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Review

Bioelectrochemical metal recovery from wastewater: A review

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ABSTRACT

Metal contaminated wastewater posts great health and environmental concerns, but it also provides opportunities for precious metal recovery, which may potentially make treatment processes more cost-effective and sustainable. Conventional metal recovery technologies include physical, chemical and biological methods, but they are generally energy and chemical intensive. The recent development of bioelectrochemical technology provides a new approach for efficient metal recovery, because it offers a flexible platform for both oxidation and reduction reaction oriented processes. While dozens of recent studies demonstrated the feasibility of the bioelectrochemical metal recovery concept, the mechanisms have been different and confusing. This study provides a review that summarizes and discusses the different fundamental mechanisms of metal conversion, with the aim of facilitating the scientific understanding and technology development. While the general approach of bioelectrochemical metal recovery is using metals as the electron acceptor in the cathode chamber and organic waste as the electron donor in the anode chamber, there are so far four mechanisms that have been reported: (1) direct metal recovery using abiotic cathodes; (2) metal recovery using abiotic cathodes supplemented by external power sources; (3) metal conversion using bio-cathodes; and (4) metal conversion using bio-cathodes supplemented by external power sources.

Contents

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1. Introduction

Rapid industrialization and human activities generate large amount of metal-laden wastewater. The metal contaminated water posts great health and environmental concerns, because most metals are not biodegradable and can be accumulated in living tissues of plants, animals, and human bodies, causing diseases and disorders (Olojo and Awoniran, 2012; Raskin et al., 1994). Physical, chemical, and biological technologies have been developed to remove metals from wastewater, and more and more efforts have been made to possibly recover precious metals, so the treatment process can be cost-effective and sustainable (Barakat, 2011; Fu and Wang, 2011; Veglio and Beolchini, 1997). Table 1 shows the concentrations of the main metals in different wastewaters, and it can be seen that industrial wastewaters contain much more metals than municipal wastewater, including those with higher market values, such as silver, gold, copper, zinc,

Table 1 – Metal concentration in common wastewaters (mg/L).

Name	Symbol	Price (USD/kg)	Municipal treatment plant	Road wash water	Tannery	Mining	Battery factory
Aluminum	Al	1.85[a]		0.467–26.1		0.161	0.2–7.3
Antimony	Sb	9.75[b]					
Arsenic	As	1.43[c]	0–0.0019				
Barium	Ba	100[c]					
Bismuth	Bi	23.4[d]					
Cadmium	Cd	1.87[e]	0–0.0033		0.056	0.004	0.02–0.12
Calcium	Ca	110[f]			255	548	83–255
Chromium	Cr	8.8[c]	0.04–0.56	0.004–0.107	391		<0.0044–0.08
Cobalt	Co	30.2[a]			1.55	0.0126	
Copper	Cu	6.72[a]	0.079–0.58	0.0111–0.177		0.244	<0.0033–0.38
Gold	Au	46378.6[a]					
Iron	Fe	0.2[g]	0.48–3.9	2.59–26.8	4.4	0.033	0.02–20
Lead	Pb	2.09[a]	0–0.039	<0.018–0.053	0.872		4.0–13
Magnesium	Mg	5.84[a]			268	29.52	15–26
Manganese	Mn	2.2[a]	0.067–1.16		0.396		0.04–0.6
Mercury	Hg	2.9[h]	0–0.0002				
Molybdenum	Mo	33.0[a]		0.0154–0.021			
Nickel	Ni	18.45[a]	0.0067–0.77	<0.006–0.0525	0.179	0.142	0.07–0.38
Potassium	K	22[i]			183	34.9	
Silver	Ag	735.8[a]	0–0.0014				
Sodium	Na	3.3[j]			25519	100.05	
Strontium	Sr	1000[c]					
Tin	Sn	22.6[a]	0–0.028				
Vanadium	V	26.5[a]					
Zinc	Zn	2.14[a]	0.26–0.75	0.105–1.56	0.684	0.023	0.6–17
Estimated monetary value (USD)[k]			0.02	0.06	121.35	61.56	28.29
Ref.			(Karvelas et al., 2003; Lipczynska-Kochany and Kochany, 2009; Varga et al., 2013)	(Paruch and Roseth, 2008)	(Tariq et al., 2005)	(Chakraborty and Chakrabarti, 2006)	(Yabe and Oliverira, 2003)

[a] http://www.infomine.com/investment/metal-prices/ (accessed on 6/21/2014).
[b] http://www.metalprices.com/p/AntimonyFreeChart?weight=KG&size=M&theme=1011 (accessed on 6/6/2014).
[c] http://en.wikipedia.org/wiki/Prices_of_elements_and_their_compounds.
[d] http://www.metalprices.com/p/BismuthFreeChart?weight=KG&size=M&theme=1011 (accessed on 6/6/2014).
[e] http://www.metalprices.com/p/CadmiumFreeChart?weight=KG&size=M&theme=1011 (accessed on 6/6/2014).
[f] http://www.ask.com/question/cost-of-calcium.
[g] http://www.chemicool.com/elements/.
[h] http://www.recycleinme.com/scrapresources/us_metal_prices.aspx (accessed on 6/21/2014).
[i] http://en.wikipedia.org/wiki/Potassium.
[j] http://en.wikipedia.org/wiki/Sodium.
[k] Suppose recovering 1000 L wastewater with 100% recovery efficiency.

and others. For example, U.S. Water Environment Research Foundation (WERF) reported in 2011 that a 10 million gallon per day (MGD, approximately 37,854 m^3/d) wastewater treatment plant may have the potential to recover \$8849–\$3,904,664 worth of silver per year (Bilyk et al., 2011), though the report didn't specify the types of wastewater used in the calculation. Another study reported that a direct contact membrane distillation with a hybrid electrolytic process can recover gold from an electroplate wastewater by concentrating the metal to 165 mg/L, which translates to approximately \$4600 worth of gold from every 10 m^3 of water treated (Chen et al., 2013). However, Table 1 also shows that the concentrations of metals in most wastewaters are relatively low, mainly ranging from μg/L to mg/L, so to make the recovery of such commodities more meaningful, technologies should be developed to treat a large amount of water while efficiently concentrating the targeted metals. Despite various challenges, research and development of metal recovery show good potential in wastewater industry, because a large amount of metal-laden wastewater needs to be treated regardless, and such recovery provides great economic incentives for technology development.

Technologies for metal recovery have been extensively studied using physical, chemical, and biological processes (Barakat, 2011; Fu and Wang, 2011; Veglio and Beolchini, 1997). In this study, we briefly compared the advantages and challenges of different technologies, but more importantly, we provided the first review of metal recovery using a new technology platform called bioelectrochemical systems (BESs). The BES platform has recently demonstrated excellent performances in removing and recovering metals from different wastewaters, suggesting the use of electrode for metal recovery can be a new efficient and effective approach.

Copper smelting	Acid mine drainage	Electroplating industry	Metal finishing industry	An acidic industrial effluent	Dying/ finishing mill	Hazardous waste landfill leachate	Industrially-contaminated groundwater	Electroplate company wastewater
	115.2							
1.5								
1979						13.8		
				<5		0.86	5.6	
85								
76.05	1.9					0.43		
				50			230	
2.3	0.2	0.71	<0.05	<5		0.24		
0.04				<5				
164.48	168	0.97	2.53–6.97	<5		0.27		
								9.9
88	2830	618		8000	0.28		65	
4.6		0.46				0.1		
				30			110	
	56			800			36	
						0.0008		
12	2.2	0.64	0.21–0.92	<5		1.8	0.11	
				15				
						0.037		
				500			170	
				<5				
						0.16		
455.6	120	584	3.50–9.56			1.15	0.51	
7.33	2.33	1.40	0.08	16.84	0.00	0.18	27.16	459.15
(Basha et al., 2011)	(Jiménez-Rodríguez et al., 2009)	(Boricha and Murthy, 2009)	(Gabaldón et al., 2007)	(Cinanni et al., 1996)	(Lin and Chen, 1997)	(Pavelka et al., 1993)	(Adey et al., 1996)	(Chen et al., 2013)

Table 2 – Common methods of metal recovery.

