Chapter 6
Recovery of Metals from Wastes Using Bioelectrochemical Systems

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6.1 Introduction

The decline of valuable metal resources, together with the increased future valuable metals demand, is likely to provide future impetus for increased metal recovery from wastes such as fly ash, sewage sludge, spent batteries, and electronic scrap materials, as well as hydroprocessing catalysts. The recovery and reuse of these wastes usually require the conversion from an insoluble to a soluble form. While a number of pyrometallurgical methods have been employed to achieve dissolution of the metal oxides, the emission of toxic gases into the environment, high energy costs, and associated expensive capital equipment costs decrease its desirable attraction. The hydrometallurgical process is thus more favorable from an environment conservation viewpoint. However, this process requires large amounts of reagents and thus augments the operational costs. In addition, it also results in the co-dissolution of other metals, increasing the complexity and cost of recovering value-added metals and treatment of unwanted elements. A biohydrometallurgical process or bioleaching offers attractive features for the extraction of metals from solid materials due to lower cost and energy requirements, environmental safety, and operational flexibility [1]. However, there are additional remaining challenges for using this approach, such as increasing leaching rates and reducing sludge generation. Electrochemical reduction is regarded as a potential strategy for the separation of the dissolved metals from solutions owing to multiple merits such as effectiveness, selectivity, robustness, versatility, controllability, less sludge production, easy operation, short retention time, reusability of the effluent, and amenability to automation and control [2]. However, electrochemical processes have high energy requirements

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and can require expensive catalysts to decrease electrode overpotentials. Development of more environmentally benign and less energy-demanding technologies would therefore be useful for treating these metal wastes and wastewaters with simultaneous value-added metal recovery.

Bioelectrochemical systems (BESs) is a newly developed technology for wastes and wastewaters treatment based on the integration of biological processes, electrochemical reduction, material science, engineering, and many related area together. BESs have recently attracted much attention owing to its high efficiency, low cost, environmental sustainability, and ambient operating temperatures with biologically compatible materials [3, 4]. BESs present potential opportunities for the microbially catalyzed conversion of electrical current into attractive value-added products, providing significant environmental benefits through the displacement of chemical production by conventional means [3–8]. Following this exploration, an emerging research field recovering metals from wastes using BESs, namely, metallurgical BESs, is being developed in an early stage and shows the most promising prospects due to its beneficial for both limited resource and environmental ecosystem. There are a few reviews about BES technologies for metal recovery [9–13]. In an effort to minimize overlap, this review gives a condensed overview of our current knowledge of metal recovery from wastes using these next-generation technologies, highlighting recent discoveries of the so-called self-driven BES processes for mixed metal recovery and discussing critically the influence of different processes and design parameters for recovery efficiencies.

6.2 Bioelectrochemical Systems (BESs)

A BES is called a microbial fuel cell (MFC) if electricity is generated and the overall reaction is exothermic. When the overall reaction is endothermic, power is needed to drive the non-spontaneous reaction, and this BES is regarded as a microbial electrolysis cell (MEC) [7]. It is reasonably believed that microbial electrosynthesis is being emerged as an alternative option to provide reducing/oxidizing power for biochemical production via electricity [4]. In terms of metal recovery, the specific cathodic condition in BESs provides preferable situation for metal reduction, and this metallurgical BES technology has thus widened the application range of BESs [14]. In the following sections, latest experimental results on bioelectroreduction for heavy metals and the developments of two aspects, namely, abiotic cathodes and biocathodes, will be briefly summarized. The newly developed MFC-MEC self-driven systems for multiple metal recovery will be emphatically discussed. Influencing factors and electron transfer mechanisms in these systems, as well as the scientific and technical challenges that have yet to be faced in the future, will be reviewed in detail.

6.3 Abiotic Cathodes

The reducing environment in the BES cathode, which is a sink for electrons originally coming from organic compounds in the anode, holds an advantage for the treatment of oxidized metal pollutants. In most cases, the oxidative electron acceptors contact with the electrode surface directly and receive the electrons released from the cathode. In addition, cathodic electrons can be also indirectly transferred through mediators such as anthraquinone analogues, riboflavin, Fe(III), and O_2 (Fig. 6.1 and Table 6.1) [15–52]. These direct and indirect electron transfer processes generally occur on the cathodes due to the high redox potentials of oxidative metal electron acceptors. Take the extensively explored Cr(VI) reduction in MFCs, for example (Table 6.1). Cr(VI) can be directly reduced to the less toxic $Cr(OH)^{2+}$ and $Cr(OH)_2^+$ in addition to $Cr(OH)_3$ on the abiotic cathodes of MFCs [15, 22]. Alternatively, Cr(VI) also indirectly accepts electrons through the in situ generated hydrogen peroxide from oxygen oxidation [15] or the external added riboflavin or Fe(III) [17, 18], which receives electrons either directly from the abiotic cathodes or via the mediator of anthraquinone-2,6-disulfonate. These mediated electron transfers explain the accelerated Cr(VI) reduction on the abiotic cathodes.

6.3.1 Individual Metal Recovery

By controlling operating conditions, some desirable metals or products can be generated from the cathode chamber. BESs thus could be used as not only an environmental remediation technology, but also a tool to produce metals from low-grade

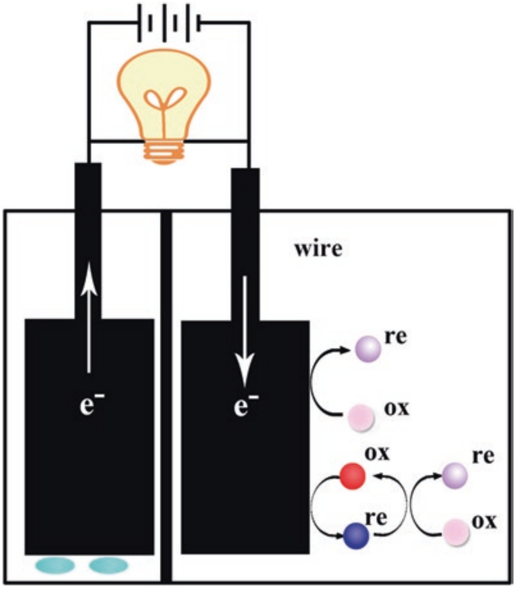

Fig. 6.1 Electron transfer pathways in the abiotic cathodes of BESs

Table 6.1 Metals removed/reduced in the abiotic cathodes of BESs

Type of substrate	Electron donor	Reactor	Anode	Cathode	Operation mode	Initial pH in catholyte	Electron acceptor	Removal/ reduction rate[a]	Product	Power production (W/m^3)[b] or applied voltage (V)[c]	References
Ag(I)	Acetate and yeast	Two-chamber MFC	Carbon fiber	Carbon cloth	Batch	7.0	Ag(I)	6.2–25	Ag	9.4[b]	[19]
Ag(I)	Acetate	Two-chamber MFC	Graphite plate	Graphite plate	Continuous	4.0	Ag(I)	18	Ag	9.8[b]	[20]
Ag(I) thiosulfate	Acetate	Two-chamber MFC	Graphite plate	Graphite plate	Continuous	10.0	Ag(I)	8.8	Ag and Ag_2O	3.2[b]	
Tetrachloroaurate	Acetate and yeast	Two-chamber MFC	Carbon fiber	Carbon cloth	Batch	2.0	Au(III)	8.3–15	Au	3.3–7.1[b]	[21]
Cr(VI)	Acetate	Two-chamber MFC	Graphite plate	Graphite plate	Batch	2.0	Cr(VI)	0.67	$Cr(OH)_3$	2.2[b]	[22]
	Acetate	Two-chamber MFC	Carbon felt	Graphite paper	Batch	2.5	Cr(VI)	8.1	$Cr(OH)_3$	16[b]	[23]
	Acetate	Two-chamber MFC	Graphite plate	Rutile-coated graphite	Batch with light irradiation	2.0	Cr(VI)	0.97	Not provided	0.25[b]	[24]
	Acetate	Two-chamber MFC	Graphite plate	Rutile-coated graphite	Batch in the dark	2.0	Cr(VI)	0.61	Not provided	0.12[b]	

	Glucose	Two-chamber MFC	Carbon felt	Carbon felt	Batch	2.0	$Cr(VI)+O_2$	2.9	Cr(III)	2.5^b	[15]
	Glucose and anthraquinone-2,6-disulfonate	Two-chamber MFC	Carbon felt	Carbon felt	Batch	2.0	$Cr(VI)+O_2$	4.9	Cr(III)	Not provided	
	Glucose	Two-chamber MFC	Carbon felt	Carbon felt	Batch	2.0	Cr(VI)	0.35	Cr(III)	0.3^b	
Cu(II)	Acetate	Two-chamber MFC	Graphite plate	Graphite foil	Continuous	3.0	Cu(II)	6.9	Cu	1.2^b	[14]
	Acetate	Two-chamber MFC	Graphite plate	Graphite foil	Continuous	3.0	$Cu(II)+O_2$	5.9	Cu	2.2^b	
	Glucose	Two-chamber MFC	Graphite plate or graphite felt	Graphite plate	Batch	4.7	Cu(II)	7.1	Cu	0.34^b	[25]
	Glucose	Membrane-free baffled MFC	Graphite plate or graphite felt	Graphite plate	Batch	7.0	Cu(II)	1.3–4.9	Cu and Cu_2O	$0.05–0.31^b$	[26]
	Acetate	Membrane-free MFC	Graphite felt	Graphite disk	Batch	2.0	Cu(II)	0.12–0.19	Cu and Cu_2O	$0.02–0.06^b$	[27]
	Acetate	Two-chamber MFC	Graphite felt	Graphite plate	Batch	9.0	Cu(II)	36	Cu and Cu_2O	3.8^b	[28]

(continued)

Table 6.1 (continued)

Type of substrate	Electron donor	Reactor	Anode	Cathode	Operation mode	Initial pH in catholyte	Electron acceptor	Removal/ reduction rate[a]	Product	Power production (W/m^3)[b] or applied voltage (V)[c]	References
	Acetate	One-chamber air-cathode MFC	Carbon fiber brush	Graphite rod	Batch	2.0	Cu(II)	13–15	Cu	18.8[b]	[29]
	Acetate	Four-chamber microbial desalination cell	Carbon felt	Graphite plate	Batch	3.0	Cu(II)	4.5–34.2	Cu and Cu_2O	1.0–5.0[b]	[30]
	Acetate	Two-chamber MFC	Graphite felt	Carbon rod, stainless steel mesh, titanium sheet, or copper sheet	Multiple batch cycle	2.0	Cu(II)	Carbon rod: 4.1 (1st cycle) −6.8 (12th cycle), stainless steel mesh: titanium sheet: 6.1 (1st cycle) −7.3 (12th cycle), copper sheet: 8.3 (1st cycle) −7.3 (12th cycle)	Cu	1.9–2.6[b]; 1.82–3.1[b]; 1.91–6.5[b]; 3.2–10.8[b]	[31]

