductive networks of filaments that transfer electrons directly to the electrode or insoluble Fe(III) oxides as the electron acceptor, which not only allows hydrocarbon degradation but also enables real-time electricity production in a BES setup. This so-called direct extracellular electron transfer (DEET) mechanism can also happen in reverse direction, where bacteria directly accept electrons from the electrodes, or between microorganisms, where electrons can be exchanged in microbial syntrophic relationships to facilitate the bioremediation and energy generation (Lovley, 2011; Rabaey and Rozendal, 2010). Alternatively, electrons can be transferred by electron shuttles, including those

bacterial self-produced phenazines, riboflavins, etc., or externally provided ones, such as humic substances (Aulenta et al., 2008; Milliken and May, 2007; Park and Zeikus, 2000; Rabaey et al., 2005; Scott and Murano, 2007; Thurston et al., 1985). While people have gained much more understandings regarding to electron transfer from cells to the anode, little is known on the cathode side on how cells uptake electrons from the cathode. It was hypothesized that possible mechanisms may include direct contact and electron transfer like DEET, shuttle mediated process, or H_2 mediated conversion (Rabaey and Rozendal, 2010; Ren, 2013). Some reports have shown that mature bioanodes may be converted into biocathodes upon changing the operating conditions, which suggested the similar roles of electrochemical active bacteria during electron-releasing and electron-accepting processes (Cheng et al., 2010; Rozendal et al., 2008). However, a recent investigation based on gene expression and deletion analysis of *Geobacter sulfurreducens* indicated that the mechanisms of electron transfer from the electrode differed significantly from the mechanisms of electron transfer to the electrode (Strycharz et al., 2011).

Due to the complexity of environmental contamination, mixed culture of microorganisms is generally used in BES studies. It was found, however, that the community structure can shift greatly in response to the contaminants present in the environment. One study found that bacterial community previously acclimated with acetate changed its composition at the rate of 48% per week to adapt to the new electron donor of 1,2-Dichloroethane (1,2-DCA), and it removed up to 95% of the 1,2-DCA when the system was stable (Pham et al., 2009). Another study showed that the increase of nitrobenzene (NB) concentration changed the electricity-generating bacteria structure, which was clearly indicated by the shift of bands location of Denaturing Gradient Gel Electrophoresis (DGGE) gels (J. Li et al., 2010). Kumru et al. reported the similar results that a major change (63%) in microbial diversity happened when adding the first dye to the reactor, which was acclimated by bakery's wastewater and sodium acetate (Kumru et al., 2012). In a hydrocarbon BES study, high-throughput culture-independent 454-pyrosequencing indicated distinctive microbial communities at the anode, in soil with electrodes, and soil without electrodes. They found that *Comamonas testosteroni*, *Pseudomonas putida*, and *Ochrobactrum anthropi* were selectively enriched on the anode, while hydrogen oxidizing bacteria were dominant in soil samples (Lu et al., 2014a). Pure cultures were also used in feasibility studies. For instance, *Geobacter metallireducens* was reported to oxidize toluene and benzoate and use the anode as electron acceptor (Zhang et al., 2010). On the other side, the cathode has been used to donate electrons for the reduction of tetrachloroethene (PCE) and trichloroethene (TCE) by *G. lovleyi* or perchlorate by *Dechloromonas* sp. PC1 (Aulenta et al., 2009; Butler et al., 2010; Strycharz et al., 2008). In addition, the possible metabolic energy gained for the bacteria lies on the standard potential of electron donor or acceptor, so artificially poised potentials may pose a selective pressure to the mixed culture and force changes of microbial community,

which may lead to more productive communities and enhance system performance (H. Wang et al., 2012; Huang et al., 2011a).

5.3. BES reactor configurations

BES reactor configurations for environmental remediation tailor to specific application needs. Different from other BES applications such as wastewater treatment or chemical production, where enclosed containers are used, many remediation processes require open structured systems due to the non-aqueous nature of the media and the large area that needs to be covered. As discussed before, a simple configuration for sediment or saturated soil remediation can be a single conductive rod spans the anaerobic and aerobic zones like a snorkel, or a graphite plate anode buried in the sediment with suspended cathode in water (Zhang et al., 2010). Such simple systems have been shown enhancing the degradation of electron donor type of contaminants, such as petroleum hydrocarbons in the sediment, but performance was generally limited due to the large distance between the anode and cathode, which results in high resistance loss. Column or tubular configurations alleviated such problem and have also been shown more effective for same types of contaminants. A typical column BES can be constructed by wrapping an assembly of anode, separator, and cathode layers around a perforated tube, with the cathode layer facing inside and exposed to air, and anode facing outside exposed to contaminated soil or sediment. Such configuration greatly improved the compactness of the reactor, reduced intrinsic loss, and can be potentially integrated with current infrastructures such as monitoring wells or piezometers (Wu et al., 2013; Yuan et al., 2010).