Category	Methods
Physical	Membrane filtration (ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED)); Ion exchange; Ion flotation; Adsorption;
Chemical	Precipitation; Cementation; Electroextraction (EE); Electrocoagulation (EC); Photocatalysis; Membrane electrolysis (ME);
Biological	Biosorption; Bioremediation

Table 3 – Summary of bioelectrochemical recovery of metals.

No.	Metal	Reactor	Reaction	Standard redox potential (vs. NHE)	Electron donor	Electron acceptor
Direct metal recovery using abiotic cathodes						
1	Au(III)	Two-chamber	$AuCl_4^- + 3e^- = Au + 4Cl^-$	1.002	Acetate (1000 mg/L)	Au^{3+} (100–2000 mg/L) $pH = 2$
2	V(V)	Two-chamber	$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O$	0.991	Glucose (812 mg/L, $pH = 7$) and sulfide (100 mg/L, $pH = 7$)	V^{5+} (500 mg/L) $pH = 2$
3	V(V)	Two-chamber	$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O$	0.991	Glucose (810 mg/L, $pH = 7$)	V^{5+} 250 mg/L or 500 mg/L $pH = 2$
	Cr(VI)		$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33	Acetate (excess, $pH = 7$)	$K_2Cr_2O_7$ 250 mg/L $pH = 2$
4	Cr(VI)	Two-chamber	$Cr_2O_7^{2-} + 8H^+ + 6e^- = Cr_2O_3 + 4H_2O$ $Cr_2O_3 + 6H^+ = 2Cr^{3+} + 3H_2O$	1.33	Acetate (1000 mg/L)	Cr^{6+} 204 mg/L (50–500 mg/L, $pH = 1–6$)
5	Cr(VI)	Two-chamber	$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33	Acetate (1640 mg/L, $pH = 7$)	Cr^{6+} (25, 50, 100 or 200 mg/L, $pH = 2,3,4,5$ or 6)
6	Cr(VI)	Two-chamber	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ $2Cr^{3+} + 7H_2O \rightarrow 2Cr(OH)_3(s) + 6H^+ + H_2O$ ($6.5 < pH < 10$)	NA	Acetate (1600 mg/L, $pH = 7$)	20-50 mg/L, $pH = 5–8$
7	Cr(VI)	Two-chamber	$Cr^{6+} \rightarrow Cr^{3+}$	NA	Acetate (1600 mg/L, $pH = 7$)	12.8–39.2 mg/L
8	Ag(I)	Two-chamber	$Ag^+ + e^- = Ag$	0.799	Acetate (1000 mg/L)	$AgNO_3$ (50, 100 or 200 mg/L)
9	Ag(I)	Two-chamber	$Ag^+ + e^- = Ag$	0.799	Acetate COD = 1500 or 1000 or 500 mg/L	$AgNO_3$ (170 mg/L) $pH = 2$ or 4 or 6.6
			$[AgS_2O_3]^- + e^- = Ag + S_2O_3^{2-}$	0.250		AgBr (188 mg/L) $Na_2S_2O_3$ (1580 mg/L) $pH = 4$ or 6.3 or 10
10	Cu(II)	Two-chamber	$Cu^{2+} + 2e^- = Cu$	0.286	Acetate (1640 mg/L) $pH = 7$	Cu^{2+} (1000 mg/L) $pH = 3$
11	Cu(II)	Two-chamber	$Cu^{2+} + 2e^- = Cu$	0.337	Acetate (1360 mg/L) $pH = 7$	Cu^{2+} (10–200 mg/L) $pH = 2,3,4,5$
12	Cu(II)	Two-chamber	$Cu^{2+} + 2e^- = Cu$ $2Cu^{2+} + H_2O + 2e^- = Cu_2O + 2H^+$ $Cu^{2+} + Cl^- + e^- = CuCl$	NA	Acetate (1000 mg/L)	$CuSO_4$ (600 or 2000 mg/L, $pH = 2$)
13	Cu(II)	Two-chamber	$Cu^{2+} + 2e^- = Cu$ $2Cu^{2+} + H_2O + 2e^- = Cu_2O + 2H^+$ $Cu_2O + 2e^- + 2H^+ = 2Cu + H_2O$ $4Cu^{2+} + SO_4^{2-} + 6H_2O = CuSO_4{\cdot}3Cu(OH)_2 + 6H^+$	0.337, 0.207, 0.059	Glucose (5000 mg/L)	(50, 200, 500, 1000 or 2000 mg/L, $pH = 4.7$)
14	Cu(II)	Two-chamber	$Cu^{2+} \rightarrow Cu_2O$ $Cu^{2+} \rightarrow Cu_2O + Cu$ $CuSO_4 \rightarrow Cu_4(OH)_6SO_4$	NA	Glucose (5000 mg/L)	Cu^{2+} (0, 200, 500 or 6400 mg/L)
15	Fe(III)	Two-chamber	$Fe^{3+} + e^- = Fe^{2+}$ $Fe^{2+} \rightarrow$ oxy(hydroxi)des	0.77	Acetate (100–12800 mg/L, $pH = 7.5–8.0$)	Fe^{3+} (500 mg/L, $pH = 2.4$)
16	Hg(II)	Two-chamber	$2Hg2^+ + 2e^- = Hg_2^{2+}$ $Hg_2^{2+} + 2e^- = 2Hg$ $Hg^{2+} + 2e^- = Hg$ $Hg_2^{2+} + 2Cl^- = Hg_2Cl_2$ $Hg_2Cl_2 + 2e^- = 2Hg + 2Cl^-$	0.911, 0.796, 0.851, 0.268	Acetate (1360 mg/L)	Hg^{2+} (25, 50 or 100 mg/L, $pH = 2,3,4$ or 4.8)
17	Se(IV)	Single-chamber	$SeO_3^{2-} + 4e^- \rightarrow Se$ (s)	NA	Sodium acetate (2000 mg/L) or glucose (1200 mg/L)	Oxygen, Se (IV)50 mg/L or 400 mg/L

2. Traditional metal recovery technologies

Metal recovery from wastewater has been studied using physical (e.g., membrane filtration, ion exchange, etc.), chemical (e.g., precipitation, electrochemical methods, etc.) and biological methods (e.g., biosorption, bioremediation, etc.), as shown in Table 2. Different processes demonstrated various efficacies for different metals. For example, membrane filtration, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), use pressures and different pore-sized membranes to physically retain metals while allowing water to pass through. In addition, membranes can be modified by chemical sorbents to selectively remove or retain metal ions. Ritchie et al. found that polycysteine functionalized MF membranes worked particularly well in sorbing high concentrations of Hg(II) and Cd(II), and polyglutamic acid

Power source (V)	Time (h)	Recovery efficiency	Max. Power (mW/m^2)	Ref.
Direct metal recovery using abiotic cathodes				
0	25	99.89 ± 0.00% (for 200 mg/L Au(III))	890–6580	(Choi and Hu, 2013)
0	72	25.3 ± 1.1%	572.4 ± 18.2	(Zhang et al., 2009)
0	240	67.9 ± 3.1%	970.2 ± 20.6	(Zhang et al., 2012)
		75.4 ± 1.9%		
0	10 or 23.3	Cr^{6+} (99.5%) total Cr (66.2%)	1600 (204 mg/L Cr^{6+})	(Li et al., 2008)
0	150	74.6–100%	150	(Wang et al., 2008)
0	4, 5	12.4–20.6 mg/g VSS/h	6.8–15 W/m^3	(Huang et al., 2011b)
0	7	2.0 ± 0.1–2.4 ± 0.2 mg/g VSS/h	0.3–2.4 W/m^3	(Huang et al., 2010)
0	8	99.91 ± 0.00–98.26 ± 0.01%	4250	(Choi and Cui, 2012)
0	2 or 36	95%	109	(Tao et al., 2012)
			35	
0	7	99.88% (anaerobic), 99.95% (aerobic)	430 (anaerobic), 800 (aerobic)	(Heijne et al., 2010)
0	11	60.1–99.9%	96.2–319	(Wang et al., 2010)
0	480, 672	92%, 48%	NA	(Tao et al., 2011c)
0	20, 360	>96%	339 mW/m^3	(Tao et al., 2011b)
0	144	70%	314 mW/m^3	(Tao et al., 2011a)
0	168	10–>99%	8.6 ± 2.3 W/m^3	(Lefebvre et al., 2012)
0	5–10	89.5–99.3%	433.1	(Wang et al., 2011)
0	42 or 72	99%	2900 (acetate) 1500 (glucose)	(Catal et al., 2009)