Hg(II)	Acetate and yeast	Two-chamber MFC	Graphite felt	Carbon paper	Batch	2.0	Hg(II)	9.8	Hg	7.6^{b}	[32]
Mn(VI)	Glucose	Two-chamber MFC	Carbon paper	Carbon cloth	Batch	3.6	Mn(VI)	5.8	MnO_2	2.2^{b}	[33]
	Glucose	Bushing MFC	Carbon paper	Carbon cloth	Batch	3.6	Mn(VI)	Not provided	MnO_2	80^{b}	
V(V)	Glucose and Na_2S	Two-chamber MFC	Carbon fiber felt	Carbon fiber felt	Batch	2.0	V(V)	1.8	V(IV)	3.7^{b}	[34]
	Glucose and Na_2S	Two-chamber MFC	Carbon fiber felt	Carbon fiber felt	Batch	1.0	V(V)	1.8	V(IV)	3.9^{b}	[35]
Co(III)	Acetate	Two-chamber MEC	Graphite felt	Graphite felt	Batch	2.0	Co(III)	3.6	Co(II)	0.2^{c}	[36]
	Acetate	Two-chamber MFC	Graphite felt	Graphite felt	Batch	2.0	Co(III)	2.6	Co(II)	0.2^{b}	[37]
	Acetate	Two-chamber MFC	Graphite felt	Graphite felt	Batch	2.0	Co(III) catalyzed by Cu(II)	8.0	Co(II)	0.8^{b}	[38]
Co(II)	Acetate	Two-chamber MEC	Graphite felt	Graphite felt	Batch	6.2	Co(II)	7.9	Co and H_2	0.5^{c}	[39]

(continued)

Table 6.1 (continued)

Type of substrate	Electron donor	Reactor	Anode	Cathode	Operation mode	Initial pH in catholyte	Electron acceptor	Removal/ reduction rate[a]	Product	Power production (W/m^3)[b] or applied voltage (V)[c]	References
	Acetate	Two-chamber MEC	Graphite felt	Nickel foam	Batch	5.8–6.0	Co(II)	1.4–6.7	Co and H_2	0.2–0.7[c]	[40]
				Stainless steel woven mesh				2.5–6.5			
				Titanium sheet				3.0–6.7			
				Carbon cloth				2.5–7.0			
				Nickel foam + graphene				2.5–6.7			
	Acetate	Two-chamber MEC self-driven by MFC	Graphite felt in MFC and MEC	Graphite felt in MFC and carbon rod in MEC	Batch	2.0 in MFC and 6.0 in MEC	Co(III) in MFC and Co(II) in MEC	Co(III): 4.2; Co(II): 3.7	Co(II) in MFC and Co in MEC	–	[41]
Ni(II)	Acetate	Two-chamber MEC	Carbon felt	Stainless steel mesh	Batch	3.0–6.0	Ni(II)	13–19	Ni	0.5–1.1[c]	[42]

Zn(II)	Acetate	One-chamber air-cathode MFC with supported liquid membrane extraction	Carbon cloth	Carbon cloth coated with Pt	Batch	5.4	O_2	5.2	Zn(II)	4.5[a]	[43]
		One-chamber air-cathode MFC alone						2.8		1.9[a]	
Cr(VI), V(V)	Glucose	Two-chamber MFC	Carbon fiber felt	Carbon fiber felt	Batch	2.0	Cr(VI), V(V)	0.8	Cr(III) and V(IV)	6.2[b]	[44]
Cu(II), Pb(II), Cd(II), Zn(II)	Acetate	Two-chamber MEC	Carbon felt	Titanium wire	Batch	2 M HCl	Cu(II), Pb(II), Cd(II), Zn(II)	Cu(II): 8.9; Pb(II): 2.3; Cd(II): 2.8; Zn(II): 1.2	Cu, Pb, Cd, Zn	0–1.7[c]	[5]
Cu(II), Ni(II), Fe(II)	Acetate	Two-chamber MEC	Graphite brush	Carbon cloth coated with Pt	Batch	2.9	Cu(II), Ni(II), Fe(II)	Cu(II): 16, Ni(II): 6.3 Fe(II): 5.0	Cu, Ni, H_2	1.0[c]	[45]

(continued)

Table 6.1 (continued)

Type of substrate	Electron donor	Reactor	Anode	Cathode	Operation mode	Initial pH in catholyte	Electron acceptor	Removal/ reduction rate[a]	Product	Power production (W/m^3)[b] or applied voltage (V)[c]	References
Cr(VI), Cd(II)	Acetate	Two-chamber MEC driven by MFC	Carbon brush	Carbon cloth	Batch	2.0 and 6.0	Cr(VI), Cd(II)	Cr(VI): 0.5–1.0 Cd(II): 0.03–0.7	Cr(III) in MFC; Cd in MEC	–	[46]
Zn(II), Cd(II)	Acetate	One-chamber air-cathode MFC	Carbon cloth	Carbon cloth coated with Pt	Batch	7.0	O_2	Zn(II): 0.6–0.7 Cd(II): 0.5–0.7	ZnS and CdS	60.7–67.7	[47]
Cr(VI), Cu(II), Cd(II)	Acetate	Two-chamber MEC driven by MFC	Graphite felt in MFC and MEC	Carbon rod in MFC and titanium sheet in MEC	Batch	2.0	Cr(VI) in MFC, Cu(II) in MFC, and Cd(II) in MEC	Cr(VI): 7.0–7.2; Cu(II): 5.8–7.5; Cd(II): 3.2–3.6	Cr(III) in MFC; Cu in MFC, and Cd and H_2 in MEC	–	[48]
				Carbon rod in both MFC and MEC				Cr(VI): 8.5; Cu(II):7.6; Cd(II): 0.0			
	Acetate	Two-chamber MEC driven by MFC	Graphite felt in MFC and MEC	Carbon rod in MFC and titanium sheet in MEC	Continuous	2.0	Mixed influent of Cr(VI), Cu(II), and Cd(II)	Cr(VI): 0.3–1.3; Cu(II): 0.3– –1.3; Cd(II): 1.3	Cr(III) and Cu in MFC, and Cd in MEC	–	[49]

Cu(II), Co(II)	Acetate	Two-chamber MEC driven by MFC	Graphite felt in MFC and MEC	Carbon rod in MFC, carbon rod, stainless steel mesh, or titanium sheet in MEC	Batch	2.0	Cu(II) in MFC and Co(II) in MEC	Cu(II): 5.6, Co(II): 3.5, 3.3, or 3.8 (carbon rod, stainless steel mesh, or titanium sheet in MEC)	Cu in MFC and Co in MEC	–	[50]
Cu(II), Co(II) and Li(I)	Acetate	Two-chamber MEC driven by MFC	Graphite felt in MFC and MEC	Various mesh size stainless steel	Continuous	2.0	Mixed influent of Cu(II), Co(II) and Li(I)	Cu(II) or Co(II): 1.1, and Li(I): 0.3 (mesh size 60#)	Cu in MFC, Co in MEC, and Li(I) in effluent	–	[51]
Cu(II) and Cd(II)	Acetate	Two-chamber MFC shifted to two-chamber MEC	Graphite felt	Carbon rod, titanium sheet, or nickel foam	Batch	2.0	Mixed Cu(II) and Cd(II)	Cu(II): 4.8–4.9, Cd(II): 5.9 (carbon rod), 5.3 (titanium sheet) and 5.0 (nickel foam)	Cu in MFC mode, Cd and H_2 in MEC mode	6.4[b] in MFC mode 0.5[c] in MEC mode	[52]

[a] Calculated on the basis of net cathodic compartment (mg/L/h)

[b] Power output calculated on the basis of net cathodic compartment (W/m^3)

ores in hydrometallurgical processes. Great attention has been paid to the finding of metals possibly used as cathodic electron acceptors in BESs. Diverse aqueous metals including Cr(VI) [18, 22, 23], V(V) [34, 35, 44], Mn(VII) [33], Hg(II) [32], Ni(II) [42], Cu(II) [14, 25–31], Ag(I) [19, 20], Au(III) [21], and Co(II) [39, 40] have been individually reduced, whereas Cd(II) was removed through biosorption, and Zn(II) was formed as sulfides precipitation or separated through supported liquid membrane extraction in one-chamber air-cathode BESs [43, 47] (Table 6.1). This list does not seem to have an end so far. Besides aqueous metal ions, metals in dissoluble particles such as Co(III) in particles $LiCoO_2$, major component of the extensively applied lithium-ion batteries, can be also reduced on the cathodes of both MFCs and MECs [36, 37]. Cathodic electrons play a synergetic interaction with HCl for cobalt leaching, leading to the decrease of apparent activation energy of cobalt leaching in both MFCs (30.6 kJ/mol) [37] and MECs (16.6 kJ/mol) [36], in comparison with the 30.8–98.7 kJ/mol in open circuit controls (OCC). The presence of Cu(II) catalyst further decreases the apparent activation energy of cobalt leaching in MFCs to 11.8 kJ/mol [38]. These results demonstrate the more efficiency of BES technologies than conventional chemical processes, and thus provide new efficient approaches for recovery of metals in solid wastes and broaden the applicable BESs for recycling spent lithium-ion batteries. In terms of net energy production/consumption, BES technologies show appreciable advantages over conventional electrochemical processes due to the always free fuels in the anodes [4]. Taking silver metal, for example, an abiotic cathode MFC can achieve recovery of pure silver metal and electrical production at a rate of 0.0143 kWh per kg of silver (69.9 kg silver per kWh energy output) in comparison with an electricity spending of 3.81 kWh per kg of silver at an optimum condition in a conventional electrowinning [19]. Thus the use of abiotic cathode MFCs for metal recovery would be to use the "green" electricity produced in the MFC to supply power for electrowinning. This process has the advantage to keep the reactions take place in only one system and thus reduce the overall energy losses. Besides, abiotic cathode BESs can also achieve higher metal removal efficiency and product purity than conventional electrolysis reactors [20, 26, 27]. In terms of endurance to high metal concentrations and acidic environments, abiotic cathodes show advantages over biological processes, in which microorganisms can only endure to a certain metal concentration at neutral or close to neutral pHs, after which inhibition of the biological processes takes over [39, 53]. Another striking feature is that abiotic cathodes can work well at a wide range of metal concentration compared to either a maximal metal concentration for conventional biological processes or a minimal metal concentration required for conventional electrolysis process [20, 26, 27]. All of these aforementioned above demonstrate the advantages of BESs over conventional technologies for individual metal leaching and/or subsequent recovery from aqueous phase to solid phase.