For remediation of aqueous contaminants, enclosed systems have been tested in different operational patterns, such as flow through, recirculation, and multi-chamber integration. Dual-chamber BESs are widely used in lab scale studies, because separation of the anode and cathode by a membrane allows simple identification of reaction pathways for a specific contaminant. For example, most studies on the reduction of electron acceptor type of contaminants, such as metals, chlorinated solvents, or perchlorate, investigated only the cathode chamber reaction by employing the cathode as the potential electron donor. However, it may not be practical to build such reactors on the field, due to their high costs and limited capacity, so alternative approaches have been used. For example, one study inserted a cathode near a perchloroethylene (PCE) plume and an anode some distance away from the cathode (Lohner et al., 2011). By adding an extra power source, hydrogen gas can be generated on the cathode to reduce PCE to *cis*-dichloroethene (*cis*-DCE), vinyl chloride (VC) and ethene. When the water containing degradation products passes through the anode, the produced metabolites can be continuously oxidized to carbon dioxide by the oxygen generated on the anode. Another study injected acetate to stimulate bioreduction of U(VI) at the anode, while an air-cathode was installed 6 m away (Williams et al., 2010). U(VI)

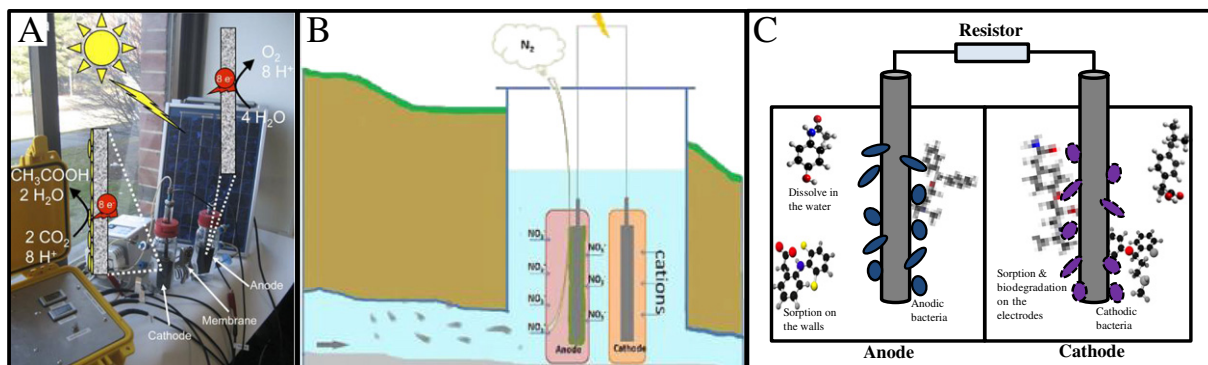


Fig. 4. Potential applications of BESs in environmental remediation: (A) carbon dioxide reduction; (B) groundwater nutrient removal, and (C) BES micropollutant degradation. (Nevin et al., 2010; Tong and He, 2013; Wang et al., 2015a).

was effectively removed with significant current production, which was hypothesized to be used for monitoring in situ microbial activity.

5.4. Co-generation of energy products

The generation of electricity and chemical energy carriers (e.g., H_2 , CH_4) from contaminant matrix treatment by BESs was discussed in the previous sections. For maximizing energy production, whether electrical or chemical, the use of expensive materials and catalysts is generally necessary. With the goal of reducing contaminant concentration in the shortest time possible, the use of BES materials for remediation needs to be cost effective, so BESs can maintain as an attractive alternative remediation technology for industries. Currently, the yield of electricity or chemical energy products generated by BESs is relatively low for the amount of contaminant that is removed. Also, the energy production is limited to the type of contaminant and the amount, where some contaminant removal processes will consume a significant portion of the energy. Again, because the goal of environmental remediation in most scenarios is to clean up an impacted environmental matrix, where the contaminant serves as the substrate for energy generation, it will ultimately be depleted and would not be expected to be replenished; therefore, generating energy from most environmental remediation applications would be temporary. Biomass or methane generation from remediating polluted gas, (i.e., high CO_2 content gas; see discussion in Section 4.1) could be an ideal application if both remediation performance and energy co-product generation are taken into the designs, thanks to the high continuous generation of the polluted medium. Nevertheless, despite the remaining challenges, BESs have demonstrated high potential as innovative alternative environmental remediation technologies, where the contaminant removal performance is the primary design concern.

5.5. Scale-up considerations for real-world applications

So far most BES studies were conducted in lab scale, but several groups have successfully demonstrated BES remediation in pilot scale as discussed in previous chapters and Tables 1–8. More scale-up studies are expected, and there are several key factors that need to be considered for real-world applications. For example, compared with BESs for wastewater treatment, the in situ field application for soil and groundwater remediation require more flexible BES configurations to adapt to different depths, soil matrix types, and other physical/chemical parameters. In addition, different contaminants are generally co-exist in soil, sediment, or groundwater, which may require integrated remediation strategy. So far most studies focused on removing one contaminant or mixed contaminants of the same type (electron donor or acceptor) in BESs, so more studies are needed to tackle co-existing yet different types of chemicals. In theory, BESs can be effective in degrading both reduced and oxidized contaminants, because reduced pollutants can be oxidized at the anode and oxidized contaminants can be reduced at the cathode, though extra energy maybe needed in some cases (Wang and Ren, 2013). Radius of influence (ROI) is another critical consideration for full-scale BES implementation, as each BES module is a “hot-spot” with the highest biodegradation activities, and its area of coverage determines the spacing and distribution of the array for remediation in a larger area. Electrode and separator materials should be biocompatible, conductive, low-cost, and resistant to corrosion. This can be more critical for remediation applications due to the higher metal concentration and long operation time in the subsurface. Lastly, how to effectively harvest, store, and utilize the BES produced energy during remediation processes can be another new area of research. The electrical current may serve as a real-time bioremediation indicator and powers wireless sensors for remote online monitoring that can significantly reduce operational cost.

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