Chapter 16
Removal and Recovery of Metals by Using Bio-electrochemical System

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16.1 Introduction

One of the potential uses of bio-electrochemical systems (BES) is the removal and recovery of metals (Nancharaiah et al. 2015). Every day, significant amounts of metals are released to the environment via anthropogenic activities such as mining, smelting, metal refining, fossil fuel combustion, waste and sewage sludge inciner- ation, electroplating discharges, disposal of electronic waste and photographic supplies as well as manufacturing of printed circuit board, semiconductor, paint, stainless steel, pigments, photoelectric cells, glass, pesticides etc. Conventionally, metals are removed by precipitation as insoluble salts, ion exchange, adsorption, biosorption and microbial reduction from metal contaminated wastewater (Elouear et al. 2009; Fu and Wang 2011; Choi and Hu 2013; Tao et al. 2011b, 2012; Wang and Ren 2014; Lim et al. 2015; Zhang et al. 2016). The conventional methods are usually impractical at low concentrations and cost-inefficient because of high operational costs, energy consumption and production of excessive amounts of hazardous wastes (Ntagia et al. 2016). The barriers in removing and recovering of metals from waste streams may be overcome by using BES.

16.2 Principles of Bioelectrochemical Systems (BESs)

BES reactors generally consist of an anode, a cathode and a separator. Biodegrad- able materials are oxidized in the anode chamber and the electrons generated as a result of oxidation are transferred to the cathode. In the cathode compartment these

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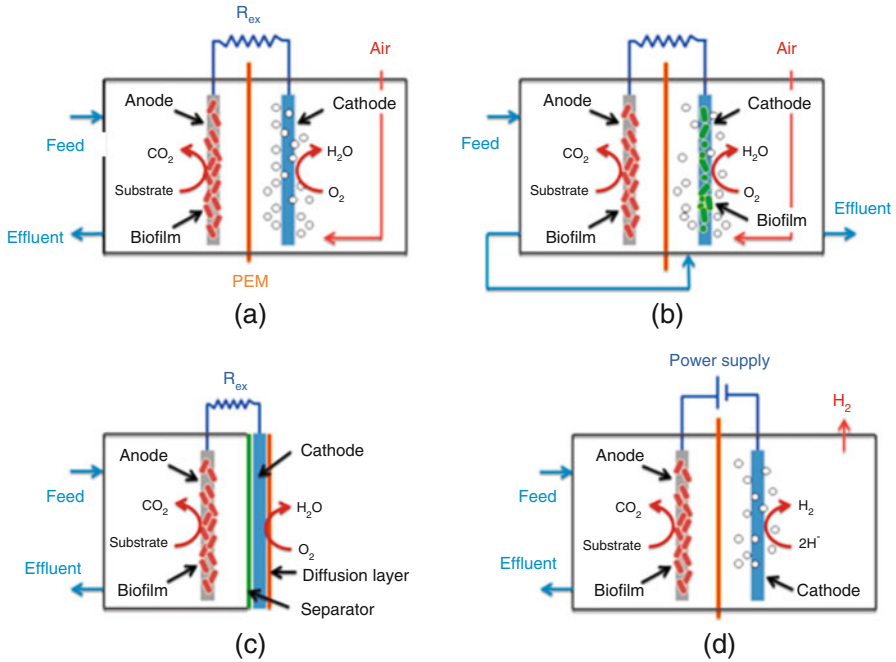
Fig. 16.1 Different BES configurations: (**a**) Two-chamber MFC; (**b**) Biocathode MFC; (**c**) Single chamber air cathode MFC; and (**d**) Two-chamber MEC for hydrogen production

electrons can be used for the direct electricity generation, reduction of chemicals or organic matter (Logan et al. 2006; Lovley 2006; Nancharaiah et al. 2016; Rabaey and Verstraete 2005; Cavdar et al. 2011; Tugtas et al. 2011, 2013). These systems have been studied intensively in terms of configuration, electrochemistry, microbiology and potential application areas and as a result microbial fuel cells (MFCs), microbial electrolysis cells (MECs) and microbial desalination cells (MDCs) have been identified as the representative of BES systems (Kelly and He 2014). In MFCs, current produced by BESs are directly harvested and used as electricity (Arends and Verstraete 2012). In MFCs, electrochemically active bacteria gain electrons by oxidizing the organic matter and transfer electrons to the surface of the anode electrode made of an inert and conductive material (e.g. carbon). The electrons are then transferred through an external resistor to the other electrode used as cathode (Fig. 16.1a–c). As a result, chemical energy in the organic matter is converted to electricity. On the surface of the cathode electrode, an oxidizing agent is used as electron acceptor, the electrons, and the protons that pass through a proton exchange membrane from anode to cathode compartment combine and form water molecules; thus the circuit is completed (He and Angenent 2006; Logan et al. 2006).

MECs (Fig. 16.1d) are the extension of MFCs; in addition to biologically produced current, some extra energy can be supplied to enhance the chemical

reactions in the cathode (Logan et al. 2006). If no external electron acceptor is supplied to the cathode chamber, electrons that arrive at the cathode can combine with the protons to generate value added products such as hydrogen, ethanol, methane, hydrogen peroxide etc. (Rozendal et al. 2008). In MECs, the electron transfer from anode to cathode does not occur spontaneously and thus an extra external energy is needed in addition to that generated by microorganisms, to drive the process (Rozendal et al. 2008).

BESs are generally configured as conventional two-chamber MFCs, bio-cathode MFCs, single chamber air cathode MFCs and two-chamber MECs (Fig. 16.1). The MFCs are operated in batch, semi-continuous, or continuous mode as other bio-reactors. The electrochemically active bacteria grow on the bio-cathode makes it a cheap and efficient alternative to chemical cathodes (Fig. 16.1b). In single chamber air cathode MFCs, cathode chamber is removed and cathode electrode is exposed directly to the air (Fig. 16.1c). Instead of producing electricity, MFCs in the form of MECs may also be used to produce hydrogen (H_2) and some valuable chemicals from soluble organic compounds. In MECs the potential generated at the anode is augmented with an additional voltage to generate H_2 at the cathode (Liu et al. 2005) (Fig. 16.1d). Figure 16.1 shows the schematics of these four BES configurations.

16.3 Metals in the Environment

Metals are ubiquitous in the biosphere and essential for the industry and infrastructure; however, industrial revolution resulted in redistribution of metals causing accumulation in terrestrial and aquatic environments (Gadd 2010). Metals have been categorized as light, toxic, heavy, semi-metal (metalloids) and trace depending on several chemical and physical properties (Sparks 2005). Thirteen metals and metalloids (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn), which can be derived from both natural and anthropogenic sources, are considered as priority pollutants (Sparks 2005). Hydrological processes are the main mechanism of metal transport and deposition in natural environments (Foster and Charlesworth 1996). Atmospheric deposition of metals originating from natural or anthropogenic sources is the major mechanism for metal input to soils and plants (Sparks 2005). In terrestrial systems, soils are the sink for metals, whereas in aquatic systems, sediments are the receiver of the metals (Sparks 2005). Natural waters are being increasingly polluted with metals worldwide, which possess adverse effects on biota and human health (Gadd 2010; Nancharaiah et al. 2016). Metals are non-biodegradable, most of them are toxic or carcinogenic and tend to accumulate in fats and tissues of living organisms (Fu and Wang 2011). Therefore, in order to decrease metal pollution, strict regulations along with appropriate treatment technologies are required worldwide.

Traditional metal removal technologies include: chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation and flocculation, flotation and electrochemical treatment (Fu and Wang 2011; Wang and Ren 2014).

In addition to traditional metal removal methods, bio-electrochemical systems have been utilized for metal removal and recovery (Lu et al. 2015; Wang and Ren 2014). In the following sections, the recent developments and progress in metal removal and recovery by using BES technology are discussed.

16.4 Bio-electrochemical Metal Removal and Recovery

16.4.1 Arsenic

Arsenic is a ubiquitous element ranking 20th in abundance in earth's crust and it naturally occurs in over 200 different mineral forms (Mandal and Suzuki 2002). Arsenic is a silver-grey brittle crystalline with atomic weight of 74.9 g mol^{-1} (Mohan and Pittman 2007). It is in the form of arsenious acid, arsenic acid, arsenites, methylarsenic acid, dimethylarsinic acid, arsenates, and arsine in the environment (Mohan and Pittman 2007). Arsenic can be found in most rocks at concentrations of 0.5–2.5 mg kg^{-1} and can be concentrated in some reducing marine sediments up to 3000 mg kg^{-1} (Mandal and Suzuki 2002). Arsenic in natural waters is a worldwide problem and many countries are suffering from contamination of groundwater resources with arsenic (Mohan and Pittman 2007). Adverse health effects of arsenic can be listed as pulmonary, cardiovascular, gastrointestinal, hematological, hepatic, renal, neurological, developmental, reproductive, immunologic, genotoxic, mutagenic and carcinogenic (Mandal and Suzuki 2002). Drinking water standard for arsenic has been adopted as 10 ppb (0.01 mg L^{-1}) by WHO and US-EPA (Mohan and Pittman 2007). Physical and chemical treatment technologies have been used to remove arsenic from water. In addition, BES has been employed to remove arsenic.

Arsenite removal was successfully achieved using MFC and zero valent iron (MFC-ZVI) hybrid system with removal efficiencies greater than 96% within 2 h (Table 16.1) (Xue et al. 2013). As a result of low voltage produced by MFC, more oxidants were driven from H_2O_2 leading effective oxidation of arsenite to arsenate which further improved the removal (Xue et al. 2013). In another study, where single stage MFC was used with carbon fibre felt anode and Pt enriched carbon paper cathode, arsenite was completely converted to arsenate within 7 days of operation (Table 16.1) (Li et al. 2016b).

16.4.2 Cadmium (Cd)

Cadmium contamination in soils and crops is mainly due to application of cadmium containing fertilizers and sewage sludge to land, mining activities and atmospheric deposition of airborne cadmium (Jarup and Akesson 2009). Cadmium is an

Table 16.1 Removal and recovery of arsenic (As) via BES

BES type	Electrode materials (A: anode, C: cathode)	Membrane	Anode inoculum	Electron donor	Electron donor removal efficiency	Metal salt used	Metal removal efficiency	Maximum power density	References
MFC-ZVI hybrid system	A: High purity iron C: Carbon felt	None	Anaerobic sludge from a WWTP	Glucose, 0.8 g L^{-1}	–	As$_2$O$_3$, 300 µg L^{-1} As(III)	> 96% (pH 8, experiment duration: 2 h)	477 mW m^{-2}	Xue et al. (2013)
Air cathode MFC	A: Carbon fibre felt C: Plain carbon paper (0.5 mg cm^{-2} Pt)	None	Anaerobic sludge	Glucose, 0.75 g L^{-1}	84% TOC removal	NaAsO$_2$, 200 µg L^{-1} As(III)	100% converted to As(V), experiment duration: 7 days	752.6 ± 17 mW m^{-2}	Li et al. (2016b)

extremely toxic element known to cause kidney damage, bone disease, cancer and increased mortality. Physical and chemical treatment technologies such as precipitation, coagulation and flocculation, ion exchange and electrochemical technologies have been used to remove cadmium from water. BES has been successfully applied to remove cadmium from water.

There are several studies in the literature investigating removal and recovery of cadmium by bioelectrochemical systems (Table 16.2). Choi et al. (2014) investigated a two chambered MEC with carbon brush anode and carbon cloth cathode electrodes where chromium was oxidized in the anode chamber and cadmium was reduced in the cathode chamber. Cadmium removal greater than 89% was observed with 2 W m^{-2} power applied. In addition, 22.5 W m^{-2} power was generated via Cr and Cd removing two chambered MEC configuration, which was approximately 11 times higher than the supplied energy (Table 16.2) (Choi et al. 2014). In another study, Cd removal was assessed using graphite fibre brush as anode and stainless steel mesh as cathode electrode and 50–67% Cd(II) removal was observed within 24 h (Table 16.2) (Colantonio and Kim 2016). In another study, 0.5 V voltage in a MEC using graphite felt was used as an anode electrode and titanium sheet (TSh), nickel foam (NF) or carbon cloth (CC) was used as cathode materials where cadmium reduction of 41.9%, 39% and 46.6% were observed, respectively (Wang et al. 2016a).

16.4.3   Chromium (Cr)

Chromium (VI) is a priority toxic chemical and it is used in industries such as electroplating, lumber and wood processing, leather tanning, dye/pigment manufacturing, cement, fungicide production (Huang et al. 2010; Tandukar et al. 2009). Chromium (VI) is a known mutagen, carcinogen and teratogen and its accumulation in the environment causes serious threat to human and other living organisms (Tandukar et al. 2009). Chromium (VI) also exerts stress on soil microbiota and enters the food chain; therefore, contaminated soils need to be remediated (Wang et al. 2016a). Chromium (VI) is highly water soluble and mobile; therefore, it needs to be converted to less toxic and less soluble Cr (III) (Wang et al. 2016b).

Removal or recovery of chromium using MFCs has been extensively studied in the literature (Table 16.3). In order to remove chromium mainly two chambered MFCs were utilized. Plain carbon felt, graphite plate, graphite brush, graphite fibre and stainless steel block were generally used as the anode electrodes, whereas plain graphite, graphite plate, graphite granules, or graphite blocks were used as the cathode materials (Table 16.3). Power generation up to 6.4 W m^{-3} was obtained and the highest hexavalent chromium efficiency of 100% was reached in the literature studies via MFCs (Huang et al. 2011; Li et al. 2008a; Tandukar et al. 2009; Wang et al. 2016b). Literature studies revealed that the complete hexavalent chromium reduction to Cr(III) can be achieved via two chambered MFCs and the

Table 16.2 Removal and recovery of cadmium (Cd) via BES

BES type	Electrode materials (A: anode, C: cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Metal salt at cathode	Metal removal efficiency	Voltage/power generated or applied	References
tMEC	A: Carbon brush C: Carbon cloth	1st cell: Cation exchange membrane 2nd cell: Anion exchange membrane	Anaerobic sludge	Abiotic	1 g L^{-1} sodium acetate + Cr (VI) reducing MFC	CdSO$_4$ (50–200 ppm Cd(II)	>89%	Generated: 22.5 W m^{-2} applied: 2 W m^{-2}	Choi et al. (2014)
Single chamber MEC	A: Graphite fibre brush C: Stainless steel mesh	None	An MEC used for WAS digestion	–	0.5 mg L^{-1} sodium acetate	CdCl$_2$, 12.26 mg L^{-1} Cd(II) in anode	50–67% Cd(II), 24 h	0.4–1.0 V cathode potential of −1.0 V vs. Ag/AgCl.	Colantonio and Kim (2016)
tMEC	A: Graphite felt C: Titanium sheet (TSh) nickel foam (NF) carbon cloth (CC)	CEM	Suspended bacteria from acetate-fed MFCs reactor	Abiotic	Sodium acetate, 1 g L^{-1}	Cd(II), 50 mg L^{-1}	TSh: 5.27 mg L^{-1} h^{-1} (41.9%) NF: 4.96 mg L^{-1} h^{-1} (39.4%) CC: 5.86 mg L^{-1} h^{-1} (46.6%)	0.5 V	Wang et al. (2016a)

Table 16.3 Removal and recovery of chromium (Cr) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor removal efficiency	Electron donor	Metal salt at cathode	Metal removal efficiency	Voltage/power generated or applied	References
tMFC	A: Plain carbon felt C: Plain graphite	Proton exchange membrane	Anaerobic digester of a WWTP	Abiotic	–	1 g L^{-1} sodium acetate	K$_2$Cr$_2$O$_7$; 204 ppm Cr^{6+}	99.5% of Cr^{6+} and 66.2% of total chromium (pH 2, 35 °C, 25 h)	1600 mW/m^2 (204 ppm)	Li et al. (2008a)
tMFC	A: Graphite plate C: Graphite plate	Proton exchange membrane	–	Denitrifying and anaerobic mixed cultures	–	Sodium acetate	K$_2$Cr$_2$O$_7$; 63 mg L^{-1} Cr^{6+}	100% Cr^{6+} (pH 7.2–7.6, 22–24 °C, 5 h)	55.5 mW m^{-2} (63 mg L^{-1})	Tandukar et al. (2009)
tMFC	A: Graphite plate C: Graphite plate submerged in granular graphite	Proton exchange membrane	–	Abiotic	–	1.6 g L^{-1} acetate	K$_2$Cr$_2$O$_7$; 39.2 mg L^{-1} Cr^{6+}	2.4 ± 0.2 mg g^{-1} VSS h^{-1}	2.4 ± 0.1 W m^{-3}	Huang et al. (2010)
tMFC	A: Porous carbon felts as anode and cathode	Cation exchange membrane	MFC effluent	Soil	–	Sodium acetate	Cr^{6+} contaminated soil	50% to 99.1%	–	Wang et al. (2016b)
Tubular tMFC	A: Graphite granules C: Graphite brush		MFC effluent	Primary clarifier effluent		1 g L^{-1} acetate	K$_2$Cr$_2$O$_7$; 20 mg L^{-1} of Cr(VI)	>98%	6.4 W m^{-3}	Huang et al. (2011)

produced Cr(III) can be removed via settling and removal of biomass from the cathode. However, the major issue of the process is the separation of adsorbed and non-adsorbed Cr (III) from the biomass which limits the practical application (Tandukar et al. 2009).

16.4.4   Cobalt (Co)

Lithium cobalt oxide ($LiCoO_2$) is extensively utilized in lithium-ion batteries (Huang et al. 2013, 2014a). Annual lithium-ion battery waste is estimated as 200–500 million tons containing 5–15% Co by weight and 2–7% Li by weight (Xu et al. 2008). Recovery of cobalt is highly desirable as it is a rare, precious and expensive metal.

Traditional methods such as hydrometallurgical, and bioleaching can be applied to recover cobalt; however, considering the economic and environmental disadvantages of the traditional methods, MFCs became an interest in cobalt recovery (Huang et al. 2014a; Jiang et al. 2014; Wang et al. 2015a). In cases where MEC systems were used to recover cobalt, voltage ranging from 0.2 V to 0.7 V was applied and greater than 75% recovery was achieved when graphite was used as an anode material and carbon, graphite, titanium sheet, nickel foam, woven mesh or carbon cloth were used as a cathode material (Table 16.4) (Huang et al. 2014a, b; Jiang et al. 2014; Wang et al. 2015b). Cobalt recovery percentages greater than 66% was achieved via MFC systems resulted in power generation ranging from 258 to 1500 mW m^{-3} (Table 16.4) (Huang et al. 2013, 2015).

16.4.5   Copper (Cu)

Copper is a crucial element for microorganisms, plants and animals at very low concentrations. It has a vital role in the synthesis of several enzymes. Nevertheless, it becomes potentially toxic to living organisms at elevated concentrations (Bilal et al. 2013). Copper can be found in waste streams generated from mining and smelting, printed circuit board, semiconductor and paint manufacturing, metallurgical, electroplating, wire drawing and copper polishing industries. Conventionally, it is removed by precipitation as insoluble salt or metallic copper, ion exchange and adsorption from wastewater (Nacharaiah et al. 2015). Copper removed from waste streams may be recovered and used in different applications (Ter Heijne et al. 2010).

Wu et al. (2016) reported that a two-chamber MFC which was operated in multiple batch cycles and had stainless steel woven mesh cathode fed with 50 mg L^{-1} of Cu (II) exhibited a maximum power density of 6.5 W m^{-3} (26.9 A m^{-3}) and a copper removal efficiency of 99.7 $\pm$ 0.4% (Table 16.5). Their results have shown

Table 16.4 Removal and recovery of cobalt (Co) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power generated or applied	References
tMEC	A: Graphite felt C: Carbon rod	Cation exchange membrane	Wastewater from a primary sedimentation tank	–	Sodium acetate, 1 g L^{-1}	0.8 g co g^{-1} COD	$CoCl_2$, 50 mg L^{-1} Co(II)	Co (II) reduction 7 mg L^{-1} h^{-1} pH 6	0.3 V from cobalt leaching MFC	Huang et al. (2014a)
tMFC	A: Graphite felt C: Graphite felt	Cation exchange membrane	Wastewater from a primary sedimentation tank	–	Sodium acetate, 0.38 g COD L^{-1}	CE, 42.7 ± 2.2% at pH 1.0	$LiCoO_2$ particles; solid/liquid ratios of 50–1000 mg L^{-1}	99.1%, 50 mg L^{-1}, 48 h, pH 1	258 ± 9 mW m^{-3}	Huang et al. (2013)
tMEC	A: Graphite fibre C: Porous graphite felt	Cation exchange membrane	Pre-acclimated MFC	Anaerobic digester of a WWTP receiving domestic and metalworking wastewaters	Sodium acetate (12.2 mM)	0.266 ± 0.001 mol Co mol^{-1} COD; 0.113 mol CH_4 mol^{-1} COD; 0.103 ± 0.003 mol acetate mol^{-1} COD	Co (II) (0.34 mM)	88.1% of Co (II)	0.2 V	Huang et al. (2014b)
tMEC	A: Graphite brush C: Graphite felt	Cation exchange membrane	Pre-acclimated MFC	Abiotic	Acetate, 1 g L^{-1}	0.81 mol Co mol^{-1} COD	847 µM Co(II)	92.2% in 6 h	0.3–0.5 V	Jiang et al. (2014)
tMFC	A: Graphite fibre C: Porous graphite felt	Cation exchange membrane	Wastewater from a primary sedimentation tank	Aerobic and anaerobic sludge, sediment and metalworking wastewater	Acetate, 1 g L^{-1}	0.24 ± 0.00 mol Co $(OH)_2$ mol^{-1} COD	$CoCl_2$; Co(II), 0.339 mM	0.079 ± 0.001 mmol L^{-1} h^{-1}	1500 mW m^{-3}	Huang et al. (2015)

that the initial deposition of Cu on the cathode is critical for efficient and continuous Cu(II) removal and power generation in the long-run.

Ntagia et al. (2016) showed the microbial hydrogen oxidation on a non-catalyzed graphite anode coupled with cathodic copper reduction in an MFC for the first time to simultaneously recover copper and produce power. They reported a maximum power density of 0.25 W m^{-2} (0.48 A m^{-2}), but no copper removal efficiency (Table 16.5). In another study, ter Heijne et al. (2010) obtained a maximum power density of 0.43 W m^{-2} (1.7 A m^{-2}) for acetate oxidation in the anode coupled to cathodic copper reduction with the same MFC configuration used by Ntagia et al. (2016). Likewise, Tao et al. (2011a) used glucose as organic electron donor for copper electrodeposition via cathodic reduction in a two-chamber MFC. They obtained a maximum power density of 339 mW m^{-3} and achieved Cu(II) removal efficiencies above 99% at 200 mg L^{-1} initial concentrations (Table 16.5).

In another study, a two-chamber membraneless MFC was successfully used for Cu(II) removal at cathode by using 5 g L^{-1} glucose as electron donor in the anode (Tao et al. 2011b). A maximum power density of 47 mW m^{-3} and 93 ± 0.1% Cu(II) removal efficiency was obtained at 200 mg L^{-1} initial Cu(II) concentration in 144 h (Table 16.5). Elemental Cu and brownish-red colour Cu$_2$O crystals were observed on the cathode as an indication of Cu deposition.

16.4.6   Mercury (Hg)

Mercury is one of the rarest elements on earth. It arises naturally through weathering of rocks, volcanic eruptions and deep-sea vents or from anthropogenic activities such as burning of fossil fuels, incineration of mercury-containing wastes (batteries, fluorescent light bulbs, etc.), use of fungicides containing mercury and catalysts. In water, it exists as soluble salts of chloride, sulphide or organic acids. Mercury which has already precipitated on the ground may evaporate back to the atmosphere. It is a neurotoxin and generally enters into the body from the environment, via the consumption of shellfish and fish from mercury-contaminated water bodies as well as through exposure to emissions from power plants and incinerators burning mercury-containing fuels and manufacturing processes. Exposure to mercury may damage the brain and kidneys and particularly children are considered under risk (Berlin et al. 2007).

There are different chemical and biological methods used to reduce soluble Hg(II) to insoluble Hg(0). The insoluble Hg(0) may then be adsorbed and removed from water. A diverse group of microorganisms are capable of reducing the soluble Hg(II) to insoluble elemental mercury (Nancharaiah et al. 2015). Because of its high standard potential, Hg(II) is a potential electron acceptor to be used in the cathode of an MFC (Wang et al. 2011). Hg(II) can be precipitated with chloride at low pH values.

Table 16.5 Removal and recovery of copper (Cu) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power output or applied	References
tMFC	A: Graphite plate C: Graphite foil pressed on titanium plate	Bipolar membrane	Mixed microbial culture from another MFC	Abiotic	Acetate, 20 mM	CE = 43%	$CuCl_2$, 1 g/L cu(II), pH 3	>99.98%	0.8 W m^{-2} (3.2 A m^{-2})	Ter Heijne et al. (2010)
tMFC	A: Graphite felt C: Graphite plate	Proton exchange membrane	Sludge from an anaerobic digester	Abiotic	Glucose, 5 g L^{-1}	CE = 3.65%	$CuSO_4$, 200 mg L^{-1} of Cu(II)	>99%, 144 h, pH 7	26 mW m^{-3}	Tao et al. (2011a)
tMFC	A: Graphite plate C: Graphite plate	Membrane-less	Sludge from an anaerobic digester	Abiotic	Glucose, 5 g L^{-1}	CE = 0.78%	$CuSO_4$, 200 mg L^{-1} of Cu(II)	93 ± 0.1%, 144 h	47 mW m^{-3}	Tao et al. (2011b)
tMFC	A: Graphite felt C: Stainless steel woven mesh	Cation exchange membrane	Mixed microbial culture from another MFCs	Abiotic	Acetate, 1 g L^{-1}	CE > 100% because of cathode corrosion	$CuCl_2$ solution (50 mg L^{-1} of Cu (II))	99.7 ± 0.4%	6.5 W m^{-3} (26.9 A m^{-3})	Wu et al. (2016)
tMEC	A: Graphite foil C: Graphite plate	Anion exchange membrane	Mixed microbial culture from an active MFC	Abiotic	3, 10 and 30 mL min^{-1} of H_2 gas	Na	$CuCl_2$ solution (1 g L^{-1} of Cu(II) at pH 4)	Na	0.48 A m^{-2} (0.25 W m^{-2})	Ntagia et al. (2016)

Wang et al. (2011) have operated an MFC by feeding the cathode chamber with Hg(II) as electron acceptor and investigated the bioelectrochemical removal of mercury from water. They obtained a maximum power density of 433.1 mW m^{-2} (1.44 A m^{-2}) and a cathodic Hg(II) removal efficiency of above 98% at pH 2 and concluded that lower the pH and higher the initial Hg (II) concentration result in a higher maximum power density (Table 16.6). The removed Hg(II) deposited as Hg (0) on the cathode surface and as Hg_2Cl_2 precipitate at the bottom of cathode chamber.

16.4.7 Gold (Au)

Gold is a rare, precious metal usually found in elemental form on earth in rocks, vein and alluvial deposits. After being extracted and refined, it is mainly used in jewellery and also in electronics due to its excellent corrosion resistance and high electrical conductivity (Spitzer and Bertazzoli 2004). If elemental gold is released into the environment it does not result in bioaccumulation or any other ecological problems because it is insoluble and its biodegradation is expected to be very poor. Electronic wastes and electroplating solutions release significant amounts of gold into the environment (Choi and Hu 2013). Therefore, currently there is a growing interest on recovery of precious metals from electronic wastes and electroplating waste streams. Gold is typically recovered from waste streams and leachate of scrap by chemical precipitation. However, chemical precipitation methods are quite inefficient at low concentrations (Nancharaiah et al. 2015). The other methods are electrochemical recovery, biosorption and microbial reduction (Choi and Hu 2013).

Choi and Hu (2013) have tested the MFC technology as a cost-effective alternative for recovery of gold from tetrachloroaurate which is used as electron acceptor at cathode. They recovered 99.89 of the Au(III) at an initial concentration of 200 mg L^{-1} and obtained 6.58 W m^{-2} maximum power density by using 2000 mg L^{-1} Au(III) and 12.2 mM acetate as catholyte and anolyte, respectively. The details of this study are given in Table 16.7.

16.4.8 Nickel (Ni)

Nickel is a hard and ductile metal used in nickel alloys, nickel-cadmium batteries, coins, industrial plumbing, machinery parts, stainless steel, spark plugs, electroplating and catalysts. Generally, very low concentration of nickel is found in soil, water and air as oxides and sulphides. Nickel chloride, sulphate and nitrate are the soluble and bioavailable nickel salts. The major sources of nickel emissions are released from fossil fuel combustion, mining, nickel metal refining, electroplating discharges, manufacturing facilities and sewage sludge incineration (ATSDR 1997).

Table 16.6 Removal and recovery of mercury (Hg) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power output or applied	References
tMFC	A: Graphite felt C: Carbon paper	Anion exchange membrane	From a waste-water treatment plant	Abiotic	0.82 g L^{-1} sodium acetate	CE = 1.6–4%	HgCl$_2$; 100 mg L^{-1} Hg(II)	98.2–99.5% at pH 2	433.1 mW m^{-2} (1.44 A m^{-2})	Wang et al. (2011)

Table 16.7 Removal and recovery of gold (Au) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power output or applied	References
tMFC	A: Carbon brush C: Carbon cloth	Cation exchange membrane	From a waste-water treatment plant	Abiotic	1 g L^{-1} sodium acetate	CE = 57%	AuCl$_4^-$; 200 and 2000 mg L^{-1}	99,89% (200 mg L^{-1}, 25 h)	6.58 W/m^{-2} (2000 mg L^{-1})	Choi and Hu (2013)

Table 16.8 Removal and recovery of nickel (Ni) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power output or applied	References
tMEC	A: Carbon felt C: Stainless steel mesh	Bipolar membrane	From a mature MFC	Abiotic	Sodium acetate, 1 g L^{-1}	CE = 35 ± 3.6%- 68 ± 3.4%	NiSO$_4$ solution; 50–1000 mg L^{-1} of Ni(II)	99 ± 0.6% at 50 mg L^{-1}; 33 ± 4.2% at 1000 mg L^{-1}	0.9 V	Qin et al. (2012)
tMEC	A: Carbon felt C: Carbon cloth coated with platinum catalyst	Bipolar membrane	Effluent of a mature MFC	Abiotic	Sodium acetate, 1 g L^{-1}	Na	NiSO$_4$ solution; 500 mg L^{-1} of Ni (II); pH = 3	96.9 ± 3.1% at 500 mg L^{-1}	0.7 V	Luo et al. (2015)
tMEC	A: Carbon fibre brush C: Copper sheet	Bipolar membrane	Anaerobic granular sludge supernatant	Abiotic	Acetate, 0.5 g L^{-1}	CE > 90%	NiSO$_4$ solution; 1 g L^{-1} of Ni (II);	40.7%; pH 3	0.5 V	Cai et al. (2016)

Although it is an essential nutrient for some microorganisms and plants, exposure of high concentration of nickel may cause a variety of adverse effects on living organisms (Klein and Costa 2007). Conventionally, nickel is removed from waste streams with coagulation/flocculation, chemical precipitation, adsorption and ion exchange. There are also very recent studies about its bioelectrochemical removal and recovery (Cai et al. 2016).

Qin et al. (2012) investigated the removal of Ni(II) using a two-chamber MEC and compared the Ni(II) removal performance to the results obtained with an identical electrolysis cell (EC) and an MFC. They reported that with 0.9 V applied voltage the Ni(II) removal efficiency of MEC was $99 \pm 0.6\%$ at 50 mg L^{-1} initial concentration and was almost three times higher than those obtained with EC and MFC. When the initial concentration increased to 1000 mg L^{-1}, Ni(II) removal efficiency of MEC decreased to $33 \pm 4.2\%$, while the amount of Ni(II) removed increased consistently with the initial concentration (Table 16.8). In another study, Luo et al. (2015) studied the selective recovery of Cu(II) and Ni(II) ions by using a fed-batch MEC following an MFC. Almost all of the Cu(II) ions and a small fraction of Ni(II) were removed at the cathode of MFC while the rest of the Ni (II) was recovered on the cathode of the subsequent MEC with an applied voltage of 0.7 V (Table 16.8). The very small amount of Ni(II) removed at the cathode of MFC was certainly due to adsorption, because the cathode potential of MFC was not adequate for the reduction of Ni(II). Likewise, Cai et al. (2016) studied the cathodic Ni(II) reduction at initial pH 3 in MECs by testing different cathode materials. The copper sheet cathode achieved the highest Ni(II) removal efficiency of 40.7% with 0.5 V applied voltage and 0.61 kWh kg^{-1} energy consumption (Table 16.8). Ni (II) was mainly removed with electrochemical reduction on the copper sheet cathode while a lesser amount with chemical precipitation.

16.4.9 Selenium (Se)

On the earth, selenium is found in water bodies, soils, rocks and the atmosphere. Through a biogeochemical cycle, it is released from sources rich in selenium such as organic-rich black shales, phosphatic rocks and coals. Pollution of the environment with selenium may occur naturally from weathering of seleniferous rocks and soils. Anthropogenic selenium contamination is caused by mining, agricultural drainage, combustion of Se containing coal, refinement of metals and manufacturing of electronics, stainless steel, pigments, semi-conductors, glass, photoelectric cells and pesticides (Nancharaiah and Lens 2015b). Release of significant amounts of selenium from agricultural and industrial activities into the environment may lead to accumulation of Se in aquatic organisms and cause acute and chronic toxicities (Catal et al. 2009).

Selenium (Se) is a critical element because of its intensive use in high-tech electronics and being an essential trace element for living organisms. However, above a certain concentration it becomes a potential toxicant. In order to remove

and recover selenium from polluted water bodies, bacterial biomineralization based applications is a promising alternative to conventional precipitation with concurrent adsorption (Nancharaiah and Lens 2015a). Having various oxidation states (−II, 0, +VI and +VI) in chemically different inorganic and organic and physically solid, liquid and gas forms make the biogeochemical selenium cycle quite complex. Generally, the oxyanions of selenium—selenite and selenate—are soluble and bioavailable under aerobic conditions. However, elemental selenium and metal selenides have limited solubilities and thus are immobilized under normal conditions (Nancharaiah and Lens 2015b). Selenite is more toxic than selenate. Therefore, bioaccumulation is more serious in water bodies contaminated with selenite (Catal et al. 2009). Stringent standards are set out to regulate the discharge of selenium in order to minimize its bioaccumulation and enrichment in food chain. For instance, the US EPA recommends a discharge limit of 5 μg L^{-1} for Se (Nancharaiah et al. 2015).

As an innovative approach, Catal et al. (2009) used air cathode MFC and evaluated the simultaneous electricity generation and selenite removal using carbon sources like acetate and glucose. They obtained removal efficiency above 88% at initial Se(IV) concentrations of 5–75 mg L^{-1} in acetate fed MFCs. When instead of acetate, glucose was used as substrate, removal efficiencies above 99% were achieved up to 200 mg L^{-1} of Se(IV). The maximum power output was 2.9 W m^{-2} and attained at 25 mg L^{-1} Se(IV) with acetate as substrate (Table 16.9). The bright red deposit observed as a result of elemental Se generation through the reduction of selenite showed that the mixed bacterial culture enriched for power generation in air cathode MFC can use selenite as electron acceptor as well as oxygen.

16.4.10   Silver (Ag)

Silver is a rare metal and occurs naturally as mineral deposits together with other metals. Anthropogenic silver emissions result from manufacture and disposal of some electrical and photographic supplies, coal combustion, smelting operations and cloud seeding. The biogeochemical silver cycling consists of natural and anthropogenic releases to the soil, water and atmosphere, wet and dry deposition, long-distance transportation of fine particulate matters in the atmosphere and sorption to sediments and soils. In nature, silver mainly occurs in the form of sulphide or exists together with sulphides of lead, copper, iron and gold, which are basically insoluble (Howe and Dobson 2002). The elemental silver is not soluble in water and within the silver salts silver nitrate ($AgNO_3$) is the only soluble one. Silver nitrate is widely used in photography, electroplating, ceramics and ink manufacturing industry. Silver ions in an aqueous solution can be recovered by ion exchange, extraction, biosorption and electrochemical reduction (Lim et al. 2015).

Table 16.9 Removal and recovery of selenium (Se) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power output or applied	References
Air cathode MFC	A: Carbon cloth C: Wet proof carbon cloth	Membrane-less	Mixed bacterial culture from a wastewater treatment plant	Sodium acetate, 2 g L^{-1} or glucose 1.2 g L^{-1}	CE = 19% with acetate at 50 mg L^{-1} of Se(IV); CE = 38% with glucose at 150 mg L^{-1} of Se(IV)	Sodium selenite; 0–400 mg L^{-1} Se (IV)	99%; 48 h; pH = 7 (acetate fed MFC)	2.9 W m^{-2} at 25 mg L^{-1} Se (IV)	Catal et al. (2009)

In the environment, high concentrations of silver may be determined close to the sewage discharge points, electroplating plants, areas seeded with silver iodide and mining sites. Generally, silver ions are very toxic to microorganisms. However, severe silver inhibitions are not experienced on microbial activity in sewage treatment plants. Because, since silver forms complexes rapidly with and adsorbed by other compounds, its bioavailability is reduced significantly (Howe and Dobson 2002). On the other hand, dissolved silver may easily bio-accumulate in living organisms.

Lim et al. (2015) studied the recovery of silver from a synthetic wastewater by using two-chamber MFC as an efficient and cost-effective technology. They achieved about 98% removal efficiency after 10 h at 1000 mg L^{-1} initial Ag (I) concentrations. The maximum power density attained was 1.93 W m^{-2} (4.25 A m^{-2}) at 2000 mg L^{-1} (Table 16.10). The results of SEM and EDS analyses verified that the shiny metal particles on the surface of graphite felt cathode electrode were metallic silver (Lim et al. 2015). In another study, Wang et al. (2013) investigated the recovery of silver from ammonia chelated silver alkaline wastewater coupled with power production in a two-chamber MFC. They achieved 99.9% Ag(I) recovery and 83% COD removal efficiencies simultaneously (Table 16.10). The maximum power output of the system was 317 mW m^{-2}. The deposit on the surface of graphite cathode was analyzed with XRD and identified as elemental silver (Wang et al. 2013). Likewise, Tao et al. (2012) showed the feasibility of metallic silver recovery from a synthetic photographic wastewater and achieved above 95% Ag(I) removal and 109 mW m^{-2} power density in a dual-chamber MFC (Table 16.10). The results of XRD analyses revealed that the deposits on the graphite cathode were metallic silver with purity above 91%.

16.4.11   Vanadium (V)

Vanadium is an abundant element occurring naturally in various minerals, phosphate rocks, iron ores and crude oil and it is released to atmosphere as a result of volcano emissions and continental dusts (Zwolak 2014). Vanadium is steel grey, corrosion resistant and most common valences are +3, +4 and +5 (Barceloux 1999). Humans are generally exposed to vanadium as a result of food consumption as vanadyl or vanadate and it is absorbed from gastrointestinal tract and transferred to tissues, liver, spleen, kidneys, testicles and bones (Zwolak 2014). Vanadium is not carcinogenic and only weakly mutagenic; generally health effects include upper respiratory tract irritation (Barceloux 1999).

Vanadium behaves as an effective electron acceptor in the cathode chambers of MFCs and removal of vanadium along with power generation is possible (Table 16.11) (Hao et al. 2016; Li et al. 2016a; Zhang et al. 2015). Single and two chambered MFC studies revealed that greater than 400 mW m^{-2} has been reached with metal removal efficiencies ranging between 25 and 76% when carbon is used as the anode and cathode material (Table 16.11). In addition to vanadium

Table 16.10 Removal and recovery of silver (Ag) via BES

BES Type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/power output or applied	References
tMFC	A: Graphite plate C: Graphite felt	Proton exchange membrane	Mixed culture from a lab BES	Abiotic	Sodium acetate, 1.28 g L^{-1}	93.6–97.8% COD removal	AgNO$_3$, 1 mM of Ag(I)	95% in 36 h, at pH 4	109 mW m^{-2}	Tao et al. (2012)
tMFC	A: Carbon cloth C: Graphite	Bipolar membrane	From a fruit waste treating anaerobic reactor	Abiotic	Sodium acetate, 1.6 g L^{-1}	83% COD removal	5 mM Ag$_2$SO$_4$	99.9% ag (I), 21 h, pH 9.2	317 mW m^{-2}	Wang et al. (2013)
tMFC	A: Graphite felt C: Graphite felt	Anion exchange membrane	From an anaerobic digester	Abiotic	Sodium acetate, 0.82 g L^{-1}	NA	AgNO$_3$, 50–4000 ppm Ag(I)	92.3–98.2%	1.93 W m^{-2} (4.25 A/m^{-2}) at 2000 mg L^{-1}	Lim et al. (2015)

Table 16.11 Removal and recovery of vanadium (V) via BES

BES type	Electrode materials (A: Anode, C: Cathode)	Membrane	Anode inoculum	Cathode inoculum	Electron donor	Electron donor removal efficiency	Metal salt at cathode	Metal removal efficiency	Voltage/ power output or applied	References
tMFC	A: Carbon fibre felt C: Carbon fibre felt	Proton exchange membrane	Anaerobic granular sludge from an UASB reactor	Abiotic	Glucose, 0.75 g L^{-1}	NA	NaVO$_3$; 75 mg L^{-1} V(V)	76.8 ± 2.9%	418.6 ± 11.3 mW m^{-2}	Zhang et al. (2015)
sMFC	A: Carbon fibre felt C: Plain carbon paper	Membrane-less	Anaerobic granular sludge from an UASB reactor	–	Glucose, 0.8 g L^{-1}	NA	NaVO$_3$,2H$_2$O; 75 mg L^{-1} V (V)	77.6% (12 h)	589.1 mW m^{-2}	Hao et al. (2016)
tMFC	A: Carbon fibre felt C: Carbon fibre felt	Proton exchange membrane	Anaerobic sludge	Abiotic	Glucose, 0.812 g L^{-1} and sodium sulphide, 100 mg S L^{-1}	NA	NaVO$_3$,2H$_2$O; 150 mg L^{-1} V (V)	NA	553.9 mW m^{-2}	Li et al. (2016a)

removal through MFC, vanadium can also be used to enhance power outputs of MFCs due to its excellent redox characteristics (Li et al. 2016a).

16.5   Conclusions

BES is considered a promising, cost-efficient and sustainable technology to remove and recover metals from wastewater and leachate. The drawbacks such as high operational cost and energy consumption, inefficiency at low concentrations and excessive hazardous waste production of conventional chemical precipitation, ion exchange, adsorption, biosorption and microbial reduction processes may be overcome with BES technology. In the literature, there are many studies demonstrating the cathodic reduction (in some cases oxidation) of the ions of arsenic, cadmium, chromium, cobalt, copper, gold, mercury, nickel, selenium, silver and vanadium in combination with the oxidation of an organic substance in the anode of a BES. Parameters affecting the efficiency of cathodic metal removal and recovery are initial metal ion concentration, pH, anode potential or applied voltage, internal resistance and conductivity of electrolytes. The biosorption and precipitation are the other mechanisms frequently contributing to cathodic metal reduction in BESs. Future studies have to focus on selective sequential recovery of metals from mixed metal solutions and real waste streams.

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