6.3.2 Multiple Metal Recovery and Self-Driven BESs

While numerous initiatives have attempted to develop abiotic cathodes for individual metal recovery, there is a trend of switch to recover multiple metals, making BES a more practical application (Table 6.1). Species of V(V) and Cr(VI), co-present in wastewaters from vanadium mining and vanadium pentoxide manufacture, are recently proved to be, respectively, reduced on the abiotic cathodes of MFCs [44]. Cr(VI) is firstly reduced as an electron acceptor due to its higher electrochemical redox potential than V(V), which leads to Cr(VI) decreasing and Cr(III) depositing, and the electrochemical redox potential of V(V) then exceeds that of Cr(VI) and begins to act as an electron acceptor to be converted into soluble V(IV). This repeatable and alternative reduction of Cr(VI) and V(V) provides an applicable abiotic cathode MFCs for separating Cr(VI) from V(V) in practical wastewaters. Closely following this report and by varying the cathode potentials of MECs, multiple metals of Cu, Pb, Cd, and Zn are selectively and sequentially separated from a simulated municipal solid waste incineration ash leachate, providing an approach for cathodic recovery of metals from municipal solid waste incineration ash leachate [5]. Similarly, simulating fly ash leachate containing multiple metals of Zn(II), Pb(II), and Cu(II) can be also successfully recovered with Zn(0) and Pb(0) in electrolysis cells and Cu(0) in MFCs [54]. While Cu(0) and Ni(0) are deposited on the same cathodes of MECs at an applied voltage of 1.0 V [45], the Cu(0) deposited in MFC mode substantially enhances the subsequent Cd(II) reduction on the same cathode but in MEC mode [52], stressing the critical catalysis role of previously deposited copper in Cd(II) reduction. Cu(0) deposited on the cathodes of titanium sheet or stainless steel woven mesh has also been observed to improve electricity generation and Cu(II) removal from cathoyte of MFCs over prolonged time [31]. Obviously, competition of electrons among protons, Cu(II), Ni(II), and Fe(II) on the cathodes of MECs was also observed, explaining the delay of each metal ion reduction in comparison with individual Cu(II), Ni(II), or Fe(II) reduction on the same cathodes [45]. While MFCs or MECs as wastes treatment methods could be potentially used for treating ash leachates, metallurgical wastewaters, and landfill leachates, the products with multiple metals require the subsequent separation of these mixed metals unless otherwise specially used. In addition, these MFCs, MECs, and electrolysis cells were separately operated, in which not only electricity generated from MFCs was not utilized but also external applied voltages of 1.0–6.0 V were required for MECs and electrolysis cells [45, 54]. In view of this point and enlightened from MFC-MEC coupled system for hydrogen production [55], a self-driven MFC-MEC system successfully carried out the two processes of Co(II) firstly released from particles $LiCoO_2$ on the cathodes of MFCs and subsequently reduced on the cathodes of the connected MECs, which are completely powered by the cobalt leaching MFCs [41]. This self-driven system thus provides a new process of linking MFCs to MECs for complete recovery of cobalt and recycle of spent lithium-ion batteries with no any external energy consumption. To develop the concept of self-driven system, Cr(VI)-reduced MFCs and Cu(II)-reduced MFCs are connected in parallel or series to successfully power Cd(II)-reduced MECs with simultaneous Cr(VI), Cu(II), and Cd(II) recovery, despite the individual metal influents in each reactor units [48]. Appropriately adjusting the composite of mixed metals of Cr(VI), Cu(II), and Cd(II) under continuous operating condition can achieve complete separation of Cr(VI), Cu(II), and Cd(II) from the mixed influents using this self-driven MFC-MEC systems [49]. For W and Mo deposition, stacked MFC-MEC made of one MEC unit serially connected with three parallel-connected MFC units outperformed other modules, achieving depositions of 27.6% (W) and 75.4% (Mo) with a separation factor of 8.1 and hydrogen production of 0.34 m^3/m^3/day in the MEC unit, compared to 12.3% (W), 52.6% (Mo), and 7.9 (separation factor) in the MFC unit [56]. In the controls of either MEC or MFC unit only, only 15.3% (W) and 60.1% (Mo) (MFC only) and 12.9% (W) and 56.1% (Mo) (MEC only) were deposited from a mixture of W(VI) and Mo(VI). Thus, this process provides a truly sustainable strategy for applicable recovery of multiple metals from electroplating wastewater and ore dressing wastewater used during W and Mo extraction processes with no need for external energy input. Ingenious designs of self-driven MFC-MEC coupled systems together with appropriate influent composites, solution chemistry, and operation modes provide guarantee for sequential metal recovery and complete separation from mixed influents using these zero energy consumption technologies. While metals deposited on the electrodes may need to be peeled from the electrode to achieve their final recovery, the in situ utilization of these deposits for photocatalytic processes may become an attractive strategy for reuse, since many metal oxides exhibit excellent photocatalytic properties [56, 57]. Multiple parameters including initial metal concentration, initial pH, electrode material, electrode distance, exoelectrogenic activities, and the copresence of multiple electron acceptors can particularly affect system performance as well as final products. It is thus essential to discuss these parameters in the following sections.

6.3.3 Critical Factors Influencing System Performance

6.3.3.1 Initial Metal Concentration

A decrease in initial metal concentration resulted in a decrease in cathode potential and an increase in internal resistance of BESs. As a result, cell voltage, current density, and cathodic efficiency decreased as well [14, 19, 20, 25–27]. Thus a high initial metal concentration will generally benefit for BES system performance [14, 29, 30]. However, in view of reduction products, this high initial metal concentration can lead to the deficient cathodic reducibility, which may change the products formed. For example, high initial Cu(II) concentrations of 500–6400 mg/L have led to the formation of non-reductive product of $Cu_4(OH)_6SO_4$ compared to the reductive products of Cu_2O and Cu at a low initial Cu(II) concentration of 200 mg/L

[25–27]. It is thus essential to control initial metal concentration in order for the formation of desirable products and in particular the preferable low metal concentrations for pure reductive metals. However, even at the same initial concentration and the identical metal ion, the variety of metal compounds also affect metal reduction rate, power production, as well as product purity. For example, at identical initial Ag(I) concentrations in the same MFC reactors, species of Ag(I) ions achieved apparent higher reduction rate and power production than Ag(I) thiosulfate complex $(AgS_2O_3)^-$ in addition to the pure Ag in the former and trace Ag_2O in the latter (Table 6.1) [20], stressing the complexity of metal reduction on the cathodes as well as the importance of various metal compounds on system performance.

6.3.3.2 Initial pH

A comparatively high cathode pH is in favor of the reduction of oxidized contaminants that require higher pH, while a low cathode pH benefits to the reduction of oxidized substrates in need of more acidic conditions. In most cases, metal reduction in the abiotic cathode requires an acidic pH such as 2.0–3.0 (Table 6.1). For example, Cr(VI) was reduced to Cr(III) in the abiotic cathode MFCs, during which a low pH substantially improved reduction rate according to Eq. 6.1 [22].

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \tag{6.1}$$

However, in the case of Ag(I) reduction, the pH effect was dependent on the original form of Ag(I) electron acceptor, in which a higher pH of 10 was favorable for the reduction of Ag(I) thiosulfate complex than the pH 4.0 for ion Ag(I) [20]. Different from this, Co(II) reduction in MECs was improved at a range of 85–97% with an increase in initial pHs from 3.8 to 6.2, mainly due to the beneficial acidic environment for hydrogen-producing process and reasonably disadvantage to its electron competitor of Co(II) reduction [39]. These results in concert imply the complex interrelated effects of initial pH, original form of metal, and hydrogen evolution on reducing metals to the same final products. Besides the aforementioned above, the formations of reductive products are also influenced by initial pH. At the tested range of low pHs, pure crystals of copper [14, 25–27], vanadium [34, 35], and mercury [32] with no trace of other corresponding oxides and hydrates were formed on the cathodes because a high pH made these metal ions precipitate as metal oxide and was unavailable for reduction. Considering the fact of low pHs in these metal containing waste streams, the chemical conditions of such wastewaters are suitable for them to act as electron acceptors in the abiotic cathodes, which prefer low pHs and directly reduce metals from wastes with no pH adjustment. However, a bioanode covered by exoelectrogens was preferably operated at near neutral pH to achieve higher power generation from MFCs [4]. A bipolar membrane was therefore more effective to prevent the pH in the catholyte from increasing and the anolyte pH from dropping although part of the energy was lost for maintaining the pH difference [58].

6.3.3.3 Electrode Material

Cathode electrode materials and their design were the most challenging aspects of BESs using air as a final electron acceptor [4]. In this case, cathodic reactions took place on the three-phase surface of solid electrode, liquid catholyte, and gaseous oxygen. Increasing cathode surface area and retaining a small anode relative to the cathode area can keep cathodic reactions from limiting rates of electron transfer at the bioanode and therefore improve power production from MFCs [4]. For soluble metal reduction on the abiotic cathodes, a certain concentration of highly soluble metals such as Cu(II) >200 mg/L at acidic conditions can preserve faster mass transfer in comparison with the occurring of mass transfer limitations of oxygen as a result of low oxygen solubility in air-cathode MFCs [14]. The overpotential for soluble metal reduction is thus much lower than that of oxygen reduction reaction. Consequently, much more porous electrode materials commonly used in aqueous air-cathodes such as granule graphite and graphite felt are not always necessary for abiotic cathodes for recovery of metals at high concentrations. Instead, carbon-based cathodes with equally apparent sizes of anodes like graphite plate and graphite foil are usually accepted [14, 20, 25–27]. However, under the mediation of dissolved oxygen, which is heavily dependent on electrode materials, reduction of metal ions such as Cr(VI) is reasonably related with cathode materials [15]. In addition, metal ions at low concentrations exhibit high overpotentials, resulting in the occurrence of electron competition with other species. For example, hydrogen is well known to be evolved in MECs, and the efficiency is heavily dependent on electrode materials [59, 60]. As a consequence, the reduction of Co(II) as low as 50 mg/L in MECs is indirectly related with electrode material via competition with hydrogen evolution [40]. In view of these considerations, species in the catholyte such as dissolved O_2 or hydrogen evolution should be carefully investigated to ensure efficient metal reduction.

In the case of self-driven MFC-MEC system for multiple metal recovery and separation, cathode material in MEC is crucial for efficient metal recovery, morphology, and crystal form of final products due to its substantial effects on electrode potential and circuit current [48, 50, 51]. Carbon rod as the cathodes of MECs cannot lead to Cd(II) or Co(II) reduction inside regardless of the serial or parallel-connected Cr(VI)-reduced MFCs and/or Cu(II)-reduced MFCs, mainly ascribed to the unsatisfied low voltage output from the MFCs and the consequent high cathode potentials unfavorable for Cd(II) reduction in MECs [50]. Conversely, titanium sheet or stainless steel mesh is a suitable cathode material used successfully for proceeding Cd(II) or Co(II) reduction in MECs with simultaneous Cr(VI) and/or Cu(II) reduction in the serially or parallel-connected MFCs [50]. Even for the same material of stainless steel mesh, Mesh #60 instead of #20 and #120 can achieve the best and complete separation of Cu(II), Co(II), and Li(I) [51]. In addition, the morphology and crystal form of final Co(II)-reduced products are substantially different and heavily dependent on the MEC cathode materials of carbon rod, titanium sheet, and stainless steel mesh [50]. These results in concert stress the importance of MEC cathode materials for multiple metal recovery and separation in the self-driven MFC-MEC systems, which should be conditionally considered as the aforementioned.