(continued on next page)

Table 3 – (*continued*)

No.	Metal	Reactor	Reaction	Standard redox potential (vs. NHE)	Electron donor	Electron acceptor
18	Cd(II)	Single-chamber	$Cd^{2+} + 2e^- = Cd$	−0.4	Acetate (4920 mg/L)	Cd^{2+}(22.5 mg/L)
	Zn(II)		$Zn^{2+} + 2e^- = Zn$	−0.764		Zn^{2+} (26 mg/L)
19	Zn(II)	Three-chamber	Zn^{2+} permeation	NA	Acetate (3280 mg/L)	400 mg/L
Metal recovery using abiotic cathodes supplemented by external power sources						
1	Ni(II)	Two-chamber	$Ni^{2+} + 2e- = Ni$	−0.25	Acetate (1000 mg/L)	Ni^{2+} (50, 100, 250, 500 or 1000 mg/L) pH = 3.0, 4.0, 5.0, Or 6.0
2	Cu(II)	Two-chamber	$Cu^{2+} + 2e^- = Cu$	0.340	Acetate (1640 mg/L) pH = 7.2	Cu^{2+}(800 mg/L)
	Pb(II)		$Pb^{2+} + 2e^- = Pb$	−0.13		Pb^{2+}(400 mg/L)
	Cd(II)		$Cd^{2+} + 2e^- = Cd$	−0.4		Cd^{2+}(800 mg/L)
	Zn(II)		$Zn^{2+} + 2e^- = Zn$	−0.762		Zn^{2+}(300 mg/L)
3	Cu(II)	Two-chamber	$Cu^{2+} \rightarrow Cu$	0.340	Acetate (1000 mg/L)	Cu^{2+} (576 mg/L, 320 mg/L)
	Ni(II)		$Ni^{2+} \rightarrow Ni$	−0.25		Ni^{2+} (531 mg/L, 295 mg/L)
	Fe(II)		$Fe^{2+} \rightarrow Fe(OH)_2$	NA		Fe^{2+} (504 mg/L) pH = 2.85
4	Cr(VI)	Two-chamber	Irradiated rutile-cathode → electron–hole pairs ($h^+_{vb} + e^-_{cb}$) Electron-hole pairs ($h^+_{vb} + e^-_{cb}$) + $e^- \rightarrow e^-_{cb}$ $6e^-_{cb} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$	1.045 (light) 0.795 (no light)	Acetate (1640 mg/L, pH = 6.5 ± 0.2)	Cr^{6+} (26 mg/L, pH = 2)
Metal conversion using bio-cathodes						
1	Cr(VI)	Two-chamber	$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$ $2Cr^{3+} + 7H_2O = 2Cr(OH)_3(s) + 6H^+ + H_2O$ (6.5 < pH < 10)	0.365	Excess acetate	Cr^{6+} = 22,31,40 and 63 mg/L
Metal conversion using bio–cathodes supplemented by external power sources						
1	Cr(VI)	Two-chamber	$Cr^{6+} \rightarrow Cr^{3+} + Cr(OH)_3$	NA	Acetate (1000 mg/L)	Cr^{6+} = 20 mg/L

Cd(II) (Ritchie et al., 2001). Electrodialysis (ED) is another physical process that applies an electrical field in a reactor with pairs of ion exchange membranes to remove metal ions from wastewater and accumulate them in concentrated solutions. General membrane-based process rejects metals together with other salts based on physical separation, and modified membranes may have higher separation selectivity and low footprint. The challenges of membrane technologies include high operational cost due to energy consumption and membrane fouling. Ion exchange uses solid resins to exchange metals from wastewater with other cations (e.g., H^+). Generally the resins are not selective but can bind metal ions sequentially based on binding preferences. Ion exchange has a high removal efficiency and fast kinetics, and it can be a good option for smaller scale industrial waste treatment processes, but it may not be suitable for high concentration wastewater due to the saturation of resins (Chiarle et al., 2000). Most ion exchange processes have been used in nano to micro gram range concentrations. Activated carbon can be effective in metal adsorption due to its high surface area, and recently low cost alternatives such as waste rice husk or fly ash were studied and showed decent adsorption for Fe^{2+}, Pb^{2+} and Ni^{2+}, or Cd^{2+} and Cu^{2+} (Hegazi, 2013). Biosorbents from natural materials derived from living biomass, dead biomass, and cellular products (e.g., polysaccharides) to remove metals have shown high efficiencies, which reduced metal concentration from ppm to ppb level (Wang and Chen, 2009).

Chemical precipitation is the most traditional and widely used technique in removing metals from aqueous systems due cipitation (e.g., $Ca(OH)_2$, NaOH, and lime), sulfide precipitation (e.g., pyrite) and chelation precipitation (e.g., trimercaptotriazine, potassium/sodiumthiocarbonate and sodium dimethyldithiocarbamate) are three main precipitation methods. However, one problem of chemical precipitation is the large amount of toxic sludge generated, which requires additional processing for disposal. Electrocoagulation (EC) is a technology that utilizes electrical current to sacrifice an aluminum or iron anode so the aluminum or iron hydroxide flocculation can adsorb and precipitate metal ions. If fine bubbles of H_2 or O_2 are produced at the cathode to float flocculation to the surface of water, the system is called electroflotation (EF). Both EC and EF do not need chemical coagulating agents, but the hazardous sludge disposal and anode replacement are main concerns. Bioremediation or phytoremediation may use microorganisms, enzymes, or living plants to clean up metal contaminated wastewater while maintaining regular metabolisms, which are considered cost-effective and environmentally friendly, but the disposal of the contaminated plants limits their applications (Gaur et al., 2014; Kikuchi and Tanaka, 2012).

3. Bioelectrochemical metal recovery

3.1. *The bioelectrochemical platform for metal recovery*

Bioelectrochemical system (BES) is a platform technology that employs microorganisms to covert the chemical energy stored in biodegradable materials to electric current and chemicals.

Power source (V)	Time (h)	Recovery efficiency	Max. Power (mW/m^2)	Ref.
0	50	90% 97%	3600	(Abourached et al., 2014)
0	72	94 ± 4%	0.233 mW	(Fradler et al., 2014)
Metal recovery using abiotic cathodes supplemented by external power sources				
0.5–1.1	19.8	99 ± 0.6%–33 ± 4.2%	0	(Qin et al., 2012)
0	2	84.3%	0	(Modin et al., 2012)
0.34	2	47.5%		
0.51	0.2–1	62%		
1.7	1–2	44.2%		
1.0	140	>97%	0	(Luo et al., 2014)
0	26	97%	–	(Li et al., 2009)
Metal conversion using bio-cathodes				
0	120–168	100%	55.5	(Tandukar et al., 2009)
Metal conversion using bio–cathodes supplemented by external power sources				
Poised potentials at −150 mV, −300 mV, −450 mV, +200 mV	72, 216, 312, 456, 624, 792, 960	19.7 mg/L/d	6.4 W/m^3	(Huang et al., 2011a)

BES offers a new solution for integrated waste treatment and energy and resource recovery, because it offers a flexible platform for both oxidation and reduction reaction oriented processes (Li et al., 2014; Logan and Rabaey, 2012; Wang and Ren, 2013). Most BES reactors consist of an anode, a cathode and an optional separator, and configurations can vary depending on target functions to be accomplished. In general, biodegradable materials, such as wastewater, are oxidized by microorganisms in the anode chamber to generate electron flow (current) to the cathode, where in the cathode chamber, the electrons can be used for direct electricity production (microbial fuel cells, MFCs), or the electrons are used for the reduction of water or oxidized chemicals, such as metal ions, CO_2, or organic chemicals (microbial electrolysis cells, MECs, or microbial electrosynthesis, MES) (Choi and Cui, 2012; Heijne et al., 2010; Logan et al., 2008; Logan and Rabaey, 2012; Lohner et al., 2011; Wang and Ren, 2013). The use of BES for wastewater treatment has been intensely investigated in recent years, and several excellent reviews discussed the suitability of BES for different wastewater conditions (Li et al., 2014; Pant et al., 2010; Wang and Ren, 2013). Most studies concluded that the advantages of BES for wastewater treatment come from the savings of aeration energy and sludge disposal. Because BES has lower energy densities than other anaerobic processes such as anaerobic digestion, it has been primarily used for lower strength wastewater treatment (Huggins et al., 2013; McCarty et al., 2011; Zhang and He, 2013). The BES platform has been shown effective in the reduction and recovery of different metals by numerous feasibility studies, and the European Union recently launched a multi-million Euro BioelectroMET project coordinated by Wetsus to research, develop, and demonstrate BESs for recovering metals from metallurgical wastewater with no or limited energy input (http://www.bioelectromet.eu/home/about-bioelectromet). However, so far there has been no review summarizing or commenting on the different fundamental mechanisms and engineering feasibilities of this new BES approach for metal removal and recovery, and this review aims to provide such information and assist in understanding the mechanisms and further developing the technology.

This study summarizes all bioelectrochemically assisted metal recovery processes published so far and divides them into 4 categories. It also offers comprehensive information on the various approaches for recovering metals with different redox potentials and provides an outlook on technology development. While all the BES assisted metal recoveries are associated with metal reduction on the cathode, as shown in Table 3 and Fig. 1, we summarize there are 4 mechanisms that need to be distinguished. The first process involves direct reduction of the metals on an abiotic cathode for those with redox potential higher than the anode potential. Such metals include Au (III), V (V), Cr (VI), Ag (I), Cu (II), Fe (III), and Hg (II), etc., and their respective reduction products are shown in Fig. 1A. The reduction is thermodynamically favorable, and the metals can be directly used as the electron acceptor without any external power consumption (Choi and Cui, 2012; Choi and Hu, 2013; Heijne et al., 2010; Lefebvre et al., 2012; Li et al., 2008; Tao et al., 2012, 2011b, 2011c, 2011a, 2011b, 2011c; Wang et al., 2008,

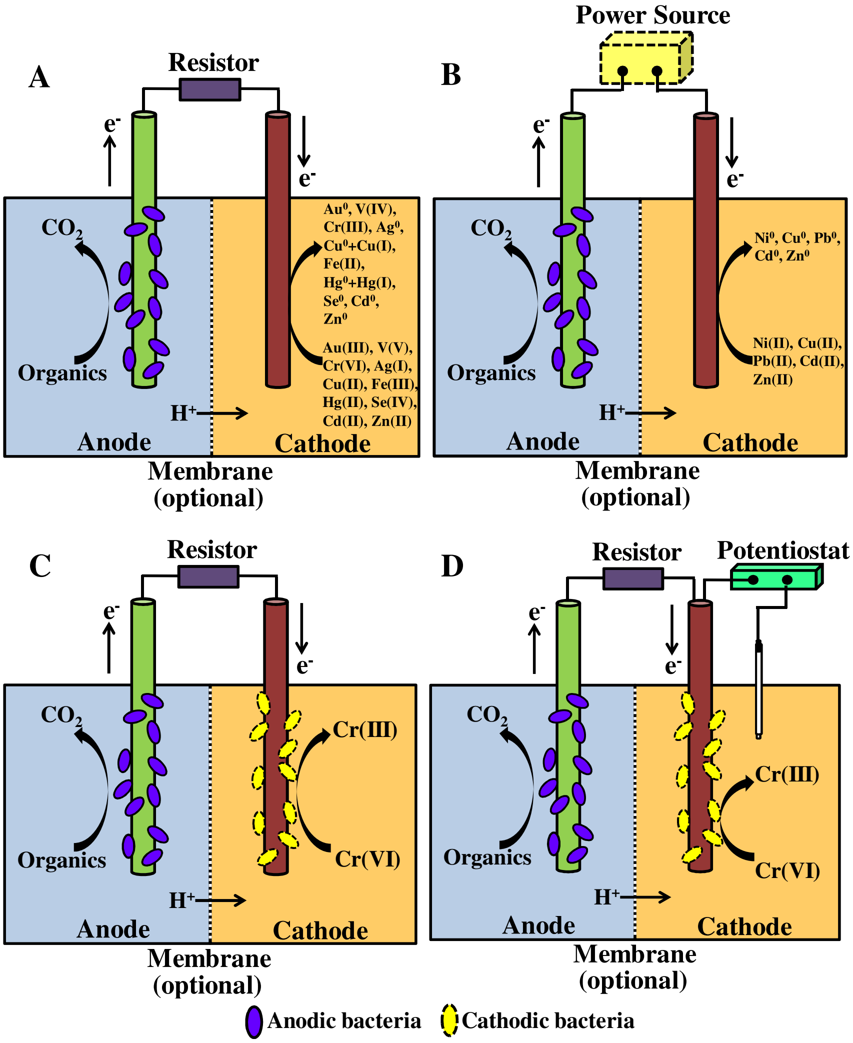

Fig. 1 – Four reported mechanisms of bioelectrochemically assisted metal recovery in bioelectrochemical systems. (A) Direct metal recovery using abiotic cathodes; (B) metal recovery using abiotic cathodes supplemented by external power sources; (C) metal conversion using bio-cathodes; (D) metal conversion using bio-cathodes supplemented by external power sources. The membrane is optional.

2011; 2010; Zhang et al., 2012, 2009). The second process requires an external power supply to force the electrons travel from the anode to the abiotic cathode, so metals with lower redox potentials than the anode potentials can be reduced. Such metals mainly include Ni (II), Pb (II), Cd (II), and Zn (II), etc., and their respective reduction products are demonstrated in Fig. 1B (Modin et al., 2012; Qin et al., 2012). The third mechanism is associated with microbial reduction of metal oxides on a cathode (Fig. 1C). For example, Cr (VI) was reduced with the assistance of microbial metabolisms on a biocathode (Tandukar et al., 2009). The last mechanism reported in literature is microbially assisted metal reduction with a poised potential (Fig. 1D), which is a combination of process 2 and 3. For instance, Huang et al. (2011a) found that Cr (VI) can be reduced at a higher rate on a biocathode with poised potentials. For mechanisms 3 and 4, only Cr (VI) has been tested so far, though other transition metals may be reduced using the similar approaches as well.

3.2. *Direct metal recovery using abiotic cathodes*

The anode potential of a BES reactor is generally around −300 mV (vs. Normal Hydrogen Electrode, NHE) when using organic electron donors, and the potential is set by the respiratory enzymes of the electrochemically active bacteria (Liu et al., 2005; Logan et al., 2006). The cathode potential can vary depending on the electron acceptors used, so for soluble metal oxides to be reduced and recovered in the cathode chamber spontaneously, their redox potentials need to be higher than the anode potential in the given condition. The actual cathode potential can be calculated by equation (a)

$$E = E^0 - (RT/nF)\ln([M_{\mathrm{red}}]/[M_{\mathrm{ox}}]), \tag{a}$$

where E is the electrochemical redox potential in a specific condition, E^0 is the electrochemical redox potential at 298.15 K and 1 atm with 1 mol/L activity of each aqueous species, *R* is the gas constant (8.31447 J/mol/K), *T* is the absolute temperature (K), *n* is the number of electrons transferred, *F* is Faraday's constant (96,485 C/mol), $[M_{red}]$ is the concentration of reduced metals, and $[M_{ox}]$ is the concentration of oxidized metals (mg/L).

Several studies have demonstrated that precious metals with higher redox potentials can be recovered in the cathode chamber, accompanied by electricity production during the oxidation of organic substrates in the anode (Table 3). For example, without using external energy, 99.89 ± 0.00% gold (Au) were recovered in a two-chamber microbial fuel cell type BES by reducing Au(III) ions in the catholyte with a maximum power production of 6.58 W/m^2 at 25 h (Choi and Hu, 2013). The same group also reported that as high as 99.91 ± 0.00% of Ag(I) was recovered after 8 h operation with a maximum power density 4.25 W/m^2 (Choi and Cui, 2012). Tao et al., also reported Ag(I) recovery and concluded that the removal rate of Ag(I) was more rapid than that of Ag(I) thiosulfate complex (Tao et al., 2012). Vanadium (V(V)) was another metal recovered using this process, with 25.3 ± 1.1% recovery yield from an initial V(V) concentration of 500 mg/L at 72 h (Zhang et al., 2009). The same group later boosted recovery to 67.9 ± 3.1% at 240 h with Cr(VI) competing for electrons (Zhang et al., 2012). Cr(VI) can be a great electron accepter due to its high oxidation potential (1.33 V vs. NHE), so some studies showed the reduction of $Cr_2O_7^{2-}$ to precipitate Cr_2O_3 in order to treat Cr(VI)-containing wastewater and recover chromium (Li et al., 2008; Wang et al., 2008). Cu(II) recovery has been widely studied using the BES approach, with initial concentrations ranged from 0 to as high as 6400 mg/L. The recovery efficiencies were reported from 60.1% to 99.9% under aerobic or anaerobic conditions (Heijne et al., 2010; Tao et al., 2011a, 2011b; Wang et al., 2010). The first pilot scale Cu(II) recovery system was built and operated by (Tao et al., 2011c), with the removal efficiency of 92% at 480 h and 48% at 672 h with initial concentrations of 600 mg/L and 2000 mg/L, respectively. In treating acid mine drainage dominated with iron, Fe^{3+} was firstly reduced to Fe^{2+} and then Fe^{2+} re-oxidatized to precipitate oxy(hydroxi)des (Lefebvre et al., 2012). Recovery of Hg(II) in the cathode chamber involved many complex reactions, but the products were verified as elemental Hg on the cathode surface and Hg_2Cl_2 as deposits on the bottom of cathode chamber (Wang et al., 2011).

While most studies used two-chamber BESs or MFCs to reduce metal ions in the anaerobic cathode by using the electrons supplied from the organic oxidization in the anode chamber, such separation may not be feasible for wastewater treatment, because both metals and organic matter co-exist in the same water stream, and the power output of the two-chamber MFC was low due to its high internal resistance. Recent studies began to consider single-chamber reactors to tackle this problem, where the same solution containing multiple pollutants is fed into a single chamber. One study showed Cd and Zn were removed through biosorption and sulfide precipitation with a higher power output of 3.6 W/m^2 (Abourached et al., 2014). The study also estimated the maximum tolerable concentrations (MTCs) of Cd and Zn were 200 mM and 400 mM, respectively. Another study showed that Se(IV) accepted electrons directly from the bacteria enriched for electricity generation, and 99% Se(IV) were recovered as the bright red deposit of elemental Se (Catal et al., 2009). However, the power density decreased from 2.9 to 2.2 W/m^2 when Se(IV) concentration increased from 25 to 75 mg/L due to the increased toxicity to microbes. The high concentration metal ions, e.g., Se(IV), can inhibit bacterial metabolisms in the single-chamber MFCs, but such effects can be avoided in the two-chamber setup due to the separation of metal-enriching solution in the cathode chamber and microbes in the anode chamber. The power output from BES has also been used as a power source for electrical metal conversion, with one study showed 99% arsenite (As(III)) removal through a hybrid processes of MFC and zerovalent iron (Xue et al., 2013).

A recent study utilized a new three-chamber system including a two-chamber MFC and a strip chamber adjacent the cathode chamber to recover Zn(II) (Fradler et al., 2014). The design enhanced the power production compared to a two-chamber MFC control, and Zn(II) in the cathode chamber was physically extracted through supported liquid membrane (SLM) and cumulated in the strip chamber. Although there were no chemical reactions happening to Zn(II), the concentration of Zn(II) in the strip chamber could be a pretreatment for further recovery.

3.3. *Metal recovery using abiotic cathodes supplemented by external power sources*

Metal ions with comparable or lower redox potentials than the BES anode potential cannot accept electrons spontaneously from the cathode, because the thermodynamic limits prevent electrons from flowing from the anode to the cathode spontaneously. However, these metal ions can still be reduced by accepting the electrons from the cathode when an extra power source is used to forcibly drive the electrons from the high potential anode to the low potential cathode. For example, nickel ion (Ni(II)) has an electrochemical redox potential of −0.25 V (vs. NHE), which cannot be naturally reduced to nickel metal under standard MFC/BES conditions. But when an external voltage of 0.5–1.1 V was applied, between 51 ± 4.6% and 67 ± 5.3% of Ni(II) was reduced from an initial concentration of 500 mg/L (Qin et al., 2012). Moreover, four different metal ions of Cu(II), Pb(II), Cd(II) and Zn(II) in a mixed catholyte were sequentially recovered when applied voltages were gradually increased (0 V, 0.34 V. 0.52 V and 1.7 V) (Modin et al., 2012). This can be an interesting approach to separate the mixed metal ions from a waste stream. Table 3 lists the standard redox potential of each metal, which can be used to design sequential removal studies. Though the voltage used in this process is generally lower than 2 V, the additional energy needed for metal reduction to some extent defeats the purpose of energy savings based on the BES principle. Theoretically, all metal ions might be reduced to metals using such an approach if enough voltage is applied, but cost-benefit analysis regarding to energy audit, chemical recovery yield and rates need to be conducted before potential engineering applications for such processes. There has been no study that discussed such considerations. Another problem of using external voltage is the unintended hydrogen production when the cathode potential dropped below hydrogen evolution potential (−0.6 V vs. NHE) (Modin et al., 2012). While gas production does reduce metal reduction efficiencies, hydrogen may also be used as a renewable energy source if possible, and it assists to keep pH balanced with the accumulation of hydroxyl ions. The increased pH facilitates metal precipitation and therefore its removal from solution. Luo et al. sequentially removed Cu^{2+}, Ni^{2+} and Fe^{2+} from artificial acid mine drainage (AMD) with simultaneous H_2 production, when applying an extra power of 1.0 V (Luo et al., 2014). They obtained the energy recovery efficiency (the ratio of the energy content of the H_2 produced to the input electrical energy) up to 100%, which suggested that the produced H_2 gas was sufficient to offset the energy consumed during the metal recovery. Different from direct voltage application, several studies utilized via exited semiconductor mediators to accomplish similar goals of electron transfer. For example, Li et al. (2009) reduced Cr(VI) photocatalytically at the irradiated rutile-coated cathode and found the reduction rate was 1.6× faster under light irradiation than that under dark condition. Visible light excited the rutile-coated cathode by producing electrons and holes, and then the electrons could be used to reduce Cr(VI) to Cr(III) with the holes been filled by electrons from the anode.

3.4. *Metal conversion using bio-cathodes*

Microorganisms play an important role in metal distribution and circulation in nature, and the interactions between microbes and metals mainly include metal assimilation and metal dissimilation. Different from assimilation, in which microbes assimilate metals into cellular materials as enzyme cofactors, the metal recovery process involves dissimilatory metal reduction by using the metal as an external electron acceptor (Holden and Adams, 2003). Table 4 lists the main dissimilatory metal reducing bacteria (DMRB) species that use metal ions as the terminal electron acceptors. DMRBs respire using metals or metalloids outside the cell membrane for cellular energetics, and they have been widely used in bioremediation of metal contaminated sites. For example, mobile and toxic Cr(VI) can be reduced by DMRBs to less mobile and less toxic Cr(III) (Daulton et al., 2007; Rahman et al., 2007; Shugaba et al., 2012; Tandukar et al., 2009; Viti et al., 2003); Se(VI) and Se(IV) can be microbially remediated to Se(0), so the metal can be precipitated (Combs et al., 1996; Garbisu et al., 1996; He and Yao, 2011; Kashiwa et al., 2000; Kessi et al., 1999; Tomei et al., 1995). DMRBs have also been used for metallic nanoparticles (NPs) production, which carry superior catalytic functions compared to the ones prepared using chemical methods (Deplanche et al., 2012). Yates et al. used *Geobacter sulfurreducens* to reduce soluble Pd(II) to Pd(0) NPs outside microbial cells (Yates et al., 2013). Spherical silver NPs were synthesized from aqueous $AgNO_3$ solutions by *Plectonema boryanum* from 25 to 100 °C both intracellularly (<10 nm) and extracellularly (1–200 nm) (Lengke et al., 2007). Several reviews discussed microbial metal or metalloids reduction mechanisms and applications (Liu et al., 2002; Lloyd, 2003; Lovley, 1993). DMRBs have also been found and used for BES anode reduction associated with organic oxidation in the anode chamber (Gorby et al., 2006; Lovley, 2006).

There have been limited studies utilizing bio-cathode for metal reduction. One study demonstrated biological

Table 4 – Microbial reduction and precipitation of metal ions.

Metal ions	Name of species	Ref.
Cr(VI)	*Trichococcus pasteurii*; *Pseudomonas aeruginosa*; *Shewanella oneidensis*; *Aspergillus niger*; *Aspergillus parasiticus*; *Pseudomonas* sp.; *Bacillus maroccanus*; *Corynebacterium hoagie*; *Bacillus megaterium*; *Cellulomonas turbata*	(Daulton et al., 2007; Rahman et al., 2007; Shugaba et al., 2012; Tandukar et al., 2009; Viti et al., 2003)
Se(VI)	*Desulfovibrio desulfuricans*; *Bacillus* sp.	(Kashiwa et al., 2000; Tomei et al., 1995)
Se(IV)	*Anaeromyxobacter dehalogenans*; *Bacillus subtilis*; *Microbacterium arborescens*; *Rhodospirillum rubrum*; *Pseudomonas fluorescens*; *Desulfovibrio desulfuricans*	(Combs et al., 1996; Garbisu et al., 1996; He and Yao, 2011; Kessi et al., 1999; Tomei et al., 1995)
Pd(II)	*Geobacter sulfurreducens*; *Cupriavidus necator*; *Cupriavidus metallidurans*; *Escherichia coli*	(Deplanche et al., 2012; Gauthier et al., 2010; Yates et al., 2013)
Au(III)	*Shewanella algae*; *Geobacillus* sp.; *Cupriavidus metallidurans*; *Verticillium luteoalbum*	(Correa-Llantén et al., 2013; Gericke and Pinches, 2006; Konishi et al., 2006; Reith et al., 2009)
U(VI)	*Desulfosporosinus* spp.; *Clostridium* spp.	(Suzuki et al., 2003)
As(V)	*Chrysiogenes arsenates*; *Desulfotomaculum auripigmentum*	(Macy et al., 1996; Newman et al., 1997)
V(V)	*Shewanella oneidensis*	(Carpentier et al., 2003)
Ag(I)	*Plectonema boryanum*	(Lengke et al., 2007)
Fe(III)	*Bacillus subterraneus*; *Shewanella putrefaciens*; *Geobacter bemidjiensis*; *Geobacter psychrophilus*	(Kanso et al., 2002; Nealson and Myers, 1992; Nevin et al., 2005)
Mn(IV)	*Bacillus subterraneus*; *Shewanella putrefaciens*	(Kanso et al., 2002; Nealson and Myers, 1992)
Hg(II)	*Bacillus cereus*; *Shewanella oneidensis*; *Anoxybacillus* sp.	(Kritee et al., 2008)
Tc(VII)	*Escherichia coli*; *Desulfovibrio desulfuricans*; *Geobacter sulfurreducens*	(Lloyd et al., 1999a, Lloyd et al. 2000; Lloyd et al., 1999b)
Mo(VI)	*Serratia* sp.; *Acinetobacter calcoaceticus*; *Klebsiella* sp.	(Lim et al., 2012; Rahman et al., 2009; Shukor et al., 2010)

conversion of Cr(VI) to $Cr(OH)_3$, which precipitated on the cathode of an MFC with a maximum power production of 55.5 mW/m^2 at the initial Cr(VI) concentration of 63 mg/L 16S rRNA analysis disclosed that Cr(VI) reducing microorganisms were closely related to *Trichococcus pasteurii* and *Pseudomonas aeruginosa* (Tandukar et al., 2009). Although Cr(VI) can be reduced directly from the abiotic cathode under acidic conditions as mentioned in Section 3.2, Cr(VI) reduction on biocathode occurred under mild pH condition in order to keep bacterial activities and reduce chemical and maintenance costs, but lower initial Cr(VI) concentrations were studied at the biotic cathode than that at the abiotic cathode (Tandukar et al., 2009).

3.5. *Metal conversion using bio-cathodes supplemented by external power sources*

Similarly to Section 3.3, for metals with lower redox potentials, external power sources can be used on biocathode to facilitate reduction. When poising the cathode potential at a certain level, although metals are not reduced electrochemically, metal ions can be extracted from solution and adsorbed into the biofilms of the electrodes, and then microorganisms on the electrodes reduce metals during microbial respiration. One study reported that U(VI) was reduced to U(IV) by *Geobacter sulfurreducens* with a poised cathode potential of −500 mV, which is much lower than the electrochemical reduction of U(VI) at −900 mV (Gregory and Lovley, 2005). Another study showed that by applying a −300 mV potential, the reduction rate of Cr(VI) and power production were both improved compared to the control reactors without set potentials (Huang et al., 2011a). The poised potential attracts the migration and adsorption of the charged metal ions onto the cathode, while the biofilm on the cathode help retain the ions from desorption when the potential is removed. Metal conversion using bio-cathodes with a small set potential can quickly remove metals from contaminated environment due to electrical and biological adsorptions, and as a result it requires less energy compared with traditional electrochemical reduction methods.

4. Outlook

While metal removal and recovery from wastewater has been a main topic in resource recovery, the use of novel bioelectrochemical platform could be a new option for more efficient and low energy approach. This review summarizes this new technique by dividing different processes into 4 categories and discussed the advantages and challenges of each scenario. Overall, the BES platform shows great potential in recovering different metals with various redox potentials due to its great flexibility, but much more needs to be done to further understand the mechanisms and investigate the feasibility of engineering applications. Here we discuss some specific challenges that require more investigations.

1. Most studies so far were conducted in lab scale using synthetic media, which demonstrates the feasibility but far from representing the reality. More studies are needed to test different real wastewater streams containing various metals for the characterization on system efficacy in real conditions. How to selectively recover and sequentially separate mixed metals from aqueous solutions can be a very interesting topic, and by controlling electrical potential, pH, retention time, and other parameters, mixed metals may be recovered and separated.
2. New reactor configurations, materials, and system integration processes need to be developed to improve metal recovery yield and rate, especially in low concentration and mixed metal conditions. Such variations may need to be customized for different metal types and conditions, and long term performance need to be investigated as well.
3. There has been limited information on how electrostatic interactions between the cathode and metal ions affect metal recovery efficiency. It is hypothesized that electrostatic attraction facilitates metal cations to move toward the cathode, while electrostatic repulsion inhibits the approaching of metal anions to the cathode, such as selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), dichromate ($Cr_2O_7^{2-}$), etc, but quantitative characterizations are needed to fully understand the effects.
4. Most studies kept a very low catholyte pH in order to keep metal dissolved in acidic condition, which generates environmental and operation concerns. The low pH also posts another challenge of H_2 evolution in poised potential conditions, which decreases metal conversion efficiency. The use of bio-cathodes may alleviate this problem.
5. While most studies showed the feasibility, few actually demonstrated actual separations of reduced metal products from the electrodes, partially because current electrode materials used including carbon cloth, activated carbon, graphite granule, etc., are hard to conduct separation, especially when live biofilms need to be kept intact for further operation. Physical and chemical removals such as heating, solvent extraction, electrolysis may need to be applied, but such methods will increase operational costs and likely to destroy the biofilm.
6. Bio-cathodes have shown good performances in removing and recovering metals, but high concentration metal solutions generally inhibit microbial activities and reduce system efficacy. More effective and tolerant biofilms need to be investigated.
7. Economic and possible life cycle analyses are needed to understand the costs and benefits of specific BES metal recovery processes before its potential scale-ups and applications. Such investigations will be very important for each specific scenario, because different waste streams may have different metal constituents, concentrations, and regulation needs for removal and recovery, and such understanding will greatly help with decision making.

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REFERENCES

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.

Adey, W.H., Luckett, C., Smith, M., 1996. Purification of industrially contaminated groundwaters using controlled ecosystems. Ecol. Eng. 7 (3), 191–212.

Barakat, M.A., 2011. New trends in removing heavy metals from industrial wastewater. Arab. J. Chem. 4, 361–377.

Basha, C.A., Somasundaram, M., Kannadasan, T., Lee, C.W., 2011. Heavy metals removal from copper smelting effluent using electrochemical filter press cells. Chem. Eng. J. 171 (2), 563–571.

Bilyk, K., Bustamante, H., Connor, M., deBarbadillo, C., Downing, L., Dupont, R., Fattah, K.P., Finch, R., Gray, D., Harper, W., Hermanowicz, S., Hong, S.-N., Jolis, D., Madubuko, J., Sharp, R., Stacklin, C., Bastian, B., Graaff, M.D., Hodges, J., Johnson, T., Stinson, B., Pramanik, A., 2011. Nutrient Recovery: State of the Knowledge. Water Environment Research Foundation.

Boricha, A.G., Murthy, Z.V.P., 2009. Preparation, characterization and performance of nanofiltration membranes for the treatment of electroplating industry effluent. Sep. Purif. Technol. 65 (3), 282–289.

Carpentier, W., Sandra, K., Smet, I.D., Brigé, A., Smet, L.D., Beeumen, J.V., 2003. Microbial reduction and precipitation of vanadium by *Shewanella oneidensis*. Appl. Environ. Microbiol. 69 (6), 3636–3639.

Catal, T., Bermek, H., Liu, H., 2009. Removal of selenite from wastewater using microbial fuel cells. Biotechnol. Lett. 31 (8), 1211–1216.

Chakraborty, P., Chakrabarti, C.L., 2006. Chemical speciation of Co, Ni, Cu, and Zn in mine effluents and effects of dilution of the effluent on release of the above metals from their metal-dissolved organic carbon (DOC) complexes. Anal. Chim. Acta 571 (2), 260–269.

Chen, T.-C., Huang, G.-H., Chen, C.-S., Huang, Y.-H., 2013. Reducing industrial wastewater and recovery of gold by direct contact membrane distillation with electrolytic system. Sustain. Environ. Res. 23 (3), 209–214.

Chiarle, S., Ratto, M., Rovatti, M., 2000. Mercury removal from water by ion exchange resins adsorption. Water Res. 34 (11), 2971–2978.

Choi, C., Cui, Y., 2012. Recovery of silver from wastewater coupled with power generation using a microbial fuel cell. Bioresour. Technol. 107, 522–525.

Choi, C., Hu, N., 2013. The modeling of gold recovery from tetrachloroaurate wastewater using a microbial fuel cell. Bioresour. Technol. 133, 589–598.

Cinanni, V., Gough, I.A., Sciuto, A.J., 1996. A water treatment and recovery plant for highly acidic heavy metal laden effluents. Desalination 106 (1–3), 145–150.

Combs, G.F., Garbisu, C., Yee, B.C., Yee, A., Carlson, D.E., Smith, N.R., Magyarosy, A.C., Leighton, T., Buchanan, B.B., 1996. Bioavailability of selenium accumulated by selenite-reducing bacteria. Biol. Trace Elem. Res. 52 (3), 209–225.

Correa-Llantén, D.N., Muñoz-Ibacache, S.A., Castro, M.E., Muñoz, P.A., Blamey, J.M., 2013. Gold nanoparticles synthesized by *Geobacillus* sp. strain ID17 a thermophilic bacterium isolated from Deception Island, Antarctica. Microb. Cell. Fact. 12 (1), 75–80.

Daulton, T.L., Little, B.J., Jones-Meehan, J., Blom, D.A., Allard, L.F., 2007. Microbial reduction of chromium from the hexavalent to divalent state. Geochim. Cosmochim. Acta 71 (3), 556–565.

Deplanche, K., Merroun, M.L., Casadesus, M., Tran, D.T., Mikheenko, I.P., Bennett, J.A., Zhu, J., Jones, I.P., Attard, G.A., Wood, J., Selenska-Pobell, S., Macaskie, L.E., 2012. Microbial synthesis of core/shell gold/palladium nanoparticles for applications in green chemistry. J. R. Soc. Interface 9 (72), 1705–1712.

Fradler, K.R., Michie, L., Dinsdale, R.M., Guwy, A.J., Premier, G.C., 2014. Augmenting microbial fuel cell power by coupling with supported liquid membrane permeation for zinc recovery. Water Res. 55, 115–125.

Fu, F., Wang, Q., 2011. Removal of heavy metal ions from wastewaters: a review. J. Environ. Manage 92 (3), 407–418.

Gabaldón, C., Izquierdo, M., Martínez-Soria, V., Marzal, P., Penya-Roja, J.M., Alvarez-Hornos, F.J., 2007. Biological nitrate removal from wastewater of a metal-finishing industry. J. Hazard Mater. 148 (1–2), 485–490.

Garbisu, C., Ishii, T., Leighton, T., Buchanan, B.B., 1996. Bacterial reduction of selenite to elemental selenium. Chem. Geol. 132 (1–4), 199–204.

Gaur, N., Flora, G., Yadav, M., Tiwari, A., 2014. A review with recent advancements on bioremediation based abolition of heavy metals. Environ. Sci. Process. Impacts 16 (2), 180–193.

Gauthier, D., Søbjerg, L.S., Jensen, K.M., Lindhardt, A.T., Bunge, M., Finster, K., Meyer, R.L., Skrydstrup, T., 2010. Environmentally benign recovery and reactivation of palladium from industrial waste by using gram-negative bacteria. ChemSusChem 3 (9), 1036–1039.

Gericke, M., Pinches, A., 2006. Microbial production of gold nanoparticles. Gold Bull. 39 (1), 22–28.

Gorby, Y.A., Yanina, S., McLean, J.S., Rosso, K.M., Moyles, D., Dohnalkova, A., Beveridge, T.J., Chang, I.S., Kim, B.H., Kim, K.S., Culley, D.E., Reed, S.B., Romine, M.F., Saffarini, D.A., Hill, E.A., Shi, L., Elias, D.A., Kennedy, D.W., Pinchuk, G., Watanabe, K., Ishii, S.i., Logan, B., Nealson, K.H., Fredrickson, J.K., 2006. Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms. PNAS 103 (30), 11358–11363.

Gregory, K.B., Lovley, D.R., 2005. Remediation and recovery of uranium from contaminated subsurface environments with electrodes. Environ. Sci. Technol. 39 (22), 8943–8947.

http://www.bioelectromet.eu/home/about-bioelectromet.

He, Q., Yao, K., 2011. Impact of alternative electron acceptors on selenium (IV) reduction by anaeromyxobacter dehalogenans. Bioresour. Technol. 102 (3), 3578–3580.

Hegazi, H.A., 2013. Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents. HBRC J. 9 (3), 276–282.

Heijne, A.T., Liu, F., Weijden, R.v.d., Weijma, J., Buisman, C.J.N., Hamelers, H.V.M., 2010. Copper recovery combined with electricity production in a microbial fuel cell. Environ. Sci. Technol. 44 (11), 4376–4381.

Holden, J.F., Adams, M.W.W., 2003. Microbe-metal interactions in marine hydrothermal environments. Curr. Opin. Chem. Biol. 7 (2), 160–165.

Huang, L., Chen, J., Quan, X., Yang, F., 2010. Enhancement of hexavalent chromium reduction and electricity production from a biocathode microbial fuel cell. Bioprocess Biosyst. Eng. 33 (8), 937–945.

Huang, L., Chai, X., Chen, G., Logan, B.E., 2011a. Effect of set potential on hexavalent chromium reduction and electricity generation from biocathode microbial fuel cells. Environ. Sci. Technol. 45 (11), 5025–5031.

Huang, L., Chai, X., Cheng, S., Chen, G., 2011b. Evaluation of carbon-based materials in tubular biocathode microbial fuel cells in terms of hexavalent chromium reduction and electricity generation. Chem. Eng. J. 166 (2), 652–661.

Huggins, T., Fallgren, P.H., Jin, S., Ren, Z.J., 2013. Energy and performance comparison of microbial fuel cell and conventional aeration treating of wastewater. J. Microb.

Biochem. Technol., S6:002. http://dx.doi.org/10.4172/1948-5948.S6-002.

Jiménez-Rodríguez, A.M., Durán-Barrantes, M.M., Borja, R.S., Sanchez, E., Colmenarejo, M.F., Raposo, F., 2009. Heavy metals removal from acid mine drainage water using biogenic hydrogen suphide and effluent from anaerobic treatment: effect of pH. J. Hazard Mater. 165 (1–3), 759–765.

Kanso, S., Greene, A.C., Patel, B.K.C., 2002. *Bacillus subterraneus* sp. nov., an iron- and manganese-reducing bacterium from a deep subsurface Australian thermal aquifer. Int. J. Syst. Evol. Microbiol. 52 (3), 869–874.

Karvelas, M., Katsoyiannis, A., Samara, C., 2003. Occurrence and fate of heavy metals in the wastewater treatment process. Chemosphere 53 (10), 1201–1210.

Kashiwa, M., Nishimoto, S., Takahashi, K., Ike, M., Fujita, M., 2000. Factors affecting soluble selenium removal by a selenate-reducing bacterium *Bacillus sp*. SF-1. J. Biosci. Bioeng. 89 (6), 528–533.

Kessi, J., Ramuz, M., Wehrli, E., Spycher, M., Bachofen, R., 1999. Reduction of selenite and detoxification of elemental selenium by the phototrophic bacterium *Rhodospirillum rubrum*. Appl. Environ. Microbiol. 65 (11), 4734–4740.

Kikuchi, T., Tanaka, S., 2012. Biological removal and recovery of toxic heavy metals in water environment. Crit. Rev. Env. Sci. Technol. 42 (10), 1007–1057.

Konishi, Y., Tsukiyama, T., Ohno, K., Saitoh, N., Nomura, T., Nagamine, S., 2006. Intracellular recovery of gold by microbial reduction of $AuCl_4^-$ ions using the anaerobic bacterium *Shewanella algae*. Hydrometallurgy 81 (1), 24–29.

Kritee, K., Blum, J.D., Barkay, T., 2008. Mercury stable isotope fractionation during reduction of Hg(II) by different microbial pathways. Environ. Sci. Technol. 42 (24), 9171–9177.

Lefebvre, O., Neculita, C.M., Yue, X., Ng, H.Y., 2012. Bioelectrochemical treatment of acid mine drainage dominated with iron. J. Hazard Mater. 241–242, 411–417.

Lengke, M.F., Fleet, M.E., Southam, G., 2007. Biosynthesis of silver nanoparticles by filamentous cyanobacteria from a silver(I) nitrate complex. Langmuir 23 (5), 2694–2699.

Li, Z., Zhang, X., Lei, L., 2008. Electricity production during the treatment of real electroplating wastewater containing Cr^{6+} using microbial fuel cell. Process Biochem. 43 (12), 1352–1358.

Li, Y., Lu, A., Ding, H., Jin, S., Yan, Y., Wang, C., Zen, C., Wang, X., 2009. Cr(VI) reduction at rutile-catalyzed cathode in microbial fuel cells. Electrochem. Commun. 11 (7), 1496–1499.

Li, W., Yu, H., He, Z., 2014. Towards sustainable wastewater treatment by using microbial fuel cells-centered technologies. Energy Environ. Sci. 7, 911–924.

Lim, H.K., Syed, M.A., Shukor, M.Y., 2012. Reduction of molybdate to molybdenum blue by *Klebsiella* sp. strain hkeem. J. Basic Microbiol. 52 (3), 296–305.

Lin, S.H., Chen, M.L., 1997. Treatment of textile wastewater by chemical methods for reuse. Water Res. 31 (4), 868–876.

Lipczynska-Kochany, E., Kochany, J., 2009. Effect of humate on biological treatment of wastewater containing heavy metals. Chemosphere 77 (2), 279–284.

Liu, C., Gorby, Y.A., Zachara, J.M., Fredrickson, J.K., Brown, C.F., 2002. Reduction kinetics of Fe (III), Co (III), U (VI), Cr (VI), and Tc (VII) in cultures of dissimilatory metal-reducing bacteria. Biotechnol. Bioeng. 80 (6), 637–649.

Liu, H., Grot, S., Logan, B.E., 2005. Electrochemically assisted microbial production of hydrogen from acetate. Environ. Sci. Technol. 39 (11), 4317–4320.

Lloyd, J.R., 2003. Microbial reduction of metals and radionuclides. FEMS Microbiol. Rev. 27 (2–3), 411–425.

Lloyd, J.R., Ridley, J., Khizniak, T., Lyalikova, N.N., Macaskie, L.E., 1999a. Reduction of technetium by *Desulfovibrio desulfuricans*: biocatalyst characterization and use in a flowthrough bioreactor. Appl. Environ. Microbiol. 65 (6), 2691–2696.

Lloyd, J.R., Thomas, G.H., Finlay, J.A., Cole, J.A., Macaskie, L.E., 1999b. Microbial reduction of technetium by *Escherichia coli* and *Desulfovibrio desulfuricans*: enhancement via the use of high-activity strains and effect of process parameters. Biotechnol. Bioeng. 66 (2), 122–130.

Lloyd, J.R., Sole, V.A., Praagh, C.V.G.V., Lovley, D.R., 2000. Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria. Appl. Environ. Microbiol. 66 (9), 3743–3749.

Logan, B.E., Rabaey, K., 2012. Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337 (6095), 686–690.

Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial fuel cells: methodology and technology. Environ. Sci. Technol. 40 (17), 5181–5192.

Logan, B.E., Call, D., Cheng, S., Hamelers, H.V.M., Sleutels, T.H.J.A., Jeremiasse, A.W., Rozendal, R.A., 2008. Microbial electrolysis cells for high yield hydrogen gas production from organic matter. Environ. Sci. Technol. 42 (23), 8630–8640.

Lohner, S.T., Becker, D., Mangold, K.-M., Tiehm, A., 2011. Sequential reductive and oxidative biodegradation of chloroethenes stimulated in a coupled bioelectro-process. Environ. Sci. Technol. 45 (15), 6491–6497.

Lovley, D.R., 1993. Dissimilatory metal reduction. Annu. Rev. Microbiol. 47, 263–290.

Lovley, D.R., 2006. Bug juice: harvesting electricity with microorganisms. Nat. Rev. Microbiol. 4 (7), 497–508.

Luo, H., Liu, G., Zhang, R., Bai, Y., Fu, S., Hou, Y., 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.

Macy, J.M., Nunan, K., Hagen, K.D., Dixon, D.R., Harbour, P.J., Cahill, M., Sly, L.I., 1996. *Chrysiogenes arsenatis* gen. nov., sp. nov., a new arsenate-respiring bacterium isolated from gold mine wastewater. Int. J. Syst. Bacteriol. 46 (4), 1153–1157.

McCarty, P.L., Bae, J., Kim, J., 2011. Domestic wastewater treatment as a net energy producer-can this be achieved? Environ. Sci. Technol. 45 (17), 7100–7106.

Modin, O., Wang, X., Wu, X., Rauch, S., Fedje, K.K., 2012. Bioelectrochemical recovery of Cu, Pb, Cd, and Zn from dilute solutions. J. Hazard Mater. 235-236, 291–297.

Nealson, K.H., Myers, C.R., 1992. Microbial reduction of manganese and iron: new approaches to carbon cycling. Appl. Environ. Microbiol. 58 (2), 439–443.

Nevin, K.P., Holmes, D.E., Woodard, T.L., Hinlein, E.S., Ostendorf, D.W., Lovley, D.R., 2005. *Geobacter bemidjiensis* sp. nov. and *Geobacter psychrophilus* sp. nov., two novel Fe(III)-reducing subsurface isolates. Int. J. Syst. Evol. Microbiol. 55 (4), 1667–1674.

Newman, D.K., Kennedy, E.K., Coates, J.D., Ahmann, D., Ellis, D.J., Lovley, D.R., Morel, F.M., 1997. Dissimilatory arsenate and sulfate reduction in *Desulfotomaculum auripigmentum* sp. nov. Arch. Microbiol. 168 (5), 380–388.

Olojo, E.A.A., Awoniran, R., 2012. Bioconcentration of heavy metals in the tissues of nile tilapia (*Oreochromis niloticus*) and African catfish (*Clarias gariepinus*) in osun river, south-west, Nigeria. Asian J. Phar. Biol. Res. 2 (2), 117–121.

Pant, D., Bogaert, G.V., Diels, L., Vanbroekhoven, K., 2010. A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Bioresour. Technol. 101 (6), 1533–1543.

Paruch, A.M., Roseth, R., 2008. Treatment of tunnel wash waters-experiments with organic sorbent materials. Part II: removal of toxic metals. J. Environ. Sci. 20 (9), 1042–1045.

Pavelka, C., Loehr, R.C., Haikola, B., 1993. Hazardous waste landfill leachate characteristics. Waste Manag. 13 (8), 573–580.

Qin, B., Luo, H., Liu, G., Zhang, R., Chen, S., Hou, Y., Luo, Y., 2012. Nickel ion removal from wastewater using the microbial electrolysis cell. Bioresour. Technol. 121, 458–461.

Rahman, M.U., Gul, S., Haq, M.Z.U., 2007. Reduction of chromium(VI) by locally isolated *Pseudomonas* sp. C-171. