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Article *in* Environmental Chemistry Letters · December 2014

DOI: 10.1007/s10311-014-0474-2

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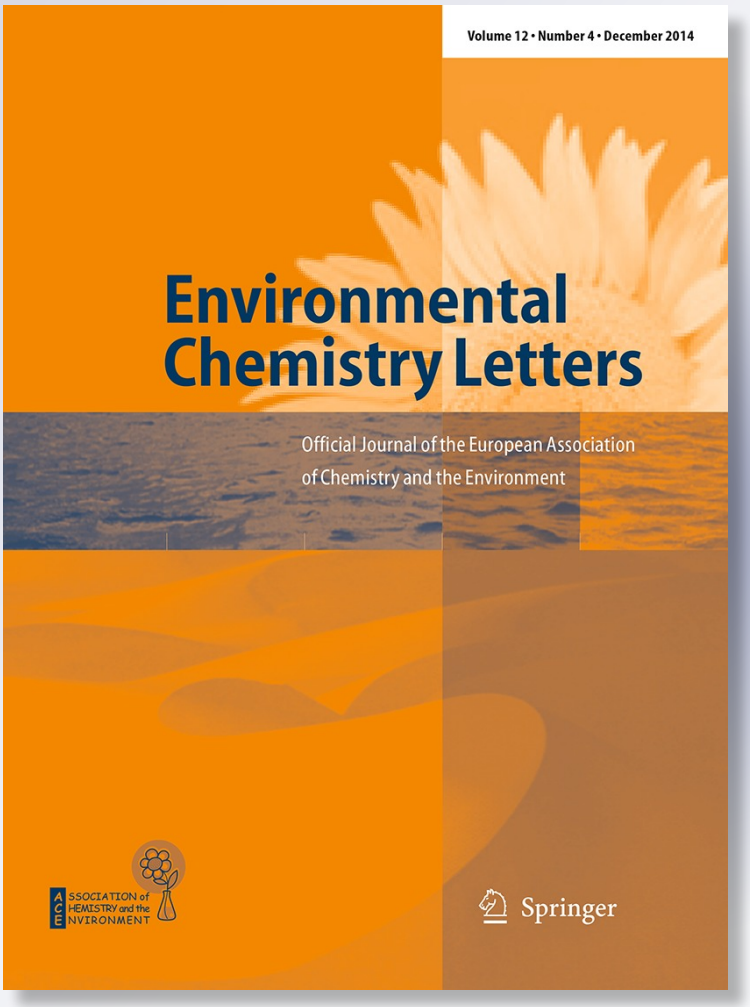
Environmental Chemistry Letters

ISSN 1610-3653
Volume 12
Number 4

Environ Chem Lett (2014) 12:483-494
DOI 10.1007/s10311-014-0474-2



Springer

Environ Chem Lett (2014) 12:483–494
DOI 10.1007/s10311-014-0474-2

REVIEW

Microbial fuel cells to recover heavy metals

Abhilasha Singh Mathuriya · J. V. Yakhmi

Received: 4 April 2014 / Accepted: 11 June 2014 / Published online: 26 June 2014

Abstract Heavy metals play a major role in several industrial, medical, and household applications. However, as constituents of effluents from many industries, heavy metals also pose a serious problem to the environment and public health due to their toxicity, bioaccumulation, and non-biodegradability. Conventional physical, chemical, and biological methodologies to treat wastewater containing heavy metals are energy-intensive and become ineffective if metals concentrations are below 1–100 mg L^{-1}. Microbial fuel cells appear promising for wastewater treatment and metal recovery by bioelectrocatalysis because metal ions can be reduced and deposited by bacteria, algae, yeasts, and fungi. Interestingly, treatment of heavy metal-containing wastewater can be attempted in both anode and cathode chambers of microbial fuel cells. Here, we review the treatment of metal-containing effluents using microbial fuel cells.

Keywords Microbial fuel cells · Heavy metals · Wastewater · Metal recovery · Bioelectricity · Waste treatment

Introduction

The term "heavy metal," in general, is applied to the group of metals and metalloids, found as natural components of the earth's crust, which have atomic density of greater than 4,000 kg m^{-3}, about 5 times more than that of water (Garbarino et al. 1995). Heavy metals are valuable in various areas of modern technology including industrial, medical, and household applications. But heavy metals are also a source of environmental pollution through various means, such as the use of coal, natural gas, paper, acid mine drainage (AMD), and chlor-alkali industries (Alloway 1995). Heavy metal poisoning can result from drinking water contamination (occurring through the use of lead pipes for supply/transport of water, or due to the contamination of water by industrial and consumer wastes), or their intake via the food chain, or due to high ambient air concentrations near the source of emission of heavy metals. Heavy metals are generally more persistent in the environment than organic contaminants such as pesticides or petroleum by-products, and thus tend to accumulate in living organisms causing toxic or carcinogenic symptoms. In order to meet the increasingly stringent environmental regulations, various treatment technologies, such as chemical precipitation, coagulation, flocculation, flotation, ion exchange, and membrane filtration, have been developed and tried for heavy metal removal from wastewater (Fu and Wang 2011) with their inherent advantages and limitations. Microbial fuel cell technology has recently emerged as a promising technology to carry out heavy metal treatment/recovery, while also producing electricity.

Microbial fuel cells are bioelectrochemical systems designed to convert the chemical energy contained in organic matter into electrical energy utilizing catalytic (metabolic) activity of microorganisms (Mathuriya and Sharma 2009). A typical two-chamber microbial fuel cell consists of an anode and a cathode, separated by a cation-specific membrane. Anode mechanism involves anaerobic oxidation of a substrate such as carbohydrate. Electrons are

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received by an enzyme-active site that acts as reduced intermediate (Shukla et al. 2004):

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (E = 0.014 \text{ Volts}) \qquad (1.1)$$

$$(\text{Intermediate})_{ox} + e^- \rightarrow (\text{Intermediate})_{re} \qquad (1.2)$$

Electrons are diverted from the electrochemical cell's metabolic pathway, across an electrode, through resistance (the *load*) into the oxygen-containing cathode (Balat 2010), according to

$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \quad (E = 1.23 \text{ Volts}) \qquad (3)$$

Microbial fuel cells prove to be superior over other competing conventional wastewater treatment technologies, in many respects, which include enhanced conversion efficiency due to direct conversion of substrate's chemical energy into electricity; capability to treat even those wastewaters that are not suitable for anaerobic digestion processes, such as low-strength wastewater (Rittmann 2008; Watanabe 2008); ability to operate at ambient temperature; safe and quite performance (Rabaey and Verstraete 2005); high conversion efficiency as compared to enzymatic fuel cells; ability to harvest up to 90 % of the electrons from the bacterial electron transport system compared to 50 % for typical fossil fuel power plants; and generation of 50–90 % less solids to be disposed of (Du et al. 2007). Besides, microbial fuel cells produce mainly carbon dioxide (CO_2) that has no useful energy content and comparatively less harmful, thus not requiring much further treatment (Jang et al. 2004). Microbial fuel cells would not generate more CO_2 than typical biological wastewater treatment processes; hence, replacement of fossil fuel power plants by microbial fuel cells would result in a net reduction of CO_2 emissions. Moreover, the generated sludge by the microbial fuel cell technology is much more stable than that produced during the aerobic treatment process, which would be an advantage (Kim et al. 2007).

In the initial stages, the efficiencies of microbial fuel cells used to be low, but with continuous development efforts, most of the microbial fuel cell architectures are now reported to remove up to 100 % pollutants (Wang et al. 2008; Liu et al. 2011; Gu et al. 2007; Zhang et al. 2009; Zhang et al. 2010a, b) and 99 % Chemical Oxygen Demand (COD) (Yu et al. 2011) from a vast variety of wastewaters. This has proved the utility of microbial fuel cells as a sustainable wastewater treatment system and their superior competency as compared with other wastewater treatment technologies such as Upflow Anaerobic Sludge Blanket (UASB) reactor (Duteanu et al. 2010) and conventional anaerobic digestion technology (Pham et al. 2006).

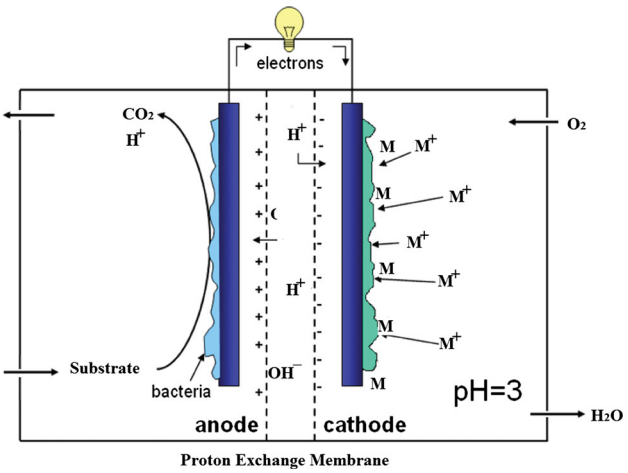

Fig. 1 Concept of heavy metal recovery in a microbial fuel cell. Microorganisms generate electrons and protons at the anode by oxidizing substrates. Electrons are transferred through an external circuit, while the protons diffuse through the solution to the cathode, where metallic ions combine with protons and reduced (M = Metal ion)

Principle of metal recovery in microbial fuel cell

In general, microbial fuel cells are applied as functional half-cell. It means that only anode chamber is used to degrade pollutants/organics through biocatalytic oxidation (Mathuriya 2014). The function of cathode chamber is mainly as microbial fuel cell circuit closure or as the destination for electrons and protons. In principle, any compound with high redox potential can serve as the cathodic electron acceptor in a microbial fuel cell. Oxygen (in ambient air) (Mathuriya and Sharma 2010), ferricyanide (Oh et al. 2004), permanganate (You et al. 2006), H_2O_2 (Tartakovsky and Guiot 2006), nitrate and trichloroethene (Clauwaert et al. 2007), and perchlorate (Thrash et al. 2007) have all been demonstrated as effective electron acceptors in the microbial fuel cell cathode chamber (Fig. 1).

Metal ions which exist as contaminants in wastewater do not biodegrade into harmless end products and therefore require special methods for treatment. Moreover, some of these heavy metal-containing groups have high redox potentials, and these could, therefore, be utilized as electron acceptors in order to get reduced and precipitate. If incorporated, this methodology could equip microbial fuel cells not only to serve the function of removing heavy metal ions in wastewater, but also as a method for recovering heavy metals.

For microbial fuel cells employed to treat wastewater simultaneously with metal recovery, three types of reactions are involved, generally, in the process for the production of electrons, their transfer, and consumption. These

include bioelectrochemical, electrochemical, and chemical reactions. The bioelectrochemical reactions occur in the anode chamber, where the electrons are released during microbial metabolism. These electrons gather at the anode and, subsequently, travel through an external load and arrive at the cathode chamber where the electrochemical reactions take over. The electrochemical reactions include the electrochemical reduction of dissolved oxygen to H_2O or H_2O_2 (Liu et al. 2011) and/or direct electrochemical reduction of metal ions.

Types of metals

Cathodic metal treatment using microbial fuel cells is still a concept being developed, and only a few metals are reported to have been treated thus. These are listed here.

Chromium

Chromium (Cr) is widely used in various industrial applications, including electroplating, tanning, dye manufacturing, and processing of wood products (Kotas and Stasicka 2000). Inappropriate and inadequate handling of effluent often leads to the introduction of Cr into the environment through soil and water, mostly as hexavalent, [Cr(VI)], or trivalent, [Cr(III)] species. The trivalent state is considered insoluble in aqueous solution and, therefore, is not a cause of much alarm. The hexavalent state, however, is of great concern due to its high solubility (Kotas and Stasicka 2000). International bodies such as the Commission of European Communities and the World Health Organization recommend 50 ppb as the maximum allowable limit (World Health Organization 2006) for Cr(VI), and any larger amounts present in the environment can be a cause of cancer, skin ulcers, and other maladies.

Since acidic Cr(VI) can be used as cathodic electron acceptor in microbial fuel cells, it makes it possible to reduce Cr(VI) to much less toxic Cr(III) with simultaneous electricity generation in an microbial fuel cell (Wang et al. 2008):

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (3.1)$$

Under standard conditions, the above half-cell reaction has a redox potential (E0) of 1.33 V (versus standard hydrogen electrode; SHE), showing that the overall reaction in the microbial fuel cell for power generation is thermodynamically feasible (Wang et al. 2008). This suggests the possibility of treating acidic Cr(VI)-containing wastewater during energy generation in a microbial fuel cell.

Many studies have reported treatment of acidic Cr(VI) using microbial fuel cells. For instance, Li et al. (2008) achieved 99.5 % Cr(VI) and 66.2 % of total Cr removal in cathode chamber of microbial fuel cell during electroplating wastewater treatment. Cr removal was achieved through reduction of $Cr_2O_7^{2-}$ to Cr_2O_3, precipitating on the surface of the cathode with a maximum power density of 1,600 mW m^{-2}. Wang et al. (2008) attained complete Cr(VI) removal (at initial concentration of 100 mg L^{-1}) in 150 h, in fed batch microbial fuel cell. Via photocatalysis at the rutile-coated cathode in the microbial fuel cells, Li et al. (2009a) observed 97 % of cathodic Cr(VI) removal within 26 h with maximal potential of 0.80 V. Using graphite plate as a cathode, Zhao et al. (2009) obtained 92.8 % Cr(VI) removal with maximal power density of 108 mW m^{-2} in 10 h. Tandukar et al. (2009) demonstrated microbial-assisted Cr(VI) reduction at the rate of 0.46 mg Cr(VI) g VSS^{-1} h^{-1}, with complete removal of Cr as $Cr(OH)_3$ precipitate at the cathode in a two-chamber microbial fuel cell along with 55.5 mW m^{-2} power density. 16S rRNA analysis revealed that the cathode biomass was largely dominated by phylotypes closely related to *Trichococcus pasteurii* and *Pseudomonas aeruginosa*. In another study, Huang et al. (2010) achieved Cr(VI) reduction rate of 2.4 ± 0.2 mg g VSS^{-1} h^{-1} and current production rate of 6.9 A m^{-3} from biocathode microbial fuel cells using indigenous bacteria from Cr(VI)-contaminated site as inoculum at an initial Cr(VI) concentration of 39.2 mg L^{-1}. Further, Huang et al. (2011) applied a biocathode potential of −300 mV, which improved microbial fuel cell performance for Cr(VI) reduction compared to a control (no set potential). With this set potential, the start-up time was reduced to 19 days, and the reduction of Cr(VI) was improved to 19.7 mg L^{-1} d^{-1}, and the maximum power density was increased to 6.4 W m^{-3} compared to the control (26 days, 14.0 mg L^{-1} d^{-1} and 4.1 W m^{-3}). Liu et al. (2011) demonstrated complete Cr(VI) removal in only 4 h using an air-bubbling carbon-felt cathode with a maximum power density of 52.1 mW cm^{-2}, with the reduction of oxygen to H_2O_2 confirmed at cathode by iron-reducing bacteria. Liu et al. (2012) also observed the association of Cr(VI) reduction with the electrogenerated H_2O_2 at the cathode. At pH 3.0, only 27.3 % of Cr(VI) was reduced after 12 h in the nitrogen-bubbling cathode microbial fuel cell, while complete reduction of Cr(VI) was achieved after 6 h in the air-bubbling cathode microbial fuel cell, with the reduction of oxygen to H_2O_2.

Another interesting study was conducted by Yeon et al. (2011) who enriched sludge, contaminated with Cr(VI) and achieved up to 93 % of 5 mg L^{-1} and 61 % of 25 mg L^{-1} Cr(VI) removal and observed the involvement of β-*Proteobacteria*, *Actinobacteria*, and *Acinetobacter* sp. for Cr(VI) reduction. Singhvi and Chhabra (2013) reported detoxification of Cr(VI)-contaminated water using algae biomass in a dual-chamber salt bridge microbial fuel cell. The device showed high Cr removal efficiency with 98 %

removal achieved in 96 h at a pH of 2 along with power density of 207 mW m^{-2}. Biocathodes for the reduction of the Cr(VI) were investigated using *Shewanella oneidensis* MR-1 (MR-1) by Xafenias et al. (2013). With MR-1 and lactate present in both anode and cathode, a maximum current density of 32.5 mA m^{-2} was produced after receiving a 10 mg L^{-1} Cr(VI) addition in the cathode, and cathodic efficiency increased steadily over an 8-day operation period with successive Cr(VI) addition.

Vanadium

The source of vanadium (V) pollutant is mainly iron and steel industry in the form of V(V) with ammonium salt, mostly as $NaVO_3$. Although it can be argued that certain amount of V is beneficial to the growth of a creature, it is toxic in nature and can inhibit the growth of the creature when its concentration is above permissible values, which should not exceed 2 mg L^{-1} according to wastewater emission standard (Li et al. 2009b). Li et al. (2009b) have suggested the following anodic mechanism for the treatment of vanadium ion complexes.

$$VO_3 + 4H^+ + e^- \rightarrow 2\,H_2O + VO^{2+} \quad (3.2)$$

Li et al. (2009b) studied the endurance to $NaVO_3$ of *Rhodoferax ferrireducens*. While adding 300 mg L^{-1} $NaVO_3$ into the anode chamber, the current output reached 0.6 mA. The reduction ratio of $NaVO_3$ was 75.8 %, and the total electron recovery of microbial fuel cell was 64 %. In an another interesting study, Zhang et al. (2010a) treated pollutants in both chambers of microbial fuel cell, by employing sulfide and vanadium as electron donor and acceptor, respectively, in dual-chamber microbial fuel cell and obtained average 82.2 and 26.1 % of sulfide and V removal with maximum power density of 614.1 mW m^{-2} within 72 h of operation. Zhang et al. (2012a) observed the reductions of V(V) and Cr(VI) together in double-chamber microbial fuel cells using V wastewater as the cathodic electron acceptor. About 67.9 ± 3.1 % V was precipitated and recovered from the exhausted catholyte, while 75.4 ± 1.9 % Cr was deposited on the cathode surface in 240 h, with a maximum power output of 970.2 ± 16.5 mW m^{-2} (Table 1).

Arsenic

Arsenic (As) is a naturally occurring, highly toxic metalloid (Oremland and Stolz 2003), and tragically, over 250 million people around the world are drinking arsenic-contaminated water and are facing arsenic toxicity, which leads to neurological damage and even death. Methods for decontaminating arsenic-laden drinking water exist, but they are costly, inefficient and need systems that require frequent servicing. Recently, Xue et al. (2013) have integrated conventional zero-valent iron (ZVI) technology with microbial fuel cell to develop microbial fuel cell-ZVI hybrid process to remove arsenite [As(III)] from aqueous solutions. Strong oxidants derived from H_2O_2 can rapidly oxidize As(III) into arsenate [As(V)], which helps to improve the As(III) removal efficiency. The resultant water qualities are compliant with the recommended standards of Environmental Protection Agency and World Health Organization.

Detection of extant life on Mars or Europa is a future goal of exobiology. For the present, biosignatures arising from life in extreme environments on Earth suggest how to search for life elsewhere. One such biosignature is the electrical current derived from the metabolic activity of microorganisms, which may be measured using microbial fuel cells (Miller et al. 2006). An arsenate respiring bacterium, *Bacillus selenitireducens*, isolated from moderately-hypersaline Mono Lake, California (US), could grow on lactate using arsenate as the electron acceptor and also grew without arsenate, using the anode as the electron acceptor. Power density of 3 μW m^{-2} was produced when arsenate was available because arsenate acted as an alternate electron acceptor to the anode (Miller et al. 2006).

Gold

Gold (Au) enjoys a celebrity status due to its industrial and ornamental demand. Microbial fuel cells recovering Au even in small concentration may be more attractive, therefore. In an interesting study, by adding a gold precursor at its cathode, a microbial fuel cell was demonstrated to form gold nanoparticles that can be used to simultaneously produce bioelectricity and hydrogen (Kalathil et al. 2013). By exploiting the quantized capacitance charging effect, the gold nanoparticles mediated the production of hydrogen without requiring an external power supply, while the microbial fuel cell produced a stable power density. In another study, Choi and Hu (2013) used tetrachloroaurate as an electron acceptor in a microbial fuel cell to investigate the parameters that influence the cost-effective recovery of gold. Models and equations for calculating the maximum actual efficiency and electrochemical impedance spectroscopic internal resistance of the microbial fuel cell were also developed. The maximum power density of 6.58 W m^{-2} with a fill factor of 0.717 was achieved for 60 mL volumes of 2,000 ppm Au(III) catholyte and 12.2 mM acetate anolyte, respectively. Additionally, the maximum actual microbial fuel cell efficiency of about 57 % was achieved, and the recovery efficiency of Au and the remaining concentration reached 99.89 ± 0.00 % and 0.22 ± 0.00 ppm, respectively, for an Au(III) concentration of 200 ppm. In an interesting study,

Table 1 Heavy metal recovery potential of microbial fuel cell technology

Sl. no.	Target metals	Original %	Source of inoculum	Time	Metal-reducing efficiency	Microbial fuel cell performance	Special note	References
1	Cr(VI)	Cr(VI) 204 ppm	Anaerobic sludge	25 h	99.5 % Cr(VI); 66.2 % total Cr	1,600 mW m^{-2}	Real electroplating wastewater treatment in TC-microbial fuel cell	Li et al. (2008)
2	Cr(VI)	200 mg L^{-1}	Domestic wastewater	150 h	Complete removal	150 mW m^{-2}	TC-microbial fuel cell	Wang et al. (2008)
3	Cr(VI)	26 mg L^{-1}	Anaerobic sludge	26 h	97 %	0.80 V	TC-microbial fuel cell with rutile-coated cathode	Li et al. (2009a)
4	Cr(VI)	177 mg L^{-1}	NIF	10 h	92.8 %	108 mW m^{-2}	TC-microbial fuel cell	Zhao et al. (2009)
5	Cr(VI)	80 mg L^{-1}	NIF	NIF	0.46 mg Cr(VI)/g VSS h	55.5 mW m^{-2}	Biocathodic TC-microbial fuel cell	Tandukar et al. (2009)
6	Cr(VI)	10 mg L^{-1}	*Shewanella decolorationis S12, Klebsiella pneumoniae L17* and mixed culture	4 h	Complete reduction	52.1 mW cm^{-2}	air-bubbling cathode (carbon-felt) TC-microbial fuel cell	Liu et al. (2011)
7	Cr(VI)	5 and 25 mg L^{-1}	β-*Proteobacteria, Actinobacteria, Acinetobacter*	6 days	93 % of 5 mg L^{-1} and 61 % of 25 mg L^{-1} Cr(VI)	0.5–0.6	TC-microbial fuel cell	Yeon et al. (2011)
8	Cr(VI)	39.2 mg L^{-1}	Indigenous bacteria from Cr(VI)-contaminated site	NIF	2.4 ± 0.2 mg g VSS^{-1} h^{-1}	6.9 A m^{-3}	Biocathode microbial fuel cells	Huang et al. (2010)
9	Cr(VI)	NIF	NIF	19 days	19.7 mg L^{-1} d^{-1},	6.4 Wm^{-3}	Biocathode microbial fuel cells	Huang et al. (2011)
10	Cr(VI)	NIF	Iron-reducing bacteria	4 h	Complete removal	52.1 mW cm^{-2}	Air-bubbling carbon-felt cathode microbial fuel cell	Liu et al. (2011)
12	Cr(VI)	–	Algae biomass	96 h	98 % removal	207 mW m^{-2}	Dual-chamber salt bridge microbial fuel cell	Singhvi and Chhabra (2013)
13	Cr(VI)	10 mg L^{-1} Cr(VI)	*Shewanella oneidensis* MR-1	8 day	–	32.5 mA m^{-2}	Biocathode microbial fuel cells	Xafenias et al. (2013)
14	$NaVO_3$	300 mg/L	*Rhodoferax ferrireducens*	7d	75.8 %	0.6 mA	TC-microbial fuel cell	Li et al. (2009b)
15	Sulfide and vanadium	Sulfide (anode): 50–200 mg L^{-1}; V(V) (cathode): 250–1,000 mg L^{-1}	Anaerobic granular sludge	72 h	82.2 % sulfide; 26.1 % vanadium	614.1 mW m^{-2}	Pollutants treatment in both chambers of TC-microbial fuel cell	Zhang et al. (2010a)
16	Cr(VI) and V(V)	NIF	NIF	240 h	67.9 ± 3.1 % V(V); 75.4 ± 1.9 % Cr(VI)	970.2 ± 16.5mW/m^2	TC-microbial fuel cell	Zhang et al. (2012a)

Table 1 continued

Sl. no.	Target metals	Original %	Source of inoculum	Time	Metal-reducing efficiency	Microbial fuel cell performance	Special note	References
18	Tetrachloroaurate	60 ml; 2,000 ppm Au(III) catholyte; 12.2 mM acetate anolyte	–	–	99.89 ± 0.00 % and 0.22 ± 0.00 ppm	6.58 W m^{-2}	–	Choi and Hu (2013)
19	Au^{3+}	200 ppm Au^{3+} with 1,000 ppm standard solutions of $HAuCl_4$	*Shewanella putrefaciens*.	–	–	–	Electrodeposition of gold on grade G-10 graphite electrodes	Varia et al. (2014)
20	Ag-ion-containing wastewaters	50–200 ppm	Sludge	8 h	99.91 % Ag recovery	4.25 W m^{-2}	TC-microbial fuel cell	Choi and Cui (2012)
21	Ag(I) ions and Ag(I) thiosulfate complex	–	–		91 %	–	Dual-chamber bioelectrochemical systems	Tao et al. (2012)
22	Ammonia-chelated Ag alkaline wastewater	–	–		1.6 g pure Ag; 99.9 % silver ions removed	–	Dual-chamber bioelectrochemical cell	Wang et al. (2013)
23	Organic wastewater (Copper)	NIF	NIF	NIF	68.67 %	147.4 mW cm^{-2}	Tank with the oxidation as the battery anode; heavy metal wastewater tank with reduction as the battery cathode	Zhang et al. (2011)
24	Cu^{2+}-containing wastewater	1,000 mg L^{-1}	Excess sludge as anolyte and $CuSO_4$ solution as the catholyte.	288 h	97.8 %	536 mW m^{-3} at Cu^{2+} concentration of 6,400 mg L^{-1}	TC-microbial fuel cell	Liang et al. (2011)
25	Metal Cu and/or cuprous oxide (Cu_2O)	–	Anaerobic sludge	–	>99 % of Cu(II) was reduced to Cu_2O and metallic Cu on the cathodes	339 mW m^{-3}	Dual-chamber microbial fuel cell	Tao et al. (2011a)
26	Synthetic Cu(II) sulfate-containing wastewater	500 mg L^{-1}	–	144 h	70 % cathodic reduction of Cu(II)	314 mW m^{-3}	Membrane-free baffled microbial fuel cell	Tao et al. (2011b)
27	Spent lithium ion batteries	–	–	–	Co(III) leaching in lithium oxide	–	–	Huang et al. (2013a)
28	Particulate lithium cobalt oxide ($LiCoO_2$)	20 mg/100 ml deionized water	Pre-established bioanode	NIF	Cobalt leaching of 57.0 ± 0.7 %	Energy efficiency of 134.0 ± 5.6 %	TC-microbial electrolysis cell	Huang et al. (2013b)
30	Se in glucose	100 mg L^{-1}	*Shewanella oneidensis* MR-1	100 h	92 %	–	–	Zhang et al. (2014)

Table 1 continued

Sl. no.	Target metals	Original %	Source of inoculum	Time	Metal-reducing efficiency	Microbial fuel cell performance	Special note	References
31	Selenium	200 mg L^{-1} Se	–	72 h	98 % Se	12.8 mW m^{-2}	Wetland-microbial fuel cell (constructed wetland-microbial fuel cell)	Yang et al. (2014)
32	Oil sands tailings	–	–	1700 h	97.8 % ^{78}Se; 96.8 % Ba; 94.7 % ^{88}Sr; 81.3 % ^{66}Zn; 77.1 % ^{95}Mo; 66.9 % ^{63}Cu; 44.9 % ^{53}Cr; 32.5 % Pb	392 ± 15 mW m^{-2}	–	Jiang et al. (2013)
33	Cd and Zn	200 mM Cd; 400 mM for Zn	Electrochemically active microorganisms	–	90 % Cd and 97 % Zn removal	3.6 W m^{-2}	Single-chamber membrane-less air–cathode microbial fuel cell	Abourached et al. (2014)
	Selenium	50 and 200 mg Se L^{-1}	Mixed bacterial culture of domestic wastewater	48 and 72 h	99 %	1,500 mW m^{-2}	Single-chamber microbial fuel cell with acetate and glucose as carbon sources	Catal et al. (2009)

TC-microbial fuel cell two-chamber microbial fuel cell, *SC-microbial fuel cell* single-chamber microbial fuel cell, *SCac-microbial fuel cell* single-chamber air cathode microbial fuel cell, *NIF* no information found

Varia et al. (2014) demonstrated electrodeposition of gold on grade G-10 graphite electrodes from aqueous electrolyte solutions of 200 ppm Au^{3+} with 1,000 ppm standard solutions of $HAuCl_4$ investigated in the presence of electroactive bacterial cells of the *Shewanella putrefaciens*.

Silver

Silver (Ag) attracts the attention of researchers because of its demand for industrial and decorative uses, photography, jewellery, and silverware. Various types of technologies to recover silver from photographic waste materials and industrial wastewater, such as replacement (Ye et al. 2009), ion exchange, and chemical reduction (Blondeau and Veron 2010) have been developed. Electrolysis is the most common effective method for Ag recovery from solution by electroplating it on a cathode (Chatelut et al. 2000). A cost-effective microbial fuel cell was developed by Choi and Cui (2012), in order to recover Ag metal from Ag-ion-containing wastewaters. In an 8-h operation, as high as 99.91 %, Ag recovery was attained with the initial concentrations from 50 ppm to 200 ppm of Ag. Another novel approach was tested by Tao et al. (2012), for metallic Ag recovery and power generation by using cathodic reduction in dual-chamber bioelectrochemical systems. With acetate as electron donor on anode, both Ag(I) ions and Ag(I) thiosulfate complexes in catholyte were reduced on cathode. X-ray diffraction (XRD) analysis indicated that electrodeposits on cathodes from both catholytes were metallic Ag with >91 % purity. Very recently, Wang et al. (2013) reported the efficient recovery of Ag from ammonia-chelated Ag alkaline wastewater, along with 83 % COD removal from acetate wastewater along with 3.2 Joule energy and 160 Coulomb charge production in a dual-chamber bioelectrochemical cell. The results indicated that 1.6 g Ag could be deposited on cathode with over 99.9 % silver ions removed from the catholyte.

Copper

Copper (Cu) is among important engineering metals, but is toxic and can cause health hazards and harmful biochemical effects on living beings, when disposed in water bodies, requiring treatment; therefore, Heijne et al. (2010) attained cathodic Cu recovery of 84 % (0.43 W m^{-2} power density) and 43 % (0.80 W m^{-2} power density) under anaerobic and aerobic conditions of cathode chamber, respectively, in a microbial fuel cell with bipolar membrane as a pH separator. Wang et al. (2010) also achieved more than 99 % Cu recovery along with 143.6 mW m^{-2} of power density. Zhang et al. (2011) developed a battery system using Cu-ion solution as catholyte and 147.4 mW cm^{-2} power density and COD removal rate of

68.67 % was obtained. About 97.8 % of cathodic Cu(II) was removed in a dual-chamber microbial fuel cell at the end of 288 h using $CuSO_4$ solution as the catholyte (Liang et al. 2011). The 96 % cathodic reduction of Cu(II) for an initial concentration of 350 mg Cu L^{-1} was achieved by Zhang et al. (2012b) at pH 9.0 over 12 h. Tao et al. (2011a) attempted cathodic recovery of metal Cu and/or cuprous oxide (Cu_2O) in a dual-chamber microbial fuel cell. With glucose as a substrate and anaerobic sludge as an inoculum, the maximum power density generated was 339 mW m^{-3} along with >99 % removal efficiency of Cu(II). X-ray diffraction analysis confirmed that Cu(II) was reduced to Cu_2O and metallic Cu on the cathodes. In addition, the same research group developed a membrane-free baffled microbial fuel cell to treat synthetic Cu(II) sulfate-containing wastewater with maximum power density of 314 mW m^{-3} using initial Cu(II) concentration of 6,400 mg L^{-1}. Up to 70 % cathodic reduction of Cu(II) was observed within 144 h using initial concentration of 500 mg L^{-1} and to Cu_2O or Cu_2O + Cu, which deposited on the cathode (Tao et al. 2011b). Very recently, organic matters and Cu-ions were together removed from wastewater by Cheng et al. (2013). About 83 % COD removal and 87 % Cu-ion removal were obtained along with cathodic efficiency of 80 % for Cu-ion removal and a maximum power density of 2.0 W m^{-2}.

Cobalt

Cobalt (Co) is a naturally occurring element in the earth's crust and is essential component of cyanocobalamin (vitamin B_{12}), an essential vitamin (Martens et al. 2002). It plays an important role as a component in alloys, batteries, crystal sets, dyes and pigments (Co Blue), magnets, and tires. Co-salts are used to impart permanent brilliant blue colors to glass, pottery, enamels, tiles, and porcelain. Yet, cobalt is highly toxic and can affect lungs, eyes, and skin (Darolles et al. 2013), thus requires treatment. Huang et al. (2013a) reported Co recovery and recycling of spent lithium ion batteries in microbial fuel cells. Rapid Co(III) leaching in lithium oxide at a rate 3.4 times the sum of rates by conventional chemical processes and no-acid controls was obtained. In addition, two-chamber microbial electrolysis cells were also examined (Huang et al. 2013b) for Co leaching from particulate lithium cobalt oxide ($LiCoO_2$), one main cathodic component in spent Li-ion batteries. In optimized performance, Co leaching of 57.0 ± 0.7 % and energy efficiency of 134.0 ± 5.6 % were achieved at an applied voltage of 0.2 V and pH 2.0. Higher applied voltage and more acidic pH enhanced Co leaching (Fig. 2).

Enhancement of both Co leaching from $LiCoO_2$ and acid utilization efficiency in microbial fuel cells was

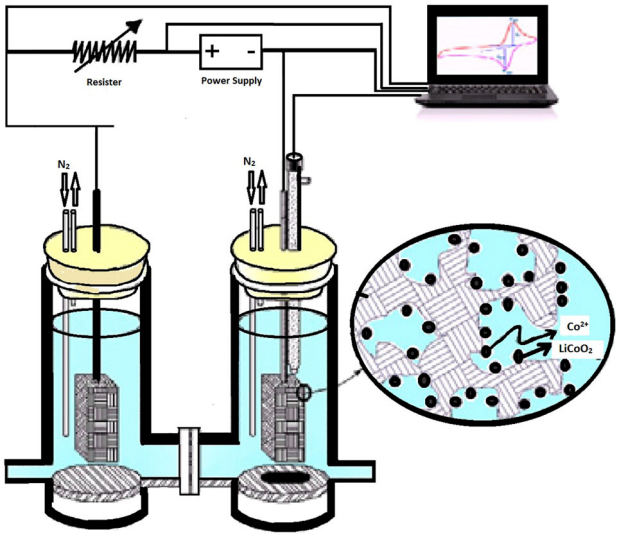

Fig. 2 A two-chamber microbial electrolysis cells used by Huang et al. (2013b) for cobalt leaching (Figure included and reproduced after permission from publisher)

successfully achieved by Liu et al. (2013) by the addition of Cu(II). A dosage of 10 mg L^{-1} Cu(II) improved both cobalt leaching up to 308 % compared to the controls with no presence of Cu(II). The results demonstrate that cobalt leaching in microbial fuel cells using Cu(II) as a catalyst may be an effective strategy for Co recovery and recycle of spent Li-ion batteries. Very recently, Jiang et al. (2014) recovered flakey Co recovered from aqueous Co(II) with simultaneous hydrogen production in microbial electrolysis cell, thus provides a new way for the recovery of Co and recycle of spent lithium ion batteries with concomitant hydrogen generation. Cathode-accumulated flakey crystals were verified as Co using both a scanning electron microscope capable of energy-dispersive spectroscopy (SEM–EDS) and X-ray diffraction analysis (XRD).

Selenium

Selenium (Se) is a metal required, though only in trace amounts for human and animal metabolism, due to its role in key physiological oxidative stress and immune functions (Hamilton 2004). However, Se is very toxic and its release in large amounts into the environment from industrial and agricultural activities can lead to its accumulation in living systems (Hamilton 2004) and cause both acute and chronic toxicities in aquatic organisms (Catal et al. 2009). Se and its compounds are widely used in various industries, such as glass manufacturing and electronic industries, and waste streams from these industries may contain high concentration of Se. Selenite (SeO_3^{2-}) and Selenate (SeO_4^{2}) are two major species of inorganic Se. Selenite is taken up faster by aquatic plants and is more toxic than selenate.

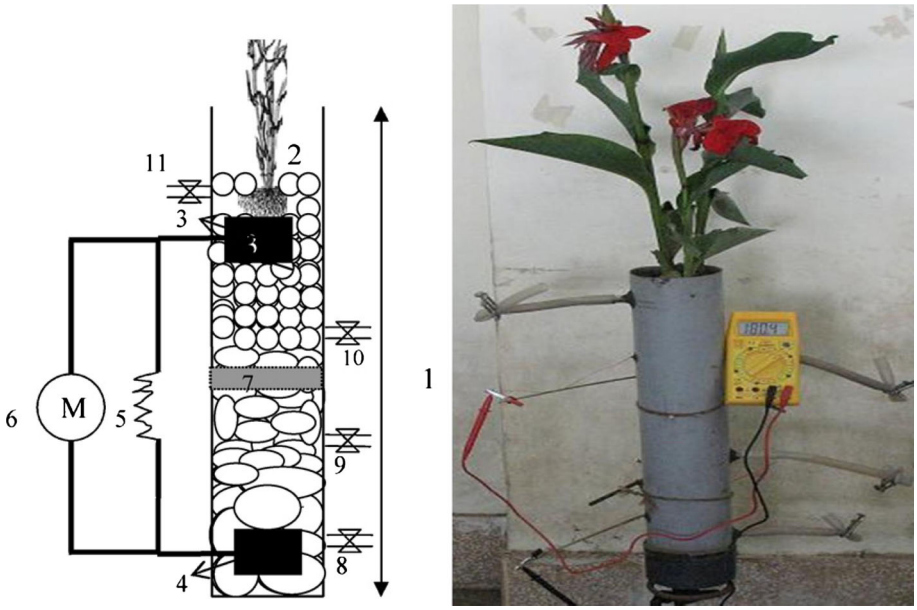

Fig. 3 Schematic of wetlands cum microbial fuel cell as described in Yadav et al. (2012). *1* Gravel filled constructed wetlands cum microbial fuel cell microcosm planted with Canna indica, *2* rhizospheric zone, *3* cathode, *4* anode, *5* resistance, *6* multimeter, *7* layer of glass wool, *8–11* sampling ports. (Figure included and reproduced after permission from publisher)

Catal et al. (2009) demonstrated selenite removal in single-chamber microbial fuel cell with acetate and glucose as carbon sources. About 99 % of 50 and 200 mg Se L^{-1} selenite was removed in 48 and 72 h using microbial fuel cells fed with acetate and glucose, respectively. A bright red deposit was observed on the microbial fuel cell electrodes as well as in the solution with the increase in selenite concentration, which was thought to be elemental Se (Narasingarao and Häggblom 2007) generated through the reduction of selenite by the microorganisms on electrode surface and in solution. Zhang et al. (2014) evaluated Se removal using *Shewanella oneidensis* MR-1 in two-chamber microbial fuel cell. About 92 % of Se 100 mg L^{-1} as selenite was removed in 100 h for microbial fuel cell fed with glucose. Power output was not affected by selenite concentration of up to <200 mg L^{-1} with glucose as substrate. Coulombic efficiencies of microbial fuel cells with glucose increased from 22 to 33 % at <200 mg Se L^{-1} (Fig. 3).

Constructed wetlands are effective and inexpensive wastewater treatment systems, which could be used in the remediation of waters contaminated with heavy metals and other toxic trace elements (Lin et al. 2010). Yang et al. (2014) constructed wetland-microbial fuel cell based on the ideas of Yadav et al. (2012), to investigate Se removal in conjunction with the production of electricity from wastewater. About 98 % of Se removed after 72 h of treatment from wastewater containing 200 mg L^{-1} Se along with power density of 12.8 mW m^{-2}. The possible removal mechanism of Se in the system appears to be the volatilization, and adsorption of Se on the surface of gravels, accumulation and biotransformations by plants and microbes in the constructed wetland-microbial fuel cell microcosm. This observation indicates that Se removal was achieved primarily by abiotic mechanisms.

Other attempts

Some research groups also described remarkable results directly or indirectly associated with electrochemical metal recovery. Metal contaminants create difficulties in the bioremediation of subsurface environments. To solve this, Lovley attempted microbial reduction of the oxidized form of uranium (U) from contaminated subsurface environments with an electrode serving as the electron donor for the bioremediation of groundwater contaminated with U (Gregory and Lovley 2005; Lovley 2006).

In an interesting study, Cheng et al. (2011) generated spherical nanoparticles of iron oxide in an microbial fuel cell that upon drying got transformed to goethite (α-FeOOH). Particle diameters ranged from 120 to 700 nm, with sizes that could be controlled by varying the fuel cell parameters, especially current density (0.04–0.12 mA cm^{-2}), pH (4–7.5), and initial Fe(II) concentration (50–1,000 mg L^{-1}). In a patent claim, Choi (2012) disclosed the elimination of mercury ions [Hg(II)] in the form of a solid precipitate or as a deposit of Hg or Hg_2Cl_2, in microbial fuel cell along with attractive power generation.

In a very interesting study, Jiang et al. (2013) achieved effective removal of eight heavy metals: 97.8 % of selenium (^{78}Se), 96.8 % of barium (Ba), 94.7 % of strontium (^{88}Sr), 81.3 % for zinc (^{66}Zn), 77.1 % of molybdenum (^{95}Mo), 66.9 % of ^{63}Cu, 44.9 % of ^{53}Cr, and 32.5 % of lead (Pb), in an microbial fuel cell during the treatment of oil sands tailings (27.8 % of the total COD, 81.8 % of the soluble COD, and 32.9 % of the total acid extractable

organics removal) along with a power density output of 392 ± 15 mW m^{-2} during 1,700-h operation. Very recently, in another very interesting study, Abourached et al. (2014) selected two heavy metals (Cd and Zn) on the basis of their toxicity and redox potential to be treated in a single-chamber membrane-less air–cathode microbial fuel cell. They demonstrated that 90 % Cd and 97 % Zn removal efficiencies obtained along with 3.6 W m^{-2}. Here, biosorption and sulfide precipitation were found to be the major mechanisms. The estimated maximum concentrations of Cd and Zn for the electrochemically active microorganisms were 200 mM for Cd and 400 mM for Zn, respectively. Heavy metals affected the microbial fuel cell anode performance mainly through their toxic inhibition to anodic microbes rather than competing with the microbial fuel cell anode for electron acceptance. Luo et al. (2014) developed a dual-chamber microbial electrolysis cell system to produce H_2 and remove Cu(II), Ni(II), and Fe(II) concurrently from acid mine drainage (AMD) under single and mixed metal conditions. With an applied voltage of 1.0 V, Cu(II) in the AMD got recovered first at the cathode, followed by Ni(II), and finally Fe(II). H_2 production rates of 0.4–1.1 m^3 m^{-3} d^{-1} were achieved during the AMD treatment, and the highest rate was obtained with the AMD containing Cu(II) alone. The highest efficiency of cathode electron recovery reached 89 %, which was obtained with the AMD containing mixed metals.

Tao et al. (2014) developed a combined system using bioelectrochemical systems followed by electrolysis reactors for heavy metals removal from fly ash leachate. Acetic acid was used as the fly ash leaching agent, and it was confirmed that the removal of heavy metals from fly ash leachate with the combination of bioelectrochemical systems and electrolysis reactors is feasible. Up to 98.5 % of Cu(II), 95.4 % of Zn(II), and 98.1 % of Pb(II) removal efficiency was achieved. Cu(II) was found to be reduced and recovered as metal Cu on cathodes, while Zn(II) and Pb(II) electrolyzed in the electrolysis reactors. Very recently, Fradler et al. (2014) attempted cathodic treatment of 400 mg/l Zn(II), via microbial fuel cell-supported liquid membrane combination. The system demonstrated 93 ± 4 % of the Zn(II) removal and 0.233 mW power within 72 h.

Prospects and concluding remarks

This article summarizes the recent developments in microbial fuel cells for metal recovery as an additional advantage along with conventional power generation and waste treatment. Recovery of metallic species during conventional microbial fuel cell function takes microbial fuel cells one step ahead of other waste treatment technologies. When contaminants serve as electron acceptors in the microbial fuel cell cathode chamber, the environmental benefits of microbial fuel cells could be further enhanced. Recovering metals during electricity generation certainly eliminates the energy need for treatment process. In addition, microbial fuel cells can remove and recover metals even in very low concentration, which is not possible in any other process. Till date, most studies were conducted on Cr removal. The reason may be the high redox potential of Cr. This is an emerging application of microbial fuel cells, and many other metal complexes are eligible to be studied for reduction and/or purification. Yet, there are difficulties in direct recovery of metals in microbial fuel cells by cathodic reduction due to their low standard reduction potentials. Therefore, extensive research is required to optimize and enhance the process efficiency. Presently, microbial fuel cells are facing shortfalls in many parameters: process scale up, lack of effectiveness for industrial wastewater if applied alone, or other available electron acceptors in real wastewater. The proton exchange membrane in two-chamber microbial fuel cells is also a major limitation due to its high cost, fouling, and chocking (Mathuriya 2014). As the metal recovery concept of microbial fuel cells is still in nascent state, it requires a detailed study. For example, Liu et al. (2011) observed that the efficiency of Cr(VI) reduction was strongly related to the catholyte pH, the anodic iron-reducing species, and the addition of extracellular mediators. Furthermore, the reduction of metal ions could apparently be accelerated by adding extracellular mediators, such as AQDS, into the anode of the microbial fuel cell (Liu et al. 2011). The effect of metal on biotic electrode is another aspect of study. As Abourached et al. (2014) observed that heavy metals affect the anode performance through their toxic inhibition to anodic microbes. Meanwhile, the microbial fuel cell technology might also be expected to contribute in the treatment of other metallic wastewaters, not yet studied, to reduce their toxicity. Hope, that this article will encourage the researchers to attempt the recovery of other metals of interest by applying microbial fuel cell technology.

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