6.3.3.4 Initial Concentration and Ratio of Different Metals

The ratios of different metals in the influent of MFC-MEC coupled system play critical roles in the separation of these metals from mixed influents. Mixed Cu(II) and Co(II) at a same concentration of 50 mg/L was firstly fed in the cathodes of MFCs, followed by the cathodes of the connected MECs. This sequential MFC-MEC cannot achieve the complete separation of Cu(II) and Co(II), leading to the mixed reduced products of Cu(0) and Co(0) on the same cathodes of MECs [50]. Similarly, metals of Cr(VI), Cu(II), and Cd(II) with each of 5 mg/L cannot be completely removed using the self-driven MFC-MEC system, whereas a composite of either 5 mg/L Cr(VI), 1 mg/L Cu(VI), and 5 mg/L Cd(II) or 1 mg/L Cr(VI), 5 mg/L Cu(II), and 5 mg/L Cd(II) can be completely and sequentially recovered from the mixed metals, illustrating the importance of metal composite and ratios for complete metal recovery and separation [49].

6.3.3.5 Electrode Distance

A properly closed anode and cathode distance can decrease internal resistance and thus improve electron transportation from anode to the cathode, and consequently benefit to completely metal reduction. For example, in a pilot and membrane-free MFC using Cu(II) as an electron acceptor, the internal resistance can be decreased from 1694 Ω at a distance of 65 cm to 304 Ω at 35 cm [25]. It was thus concluded that a close anode and cathode created a high circuit current and provided more sufficient electrons for Cu(II) reduction for pure copper, whereas the limited electrons or lower currents at a far anode and cathode distance resulted in the less reduced copper species such as partial Cu(II) reduction to Cu_2O or CuCl [25]. In terms of reactor size, however, a far anode and cathode distance is generally observed in large reactors and results in the consequent low system performances. For example, a large volume up to 16 L in pilot-scale membrane-free MFC substantially decreased system performance for both Cu(II) reduction and power generation compared to other smaller volume MFCs (Table 6.1) [25]. In view of practical application, scale-up reactors with large volumes will satisfy the requirement of large amount wastewater treatment. Based on these considerations, performance in stack cells where many small reactors are connected in parallel or in series may be an alternative choice. However, the variability in the capacity for individual reactor in the stack may lead to voltage reversal in some reactors [61]. In view of this point, a same hydraulic condition and a same substrate concentration are beneficial for less voltage reversal [62]. In addition, various types of control circuit for each cell in the stack system may also avoid this phenomenon [63]. Much effort is still in great need along this direction for more efficient and practically applied metal recovery from wastes.

6.3.3.6 Exoelectrogenic Activities

Cathodic electrons originally come from organic compounds oxidized by exoelectrogens on the anodes. Exoelectrogenic activities reasonably affect metal reduction on the abiotic cathodes. For example, bioanodes catalyzed by either *Shewanella decolorationis* S12 or *Klebsiella pneumoniae* L17 exhibited slower Cr(VI) reduction than anaerobic activated sludge, mainly ascribed to their different exoelectrogenic activities [15]. In the case of Co(III) reduction on the abiotic cathodes, exoelectrogenic activities were substantially different from those using pentachlorophenol as an electron acceptor in the cathodes in spite of their similar microbial community compositions [37, 64], stressing the changes of exoelectrogenic activities with cathodic electron acceptors. While bacterial community collaboration may occur among many other bacteria and exoelectrogens on the anodes [4, 65], exoelectrogenic activities in linkage with cathodic metal acceptors have attracted less attention. Further investigation of the exoelectrogenic activities of bacteria with diverse metal reductions on the cathodes is still needed.

6.3.3.7 Other Electron Acceptors

Other electron acceptors such as oxygen can heavily affect system performance due to its higher redox potential and competitive ability than the metals present in the cathode. In the case of Cu(II) or Co(II) reduction, the presence of oxygen also consumed electrons and consequently resulted in adverse effects on Cu(II) or Co(II) reduction as well as low cathodic efficiencies [14, 40]. For W(VI) and Mo(VI) deposition in MFCs, however, the presence of oxygen can enhance W and Mo deposition through the in situ produced H_2O_2 and the consequent predominant peroxotungstate and peroxo-polymolybdate despite the always occurrence of competition between oxygen reduction and metal deposition for H^+ ions [66]. The purity of reduced products was also dependent on aerobic and anaerobic environments, where pure copper crystals were attributable to the anaerobic condition, and CuO and Cu_2O other than Cu(0) were formed under an aerobic environment [25–27]. In terms of power production, it is understandable that the multiple electron acceptors of oxygen and Cu(II) had higher current densities than the Cu(II) individually due to a high redox potential of 0.8 V for oxygen [13, 14]. In fact, in view of oxygen reduction, copper here may also function as a catalyst, although the catalysis mechanism was still unclear [14]. Quantitative competition between metal ions and other electron acceptors for electrons transferred from the anode may need to be further reinforced to stress the greater efficiencies and advantages of abiotic cathodes compared to conventional processes for metal recovery.

6.4 Biocathodes

6.4.1 Recovered Metal

While an abiotic cathode employed as a direct electron donor in the reduction of metals has been proposed, development of microbially catalyzed cathodes (microbial cathodes or biocathodes) revealed that certain electrochemically active bacteria (electrotrophs) are capable of “picking” electrons from the surface of cathodic electrodes and using them to metabolically reduce the oxidative metals in the catholytes. The use of bacteria can avoid some of the drawbacks such as much acidic condition and low sustainability in abiotic cathodes [67, 68]. Metal reduction on the biocathodes can be dated back to 2005, in which Gregory and Lovley [69] demonstrated the occurrence of U(VI) reduction on a graphite plate cathode at a poised potential of −0.3 V (vs SHE) under the catalysis of either *Geobacter sulfurreducens* or enrichment culture (Table 6.2). A substantially higher U(VI) reduction rate of 0.58–0.77 mg/L/h with the presence of *G. sulfurreducens* implies the preferable *G. sulfurreducens* instead of enrichment culture to U(VI) reduction. The pure culture of *G. sulfurreducens* can get energy from reducing or adding electrons to U(VI) and reduce uranium dissolved in groundwater and thus make this metal much less soluble and abate the spread of its contamination. Similar to U(VI) reduction, *Shewanella species* was recently proved to use electrode as electron donor for Cr(VI) reduction [17, 70]. Instead of pure culture, Tandukar et al. [71] constructed a complete biological MFC with mixed culture at both the anode and the cathode and achieved a Cr(VI) reduction rate of 0.17–0.42 mg/L/h on the cathode with spontaneous electricity production of 0.9 W/m^3 (Table 6.2). The Cr(VI)-reducing biocathode was further demonstrated with preferable electrode materials for electrotrophic attachment [67], modifications to reactor architecture [72], and minimization of start-up period and enhancement of system performance [73]. The newly established biocathode MECs dominantly composed of *G. psychrophilus*, *Acidovorax ebreus*, *Diaphorobacter oryzae*, *Pedobacter duraquae*, and *Prolixibacter bellariivorans* provide a new approach for aqueous Co(II) recovery concomitant with production of other biomaterials such as gaseous methane and liquefied acetate [53]. Besides metal recovery and other biomaterials production with simultaneous wastes treatment and environmental remediation, another potentially applicable field for biocathodes is metal nanoparticles synthesis, which is a very exciting field because of its potential application in bioenergy, catalysis, electronics, optics, medicine, and environmental remediation. While a large number of bacteria including *Shewanella oneidensis* have been illustrated to act as nanofactories, showing advantages over chemical methods due to the consumption of strong reducing agents and large quantities of chemicals that can contaminate the nanoparticles [74], biocathodes are expected to develop microbial consortia or pure culture exhibiting both electrotrophic activities and synthesizing metal nanoparticle abilities [75]. However, this concept is still not extensively proved in BESs, and metal-reducing biocathodes are demonstrated in very limited literature (Table 6.2), in which only metals of U(V), Cr(VI), Se(VI), Co(II), Cu(II), and Cd(II) together with a narrow range of operating conditions including initial metal concentration, initial pH, anodic acetate dose, cathodic electrode material, and optimal start-up time were reported [69–73, 76–85]. In addition, OH^- generated from oxygen-reducing biocathode MFCs in situ reacted with Co(II) to form precipitated $Co(OH)_2$, providing a new clean approach for the production of cobalt dihydroxide with simultaneous electricity generation (Table 6.2) [81]. It is very recent that a directed production of selenium-containing nanoparticles in *S. oneidensis* MR-1 cells, with fine-tuned composition and subcellular synthetic location, was achieved by modifying the extracellular electron transfer chain, leading to the development of fine-controllable nanoparticles biosynthesis technologies [75]. Much work is still needed to be paid on this emerging alternative and inexpensive technology for devising new microbial cathode systems for efficient metal reduction and broadening applicable fields of BESs as well. On the other hand, the recovery of metals by biocathodes will likely not displace existing methods of electrochemical or chemical-physical processes, especially for high-strength metal recovery, because of detrimental effects of high concentration of metals on electrotrophic activities. Biocathodes will likely be more appropriate for treatment of relatively low-strength or dilute metal effluents [53, 81, 85]. The overall advantages of biocathodes for recovery of metals from wastes could make them an important method for metal reduction in the near future. Factors including bacterial origin and evolution, initial pH, and metal concentration can particularly influence biocathode performance since environmental conditions can shape microbial consortia in terms of various bacterial roughness, biocompatibilities, electron transfer efficiencies, and stimulus to microbial consortia [53]. In addition, electron transfer mechanisms on the biocathodes, properly different from the bioanodes, are still debatable [68, 86]. In the following sections, these aspects in linkage with metal recovery will be in particular addressed.

6.4.2 Bacterial Origin and Evolution

Microbial consortia inoculated from different sites exhibit various Cr(VI) reduction rates, in which bacteria from a wastewater treatment plant achieved a specific Cr(VI) reduction rate of 0.30 mg/g biomass/h [71] compared to 2.4 mg/g biomass/h obtained from a Cr(VI) contaminated site [72]. Although other factors including reactor architecture and electrode material may also contribute to these differences in Cr(VI) reduction rate, microbial consortia well developed at a Cr(VI) contaminated site is presumably more adaptive and favorable for the Cr(VI) environment in the biocathodes and thus attribute to more efficient Cr(VI) reduction [72]. Further

Table 6.2 Metals removed/reduced in the biocathodes of BESs

Electron acceptor	Biocatalyst	Mediator	Reactor	Anode electrode	Cathode electrode	Carbon source in catholyte	Operation mode	Initial pH	Removal/ reduction rate^{a}	Product	Power production (W/m^{3})^{b}, poised potential (V)^{c} or applied voltage (V)^{d}	References
U(VI)	*Geobacter sulfurreducens*	–	Two-chamber	Graphite plate	Graphite plate	$NaHCO_3$	Batch	6.9	0.58–0.77	U(IV)	–0.3^{c}	[69]
	Enrichment culture	–	Two-chamber	Graphite plate	Graphite plate	$NaHCO_3$	Batch	6.9	0.02	U(IV)	–0.3^{c}	
Cr(VI)	Enrichment culture	–	Two-chamber	Graphite plate	Graphite plate	$NaHCO_3$	Batch	7.2–7.6	0.17–0.42	$Cr(OH)_3$	0.9^{b}	[71]
	Enrichment culture	–	Two-chamber	Graphite plate	Graphite granule	$NaHCO_3$	Batch	7.0	4.4–5.3	$Cr(OH)_3$	2.4^{b}	[72]
	Enrichment culture	–	Two-chamber and tubular	Graphite fiber	Graphite granule	$NaHCO_3$	Batch	7.0	3.5	$Cr(OH)_3$	2.0^{b}	[73]
		–	Two-chamber and tubular	Graphite fiber	Graphite felt	$NaHCO_3$	Batch	7.0	3.1	$Cr(OH)_3$	3.8^{b}	
		–	Two-chamber and tubular	Graphite fiber	Graphite fiber	$NaHCO_3$	Batch	7.0	3.6	$Cr(OH)_3$	4.5^{b}	
	Shewanella oneidensis MR-1	–	Two-chamber	Reticulated vitreous carbon	Reticulated vitreous carbon	–	Batch	7.0	0.04	$Cr(OH)_3$	0.03^{b}	[70]

(continued)

Table 6.2 (continued)

Electron acceptor	Biocatalyst	Mediator	Reactor	Anode electrode	Cathode electrode	Carbon source in catholyte	Operation mode	Initial pH	Removal/ reduction rate[a]	Product	Power production (W/ m^3)[b], poised potential (V)[c] or applied voltage (V)[d]	References
	Shewanella putrefaciens W3–18-1	–	Two-chamber	Reticulated vitreous carbon	Reticulated vitreous carbon	–	Batch	7.0	0.04	$Cr(OH)_3$	0.16[b]	
	Shewanella amazonensis SB2B	–	Two-chamber	Reticulated vitreous carbon	Reticulated vitreous carbon	–	Batch	7.0	0.03	$Cr(OH)_3$	0.13[b]	
	Shewanella sp. ANA-3	–	Two-chamber	Reticulated vitreous carbon	Reticulated vitreous carbon	–	Batch	7.0	0.04	$Cr(OH)_3$	0.08[b]	
	Shewanella loihica PV-4	–	Two-chamber	Reticulated vitreous carbon	Reticulated vitreous carbon	–	Batch	7.0	0.03	$Cr(OH)_3$	0.03[b]	
	Shewanella sp. MR-4	–	Two-chamber	Reticulated vitreous carbon	Reticulated vitreous carbon	–	Batch	7.0	0.03	$Cr(OH)_3$	0.08[b]	
	Shewanella oneidensis MR-1	Riboflavin	Two-chamber	Graphite felt	Graphite felt	Lactate	Batch	7.0	1.3–2.0	$Cr(OH)_3$ and Cr(III)-lactate	–0.3[c]	[17]
	–	Riboflavin	Two-chamber	Graphite felt	Graphite felt	Lactate	Batch	7.0	0.17	$Cr(OH)_3$ and Cr(III)-lactate	Not provided	
	–	–	Two-chamber	Graphite felt	Graphite felt	Lactate	Batch	7.0	0.13	$Cr(OH)_3$ and Cr(III)-lactate	0.43[b]	

	Stenotrophomonas sp. YS1	–	Two-chamber	Graphite felt	Graphite felt	$NaHCO_3$	Batch	5.8	2.9	Intracellular Cr(III) ions	1.0	[76]
	Stenotrophomonas maltophilia YS2								3.0	Intracellular Cr(III) ions	1.2	
	Serratia marcescens YS3								3.4	Intracellular Cr(III) ions	2.9	
	Achromobacter xylosoxidans YS8								3.1	Intracellular Cr(III) ions	1.6	
Cu(II)	*Stenotrophomonas maltophilia* JY1	–	Two-chamber	Graphite felt	Graphite felt	$NaHCO_3$	Batch	5.8	2.9	Intracellular Cu(II) ions	0.4	[77, 78]
	Citrobacter sp. JY3								3.5	Intracellular Cu(II) ions	0.4	
	Pseudomonas aeruginosa JY5								3.6	Intracellular Cu(II) ions	0.5	
	Stenotrophomonas sp. JY6								3.6	Intracellular Cu(II) ions	1.1	
Cd(II)	*Ochrobactrum* sp. X1	–	Two-chamber	Graphite felt	Graphite felt	$NaHCO_3$	Batch	5.8	3.1	Intracellular Cd(II) ions	0.5^{d}	[79]
	Pseudomonas sp. X3								3.3	Intracellular cd(II) ions	0.5^{d}	
	Pseudomonas delhiensis X5								3.2	Intracellular Cd(II) ions	0.5^{d}	
	Ochrobactrum anthropi X7								3.1	Intracellular Cd(II) ions	0.5^{d}	

(continued)

Table 6.2 (continued)

Electron acceptor	Biocatalyst	Mediator	Reactor	Anode electrode	Cathode electrode	Carbon source in catholyte	Operation mode	Initial pH	Removal/ reduction rate[a]	Product	Power production (W/ m^3)[b], poised potential (V)[c] or applied voltage (V)[d]	References
Se(IV)	Enrichment culture	–	One-chamber air-cathode MFC	Carbon cloth	Carbon cloth coated with Pt	Glucose	Batch	7.0	1.3	Se	25[b]	[80]
						Acetate			0.47		18[b]	
Co(II)	Enrichment culture	–	Two-chamber	Graphite felt	Graphite felt	$NaHCO_3$	Batch	6.2	2.9	Co	0.2[d]	[53]
	Enrichment culture	–	Two-chamber oxygen-reducing MFC	Graphite felt	Graphite felt	Acetate	Batch	5.6	4.7	$Co(OH)_2$	1.5[b]	[81]
	Enrichment culture	–	Two-chamber MFCs driven by MECs	Graphite felt	Graphite felt	$NaHCO_3$	Batch	MFC: 2.0	Cu: 6.0	MFC: Cu	0.0	[82]
								MEC: 6.2	Co: 5.3	MEC: Co		
Cd(II)	M	–	Two-chamber	Graphite felt	Graphite felt	$NaHCO_3$	Batch	5.8	6.56	Cd and Cd(II)	0.5[d]	[83]
						Acetate			7.33			

Cr(VI), Fe(III)	Enrichment culture	–	One-chamber air-cathode MFC	Carbon brush	Carbon cloth coated with Pt	Acetate	Batch	6.5	Cr(VI): 0.08	Cr(III)	0.8–1.3[b]	[84]
									Fe(III): 0.4			
Cr(VI), Cu(II), Cd(II)	Enrichment culture	–	Two-chamber MFC and MFC	Graphite felt	Graphite felt	$NaHCO_3$	Batch	5.8	Cr(VI): 1.24	Cr(III)	0.45–0.58[b]	[85]
									Cu(II): 1.07	Cu	0.5[d]	
									Cd(II): 0.98	Cd		

[a] Calculated on the basis of net cathodic compartment (mg/L/h)

[b] Calculated on the basis of net cathodic liquid volume (W/m^3)

[c] vs standard hydrogen electrode (SHE). Values reported vs Ag/AgCl were converted to SHE by adding 0.195 V

exploration should use the same reactor architecture with identical electrode material to compare effects of different bacterial origins on metal reduction in order to deeply understand relations between microbial consortia and metal reduction.

Another important issue about the catalysts of microbial consortia is the efficient evolution strategies for specific microbial consortia. It has long been recognized that mixed species biofilm of *Klebsiella pneumoniae*, *Pseudomonas fluorescens*, and *Pseudomonas aeruginosa* grown in a flow cell fitted with two platinum wire electrodes remained changeable with the alternative anode and cathode. The biofilm expanded by approximately 4% when the wire was cathodic but was reduced to 74% of the original thickness when the wire was anodic, explained by electrostatic interactions between negatively charged groups in the biofilm and the charged wire which caused biofilm expansion when the wire was cathodic and contraction when the wire was anodic [87]. It is thus reasonably feasible to apply an optimal selected cathode potential for shortened start-up period and enhanced Cr(VI) reduction on the biocathodes of MFCs [73] based on the roles of applied electrode potential on microbial physiology, which include changing the cell surface properties, increasing the enzyme activity, as well as shortening the doubling time of the bacteria [88]. Similarly and in the case of Co(II) reduction on the biocathodes of MECs, applied voltages of 0.1–0.7 V achieved different cathode potentials, electric currents, and cathodic distributions of charges for Co(II) reduction, hydrogen evolution, methane and acetate production, as well as bacterial growth [53], reasonably resulting in diverse microbial community compositions. However, at the same applied voltage of 0.2 V, the composition of bacterial community developed for 1 month exhibited a somewhat shift from that evolved for 3 months in spite of similar Co(II) reduction [53]. Different from the strategy of applied voltage for bacterial community, carbon sources of acetate or $NaHCO_3$ at long-term bacterial community acclimation (6 months) and elevated Cd(II) concentrations (20–50 mg/L) can also enhance Cd(II) removal with simultaneous hydrogen production [83]. Cd(II) removal of 7.33 mg/L/h (acetate) and 6.56 mg/L/h ($NaHCO_3$) and hydrogen production of 0.301 m^3/m^3/day (acetate) and 0.127 m^3/m^3/day ($NaHCO_3$) were achieved at an initial Cd(II) of 50 mg/L with the observation of the same predominant species but in different proportions in the acetate or $NaHCO_3$ biofilms. Deeper understanding of the microbial consortia effects on biocathode performance is thus critical to maintain a healthy operation, and proper control of the composition of microbial consortia will also be necessary.

6.4.3 Initial pH and Metal Concentration

Initial pH and metal concentration extensively stressed in abiotic cathodes also affect the performance of biocathodes [53, 67, 71, 85] since initial pH and metal concentration are primarily responsible for structuring whole communities, and the diverse microbial taxa response differently to various environmental conditions [89]. It is generally recognized electrotrophs can only endure an appropriate metal concentration, after which inhibition of the electrotrophic activities takes over [53, 67, 85]. Take Cr(VI), for example. The presently reported Cr(VI) concentrations in the biocathodes ranged from 2.5 mg/L with pure culture of *Shewanella* to 40 mg/L with enrichment culture (Table 6.2) [70, 73], reflecting the applicable biocathodes for reducing Cr(VI) at these concentration levels. In terms of microbial characters, the pH changes may have affected the surface properties of the cells, including cell surface hydrophobicity, net surface electrostatic charge, cell surface shape and polymers, cell morphology, cell size at cell division, time to division, as well as biofilm structure [87, 88], and consequently influenced the bio-catalytic activity on electron transfer from cathode to bacteria and the subsequent metal reduction. A neutral condition is more beneficial for electrotrophic activities, whereas a more alkaline environment is inclined to form metal precipitates and not only influences electrotrophic activities but also augments metal reduction overpotential. A more acidic condition, however, favors for hydrogen evolution and detrimental to electrotrophic activities. Optimal pHs and initial metal concentrations thus benefit to both electrotrophic activities and metal reduction via electrochemical and biological reactions [53, 67, 70, 85]. Investigation is necessary to better clarify the nature of the competitive processes on the biocathodes and achieve efficient system performance for metal recovery.

6.4.4 Electron Transfer Mechanism

In contrast to electron transfer mechanisms in the bioanodes, the exact mechanisms of electron transfer from the cathode, through the bacteria, and finally, to the terminal electron acceptors in biocathodes have not yet been studied in detail. There are actually close interactions between microorganisms and the cathodic electrodes. Gene expression and deletion analysis demonstrate that the mechanisms for electron transfer from electrodes to *G. sulfurreducens* differed significantly from the mechanisms for electron transfer to electrodes [90]. To date, two main mechanisms, namely, direct and indirect electron transfers, have been reported (Fig. 6.2), which are more complex than those in abiotic cathodes (Fig. 6.1). Direct electron transfer on the biocathodes requires a physical contact between the bacterial cell membrane and the cathode electrode surface, and electrons from the electrode are directly received by the outer membrane redox macromolecules such as cytochromes (Fig. 6.2). *G. sulfurreducens* is one of the few microorganisms available in pure culture known to directly accept electrons from a negative poised electrode. It is believed that c-type cytochromes inside bacteria are essential electron-transferring proteins, and outer membrane cytochromes have the ability to catalyze the last step of the respiratory chains. Alternatively, a versatile bacterium of *S. putrefaciens* in anodic electron transfer through excreted flavins and menaquinone-related redox mediators as well as outer membrane cytochromes can utilize an outer membrane-bound redox compound for electron transfer in microbially cathodic oxygen reduction although this compound was still unidentified. In both cases, c-type cytochromes are essential electron-transferring proteins. They make the journey of respiratory electrons from the cytoplasmic membrane through periplasm and over the outer membrane possible [91]. Similarly, the absence of ferrous iron repressed the transcription of genes encoding outer membrane cytochromes necessary for the reduction of metals such as MnO_2, reflecting the importance of outer membrane cytochromes in *S. oneidensis* MR-1 for MnO_2 reduction [92]. With the presence of lactate and electrode, *S. oneidensis* MR-1 can use both as the electron donor for accelerated Cr(VI) reduction because (i) the forming chelates of Cr(III)-lactate interaction delayed the electrode deactivation by $Cr(OH)_3$ precipitate, (ii) electron mediators produced mediated electrons from the electrode to Cr(VI) and promoted indirect Cr(VI) reduction, and (iii) the presence of lactate and redox mediators produced enabled *S. oneidensis* MR-1 to be actively involved in the electrode oxidation process and drive direct or indirect Cr(VI) reduction [17]. With the help of noninvasive imaging technique of a naphthalimide-rhodamine-based Cr(III) fluorescent probe [93], four Gram-negative electrotrophs *Stenotrophomonas* sp. YS1, *Stenotrophomonas maltophilia* YS2, *Serratia marcescens* YS3, and *Achromobacter xylosoxidans* YS8 isolated from previously well-developed mixed culture biocathodes for Cr(VI) reduction [85] were imaginably and quantitatively mapped for intracellular Cr(III) ions [76]. These electrotrophs were intracellularly accumulated by chromium, shown as a total of 45.1–60.5% with a composite of Cr(III) ions (23.7–27.3%) and other forms of chromium complex (18.7–32.2%), compared to 10.2–11.7% (Cr(III) ions: 8.2–9.5%; other forms: 0.2–0.3%) in the controls in the absence of cathodic electrons, implying the direction of cathodic electrons for more intracellular chromium. In parallel, another four indigenous Gram-negative electrotrophs *Stenotrophomonas maltophilia* JY1, *Citrobacter* sp. JY3, *Pseudomonas aeruginosa* JY5, and *Stenotrophomonas* sp. JY6 isolated from well-adapted mixed cultures on the MFC cathodes for Cu(II) reduction [85] were proved to play diverse functions between cellular electron transfer processes and either Cu(II) reduction or circuital current [77]. Strains JY1 and JY5 exhibited a weak correlation between circuital current and Cu(II) reduction, whereas a much stronger correlation was observed for strain JY3 followed by strain JY6. In the presence of electron transfer inhibitor of 2,4-dinitrophenol or rotenone, significant inhibition on strain JY6 activity and a weak effect on strains JY1, JY3, and JY5 were observed, confirming a strong correlation between cellular electron transfer processes and either Cu(II) reduction or circuital current. With the help of a rhodamine-based Cu(II) fluorescent probe [94], Cu(II) ions were imaginably and quantitatively tracked in these electrotrophic subcellular sites [78]. Similar to the imaginable Cr(III) ions in the corresponding electrotrophs [76], cathodic electrons also led to more Cu(II) ions in the intracellular site compared to the prolonged appearance of more Cu(II) ions in the controls in the absence of cathodic electrons. For Cd(II) removal on the biocathodes of MECs and with the help of a quinoline-based Cd(II) fluorescent probe [95], four indigenous electrotrophs of *Ochrobactrum* sp. X1, *Pseudomonas* sp. X3, *Pseudomonas delhiensis* X5, and *Ochrobactrum anthropi* X7 isolated from mixed culture for Cd(II) removal [85] imaginably exhibited diverse distributions of Cd(II) ions at the subcellular level with heavy dependence on current and electron transfer inhibitor of 2,4-dinitrophenol (2,4-DNP) [79]. These results in concert may provide evidence for explaining the previous always observation of more efficient biocathodes for heavy metals removal at the subcellular level [53, 67, 70, 85].

In comparison with Gram-negative bacteria, little is known about Gram-positive bacteria for dissimilatory metal reduction. *Thermincola potens*, isolated from a MFC and reserving unusual abundance of multiheme c-type cytochromes localized to the cell wall or cell surface, can couple acetate oxidation to the reduction of hydrous ferric oxides or anthraquinone-2,6-disulfonate [96]. This result provides direct evidence for cell wall-associated cytochromes and supports multiheme c-type cytochromes involvement in conducting electrons across the cell envelope of a Gram-positive bacterium. In addition, a wide variety of microbially induced extracellular mechanisms have been used to explain the role of microorganisms in the increase of surface potential on passive metals, such as the generation of protons and hydrogen peroxide near the surface and the production of organometallic catalysts of metal reduction, specific enzymes, and passivating siderophores [15, 88, 89]. All the aforementioned enriches the electron transfer mechanisms in the biocathodes.

Compared with the increasing attention being paid on the electron transfer mechanisms between cathodic electrodes and microorganisms, present information about the subsequent link between the electrons derived from the electrodes and the terminal electron acceptors of metals is minimal and debatable (Fig. 6.2). Even for the extensively investigated electron acceptor of oxygen, it has not yet been demonstrated that the electron transfer is a respiratory mechanism in which electrons derived from the cathode serve as an energy-yielding electron donor for oxygen reduction, and there are a variety of other possible mechanisms by which cells

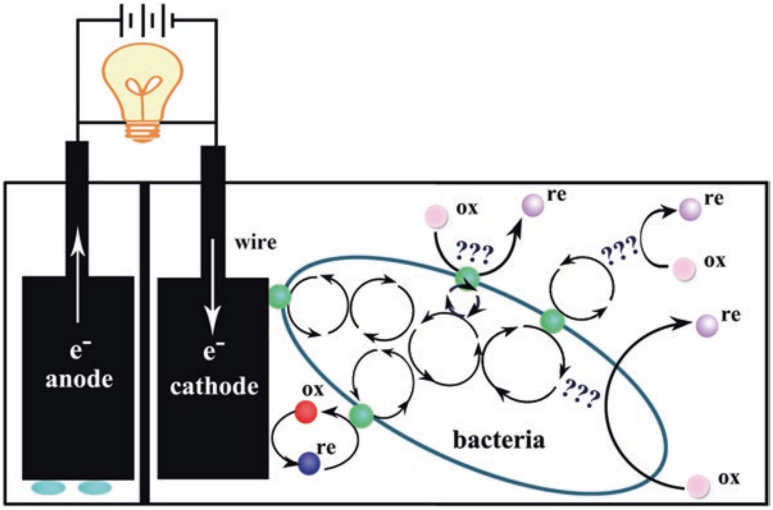

Fig. 6.2 Electron transfer pathways in the biocathodes of BESs

might catalyze enhanced oxygen reduction [68]. Riboflavin, an electron mediator naturally produced by *S. oneidensis* MR-1, was found to have a positive impact in potentiostatically controlled cathodes [17], implying its function as a mediator for electron transfer between *S. oneidensis* MR-1 and Cr(VI). While Gram-negative bacteria of *Shewanella* and *Geobacter* are model organisms enabling the dissimilatory reduction of extracellular electron acceptors, it is recently found that *G. sulfurreducens* can donate electrons through pili, a type of metal-like conductive nanofilaments or nanowires and made from protein produced by themselves, photosynthetic cyanobacteria, and thermophilic methanogens, to the external electron acceptor of uranium [97]. The bacterial pili can move charges over thousands of times the bacterium's length. Compared to the no-pili controls, in which *G. sulfurreducens* reduced uranium within the cell envelope and thus poisoned the cell in the process, the great surface area of pili had provided more occurrence of the precipitation around the pili and thus greatly increased the amount of uranium that *G. sulfurreducens* was able to remove [98]. While this result provides evidence for long-range electron transfer along the pili, *G. sulfurreducens* analogous to *S. oneidensis* [99] can reduce U(VI) much as it reduced the soluble, extracellular electron acceptors of anthraquinone-2,6-disulfonate and Fe(III) citrate without the requirement of pili, and a number of outer-surface c-type cytochromes contribute to U(VI) reduction. These results support the conclusion that pili were necessarily required for long-range electron transport to insoluble electron acceptor such as Fe(III) oxides in the *Geobacter* species [100, 101] and electron exchange between syntrophic partners [102], as well as electron conduction through current-producing biofilms [103]. Based on this observation and after fine-tuning the properties of the pili or adding different functional groups on the pili, these amended pili may be also used to precipitate other metal elements. In view of this point, the discovery of conductive pili is not only an important new principle in biology but also in materials science.

While biocathodes are presently limited to reduce U(VI), Cr(VI), Se(IV), Cu(II), Cd(II), and Co(II), few attempts have been made to elucidate the basic aspects of microbial activities such as interaction of substrate metabolism and electron transfers in the biocathodes. Although gene expression and deletion analysis are usually used for clarifying electron transfer mechanisms in U(VI)-reducing and pure-culture biocathodes [100–103], whether the cathodic electrons are the only energy source for the organisms forming the biofilm, which would make these microorganisms electrochemical lithotrophs, and what function this property plays in nature remain to be elucidated. Development of novel noninvasive imaging techniques to characterize the structure and biochemical composition of the electrotrophic biofilm is of particular importance. That a number of highly selective metal ion-sensitive fluorescence probes are synthesized and combined with confocal laser scanning microscopy for metal detection in cell biology [104] will potentially provide critical insights into metal distribution and electron transfer within the electrotrophs, as well as tools to characterize the mechanisms of electron transfer, leading to a better understanding of the electrotrophic roles in electron transfer mechanisms [76, 78, 79].

6.5 Conclusion

Metallurgical BES processes have been proved in labs and will be well established. However, these technologies are still far from finding real applications in wastes treatment. In addition, much is known about recovering single metals from individual abiotic cathodes; more attention should be paid to MFC-MEC coupled systems and/or BES-other technology combined processes for sequential metal recovery from wastes. Electron transfer mechanisms on the biocathodes are ultimately required to be elucidated in order to understand their limitations and hence maximize metal recovery in the near future.

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References

1. Xin B, Zhang D, Zhang X et al (2009) Bioleaching mechanism of Co Li from spent lithium-ion battery mixed culture acidophilic sulfur-oxidizing iron-oxidizing bacteria. Bioresour Technol 100:6163–6169
2. Chen G (2004) Electrochemical technologies in wastewater treatment. Sep Purif Technol 38:11–41
3. Rabaey K, Rozendal RA (2010) Microbial electrosynthesis-revisiting the electrical route for microbial production. Nat Rev Microbiol 8:706–716
4. Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337:686–690
5. Modin O, Wang X, Wu X et al (2012) Bioelectrochemical recovery of Cu, Pb, Cd, and Zn from dilute solutions. J Hazard Mater 235:291–297
6. Huang L, Yang X, Quan X et al (2010) A microbial fuel cell–electro-oxidation system for coking wastewater treatment and bioelectricity generation. J Chem Technol Biotechnol 85:621–627
7. Huang L, Cheng S, Chen G (2011) Bioelectrochemical systems for efficient recalcitrant wastes treatment. J Chem Technol Biotechnol 86:481–491
8. Kelly PT, He Z (2014) Nutrients removal and recovery in bioelectrochemical systems: a review. Bioresour Technol 153:351–360
9. Wang H, Ren Z (2014) Bioelectrochemical metal recovery from wastewater: a review. Water Res 66:219–232
10. Nancharaiah YV, Mohan SV, Lens PNL (2015) Metals removal and recovery in bioelectrochemical systems: a review. Bioresour Technol 195:102–114
11. Nancharaiah YV, Mohan SV, Lens PNL (2016) Biological and bioelectrochemical recovery of critical and scarce metals. Trends Biotechnol 34:137–155
12. Lu Z, Chang D, Ma J (2015) Behavior of metal ions in bioelectrochemical systems: a review. J Power Sources 275:243–260
13. He C, Mu Z, Yang H et al (2015) Electron acceptors for energy generation in microbial fuel cells fed with wastewaters: a mini-review. Chemosphere 140:12–17
14. Ter Heijne A, Liu F, van der Weijden R et al (2010) Copper recovery combined with electricity production in a microbial fuel cell. Environ Sci Technol 44:4376–4343
15. Liu L, Yuan Y, Li F et al (2011) In-situ Cr(VI) reduction with electrogenerated hydrogen peroxide driven by iron-reducing bacteria. Bioresour Technol 102:2468–2473

16. Pang Y, Xie D, Wu B et al (2013) Conductive polymer-mediated Cr(VI) reduction in a dual-chamber microbial fuel cell under neutral conditions. Synth Met 183:57–62
17. Xafenias N, Zhang Y, Banks CJ (2013) Enhanced performance of hexavalent chromium reducing cathodes in the presence of Shewanella oneidensis MR-1 and lactate. Environ Sci Technol 47:4512–4520
18. Wang Q, Huang L, Pan Y et al (2017) Impact of Fe(III) as an effective mediator for enhanced Cr(VI) reduction in microbial fuel cells: reduction of diffusional resistances and cathode overpotentials. J Hazard Mater 321:896–906
19. Choi C, Cui Y (2012) Recovery of silver from wastewater coupled with power generation using a microbial fuel cell. Bioresour Technol 107:522–525
20. Tao H, Gao Z, Ding H et al (2012) Recovery of silver from silver(I)-containing solutions in bioelectrochemical reactors. Bioresour Technol 111:522–525
21. Choi C, Hu N (2013) The modeling of gold recovery from tetrachloroaurate wastewater using a microbial fuel cell. Bioresour Technol 133:589–598
22. Wang G, Huang L, Zhang Y (2008) Cathodic reduction of hexavalent chromium [Cr(VI)] coupled with electricity generation in microbial fuel cells. Biotechnol Lett 30:1959–1966
23. Li Z, Zhang X, Lei L (2008) Electricity production during the treatment of real electroplating wastewater containing Cr(VI) using microbial fuel cell. Process Biochem 43:1352–1358
24. Li Y, Lu A, Ding H et al (2009) Cr(VI) reduction at rutile-catalyzed cathode in microbial fuel cells. Electrochem Commun 11:1496–1499
25. Tao H, Zhang L, Gao Z et al (2011) Copper reduction in a pilot-scale membrane-free bioelectrochemical reactor. Bioresour Technol 102:10334–10339
26. Tao H, Li W, Liang M et al (2011) A membrane-free baffled microbial fuel cell for cathodic reduction of Cu(II) with electricity generation. Bioresour Technol 102:4774–4778
27. Tao H, Liang M, Li W et al (2011) Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. J Hazard Mater 189:186–192
28. Zhang Q, Wei Z, Liu C et al (2012) Copper-doped cobalt oxide electrodes for oxygen evolution reaction prepared by magnetron sputtering. Int J Hydrog Energy 37:822–830
29. Cheng S, Wang B, Wang Y (2013) Increasing efficiencies of microbial fuel cells for collaborative treatment of copper and organic wastewater by designing reactor and selecting operating parameters. Bioresour Technol 147:115–121
30. An Z, Zhang H, Wen Q et al (2014) Desalination combined with copper(II) removal in a novel microbial desalination cell. Desalination 346:115–121
31. Wu D, Huang L, Quan X et al (2016) Electricity generation and bivalent copper reduction as a function of operation time and cathode electrode material in microbial fuel cells. J Power Sources 307:705–714
32. Wang Z, Lim B, Choi C (2011) Removal of Hg^{2+} as an electron acceptor coupled with power generation using a microbial fuel cell. Bioresour Technol 102:6304–6307
33. You S, Zhao Q, Zhang J et al (2006) A microbial fuel cell using permanganate as the cathodic electron acceptor. J Power Sources 162:1409–1415
34. Zhang B, Zhao H, Shi C et al (2009) Simultaneous removal of sulfide and organics with vanadium (V) reduction in microbial fuel cells. Technol Biotechnol 84:1780–1786
35. Zhang B, Zhou S, Zhao H et al (2010) Factors affecting the performance of microbial fuel cells for sulfide and vanadium (V) treatment. Bioprocess Biosyst Eng 33:187–194
36. Huang L, Guo R, Jiang L et al (2013) Cobalt leaching from lithium cobalt oxide in microbial electrolysis cells. Chem Eng J 220:72–80
37. Huang L, Li T, Liu C et al (2013) Synergetic interactions improve cobalt leaching from lithium cobalt oxide in microbial fuel cells. Bioresour Technol 128:539–546
38. Liu Y, Shen J, Huang L et al (2013) Copper catalysis for enhancement of cobalt leaching and acid utilization efficiency in microbial fuel cells. J Hazard Mater 262:1–8
39. Jiang L, Huang L, Sun Y (2014) Recovery of flakey cobalt from aqueous Co(II) with simultaneous hydrogen production in microbial electrolysis cells. Int J Hydrog Energy 39:654–663

40. Wang Q, Huang L, Yu H et al (2015) Assessment of five different cathode materials for Co(II) reduction with simultaneous hydrogen evolution in microbial electrolysis cells. Int J Hydrog Energy 40(2015):184–196
41. Huang L, Yao B, Wu D et al (2014) Complete cobalt recovery from lithium cobalt oxide in self-driven microbial fuel cell-microbial electrolysis cells systems. J Power Sources 259:54–64
42. Qin B, Luo H, Liu G et al (2012) Nickel ion removal from wastewater using the microbial electrolysis cell. Bioresour Technol 121:458–461
43. Fradler KR, Michie I, Dinsdale RM et al (2014) Augmenting microbial fuel cell power by coupling with supported liquid membrane permeation for zinc recovery. Water Res 55:115–125
44. Zhang B, Feng C, Ni J et al (2012) Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology. J Power Sources 204:34–39
45. Luo H, Liu G, Zhang R et al (2014) Heavy metal recovery combined with H_2 production from artificial acid mine drainage using the microbial electrolysis cell. J Hazard Mater 270:153–159
46. Choi C, Hu N, Lim B (2014) Cadmium recovery by coupling double microbial fuel cells. Bioresour Technol 170:361–369
47. Abourached C, Catal T, Liu H (2014) Efficacy of single-chamber microbial fuel cells for removal of cadmium and zinc with simultaneous electricity production. Water Res 51:228–233
48. Zhang Y, Yu L, Wu D et al (2015) Dependency of simultaneous Cr(VI), Cu(II) and Cd(II) reduction on the cathodes of microbial electrolysis cells self-driven by microbial fuel cells. J Power Sources 273:1103–1113
49. Li M, Pan Y, Huang L et al (2017) Continuous flow operation with appropriately adjusting composites in influent for recovery of Cr(VI), Cu(II) and Cd(II) in self-driven MFC-MEC system. Environ Technol 38:615–628
50. Wu D, Pan Y, Huang L et al (2015) Comparison of Co(II) reduction on three different cathodes of microbial electrolysis cells driven by Cu(II)-reduced microbial fuel cells under various cathode volume conditions. Chem Eng J 266:121–132
51. Wu D, Pan Y, Huang L et al (2015) Complete separation of Cu(II), Co(II) and Li(I) using self-driven MFCs-MECs with stainless steel mesh cathodes under continuous flow conditions. Sep Purif Technol 147:114–124
52. Wang Q, Huang L, Pan Y et al (2016) Cooperative cathode electrode and in situ deposited copper for subsequent enhanced Cd(II) removal and hydrogen evolution in bioelectrochemical systems. Bioresour Technol 200:565–571
53. Huang L, Jiang L, Wang Q et al (2014) Cobalt recovery with simultaneous methane and acetate production in biocathode microbial electrolysis cells. Chem Eng J 253:281–290
54. Tao H, Lei T, Shi G et al (2014) Removal of heavy metals from fly ash leachate using combined bioelectrochemical systems and electrolysis. J Hazard Mater 264:1–7
55. Sun M, Sheng G, Zhang L et al (2008) An MEC-MR-coupled system for biohydrogen production from acetate. Environ Sci Technol 42:8095–8100
56. Huang L, Li M, Pan Y et al (2017) Efficient W and Mo deposition and separation with simultaneous hydrogen production in stacked bioelectrochemical systems. Chem Eng J 327:584–596
57. Ramabhadran RO, Mann JE, Waller SE et al (2013) New insights on photocatalytic H_2 liberation from water using transition-metal oxides: lessons from cluster models of molybdenum and tungsten oxides. J Am Chem Soc 135:17039–17051
58. Chen Q, Liu J, Liu Y et al (2013) Hydrogen production on TiO_2 nanorod arrays cathode coupling with bio-anode with additional electricity generation. J Power Sources 238:345–349
59. Kundu A, Sahu JN, Redzwan G et al (2013) An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell. Int J Hydrog Energy 38:1745–1757

60. Ribot-Llobet E, Nam JY, Tokash JC et al (2013) Assessment of four different cathode materials at different initial pHs using unbuffered catholytes in microbial electrolysis cells. Int J Hydrog Energy 38:2951–2956
61. Oh SE, Logan BE (2007) Voltage reversal during microbial fuel cell stack operation. J Power Sources 167:11–17
62. Modin O, Fukushi K (2014) Development and testing of bioelectrochemical reactors converting wastewater organics into hydrogen peroxide. Water Sci Technol 69:1359–1372
63. Kim Y, Hatzell MC, Hutchinson AJ et al (2011) Capturing power at higher voltages from arrays of microbial fuel cells without voltage reversal. Energy Environ Sci 4:4662–4667
64. Huang L, Chai X, Quan X et al (2012) Reductive dechlorination and mineralization of pentachlorophenol in biocathode microbial fuel cells. Bioresour Technol 111:167–174
65. Wang H, Ren Z (2013) A comprehensive review of microbial electrochemical systems as a platform technology. Biotechnol Adv 31:1796–1807
66. Wang Q, Huang L, Quan X et al (2017) Preferable utilization of in-situ produced H_2O_2 rather than externally added for efficient deposition of tungsten and molybdenum in microbial fuel cells. Electrochim Acta 247C:880–890
67. Huang L, Chai X, Cheng S et al (2011) Evaluation of carbon-based materials in tubular biocathode microbial fuel cells in terms of hexavalent chromium reduction and electricity generation. Chem Eng J 166:652–661
68. Huang L, Regan JM, Quan X (2011) Electron transfer mechanisms, new applications, and performance of biocathode microbial fuel cells. Bioresour Technol 102:316–323
69. Gregory KB, Lovley DR (2005) Remediation and recovery of uranium from contaminated subsurface environments with electrodes. Environ Sci Technol 39:8943–8947
70. Hsu L, Masuda SA, Nealson KH et al (2012) Evaluation of microbial fuel cell *Shewanella* biocathodes for treatment of chromate contamination. RSC Adv 2:5844–5855
71. Tandukar M, Huber SJ, Onodera T et al (2009) Biological chromium(VI) reduction in the cathode of a microbial fuel cell. Environ Sci Technol 43:8159–8165
72. Huang L, Chen J, Quan X et al (2010) Enhancement of hexavalent chromium reduction and electricity production from a biocathode microbial fuel cell. Bioprocess Biosyst Eng 33:937–945
73. Huang L, Chai X, Chen G et al (2011) Effect of set potential on hexavalent chromium reduction and electricity generation from biocathode microbial fuel cells. Environ Sci Technol 45:5025–5031
74. De Windt W, Boon N, van den Bulcke J et al (2006) Biological control of the size and reactivity of catalytic Pd(0) produced by *Shewanella oneidensis*. Antonie Van Leeuwenhoek 90:377–389
75. Tian LJ, Li WW, Zhu TT et al (2017) Directed biofabrication of nanoparticles through regulating extracellular electron transfer. J Am Chem Soc 139:12149–12152
76. Xue H, Zhou P, Huang L et al (2017) Cathodic Cr(VI) reduction by electrochemically active bacteria sensed by fluorescent probe. Sensor Actuat B Chem 243:303–310
77. Shen J, Huang L, Zhou P et al (2017) Correlation between circuital current, Cu(II) reduction and cellular electron transfer in EAB isolated from Cu(II)-reduced biocathodes of microbial fuel cells. Bioelectrochemistry 114:1–7
78. Tao Y, Xue H, Huang L et al (2017) Fluorescent probe based subcellular distribution of Cu(II) ions in living electrotrophs isolated from Cu(II)-reduced biocathodes of microbial fuel cells. Bioresour Technol 225:316–325
79. Huang L, Xue H, Zhou Q et al (2018) Imaging and distribution of Cd(II) ions in electrotrophs and its response to current and electron transfer inhibitor in microbial electrolysis cells. Sensor Actuat B Chem 255:244–254
80. Catal T, Bermek H, Liu H (2009) Removal of selenite from wastewater using microbial fuel cells. Biotechnol Lett 31:1211–1216

81. Huang L, Liu Y, Yu L et al (2015) A new clean approach for production of cobalt dihydroxide from aqueous Co(II) using oxygen-reducing biocathode microbial fuel cells. J Clean Prod 86:441–446
82. Shen J, Sun Y, Huang L et al (2015) Microbial electrolysis cells with biocathodes and driven by microbial fuel cells for simultaneous enhanced Co(II) and Cu(II) removal. Front Environ Sci Eng 9:1084–1095
83. Chen Y, Shen J, Huang L et al (2016) Enhanced Cd(II) removal with simultaneous hydrogen production in biocathode microbial electrolysis cells in the presence of acetate or $NaHCO_3$. Int J Hydrog Energy 41:13368–13379
84. Li Y, Wu Y, Puranik S et al (2014) Metals as electron acceptors in single-chamber microbial fuel cells. J Power Sources 269:430–439
85. Huang L, Wang Q, Jiang L et al (2015) Adaptively evolving bacterial communities for complete and selective reduction of Cr(VI), Cu(II) and Cd(II) in biocathode bioelectrochemical systems. Environ Sci Technol 49:9914–9924
86. Rosenbaum MA, Franks AE (2014) Microbial catalysis in bioelectrochemical technologies: status quo, challenges and perspectives. Appl Microbiol Biotechnol 98:509–518
87. Stoodley P, De Beer D, Lappin-Scott HM (1997) Influence of electric fields and pH on biofilm structure as related to the bioelectric effect. Agent Chemother 41:1876–1879
88. Luo Q, Wang H, Zhang X et al (2005) Effect of direct electric current on the cell surface properties of phenol-degrading bacteria. Appl Environ Microbiol 71:423–427
89. Liu J, Hua Z, Chen L et al (2014) Correlating microbial diversity patterns with geochemistry in an extreme and heterogeneous environment of mine tailings. Appl Environ Microbiol 80:3677–3686
90. Strycharz SM, Glaven RH, Coppi MV et al (2011) Gene expression and deletion analysis of mechanisms for electron transfer from electrodes to *Geobacter sulfurreducens*. Bioelectrochemistry 80:142–150
91. Richter K, Schicklberger M, Ge scher J (2012) Dissimilatory reduction of extracellular electron acceptors in anaerobic respiration. Appl Environ Microbiol 78:913–921
92. Kouzuma A, Hashimoto K, Watanabe K (2012) Roles of siderophore in manganese-oxide reduction by *Shewanella oneidensis* MR-1. FEMS Microbiol Lett 326:91–98
93. Mao J, Wang L, Dou W et al (2007) Tuning the selectivity of two chemosensors to Fe(III) and Cr(III). Org Lett 9:4567–4570
94. Zhao Y, Zhang X, Han Z et al (2009) Highly sensitive and selective colorimetric and off-on fluorescent chemosensor for Cu^{2+} in aqueous solution and living cells. Anal Chem 81:7022–7030
95. Xu L, He MI, Yang HB et al (2013) A simple fluorescent probe for Cd^{2+} in aqueous solution with high selectivity and sensitivity. Dalton Trans 42:8218–8222
96. Carlson HK, Iavarone AT, Gorur A et al (2012) Surface multiheme c-type cytochromes from Thermincola potens and implications for respiratory metal reduction by gram- positive bacteria. Proc Natl Acad Sci U S A 109:1702–1707
97. Cologgi DL, Lampa-Pastirk S, Speers AM et al (2011) Extracellular reduction of uranium via *Geobacter* conductive pili as a protective cellular mechanism. Proc Natl Acad Sci U S A 108:15248–15252
98. Orellana R, Leavitt JJ, Comolli LR et al (2013) U(VI) reduction by diverse outer surface c-type cytochromes of *Geobacter sulfurreducens*. Appl Environ Microbiol 79:6369–6374
99. Marshall MJ, Beliaev AS, Dohnalkova AC et al (2006) c-type cytochrome-dependent formation of U(IV) nanoparticles by *Shewanella oneidensis*. PLoS Biol 4:e268
100. Reguera G, McCarthy KD, Mehta T et al (2005) Extracellular electron transfer via microbial nanowires. Nature 435:1098–1101
101. Smith JA, Lovley DR, Tremblay PL (2013) Outer cell surface components essential for Fe(III) oxide reduction by *Geobacter metallireducens*. Appl Environ Microbiol 79:901–907

102. Summers ZM, Fogarty HE, Leang C et al (2010) Direct exchange of electrons within aggregates of an evolved syntrophic coculture of anaerobic bacteria. Science 330:1413–1415
103. Malvankar NS, Vargas M, Nevin KP et al (2011) Tunable metallic-like conductivity in microbial nanowire networks. Nat Nanotechnol 6:573–579
104. Hao L, Li J, Kappler A et al (2013) Mapping of heavy metal ion sorption to cell-extracellular polymeric substance-mineral aggregates by using metal-selective fluorescent probes and confocal laser scanning microscopy. Appl Environ Microbiol 79:6524–6534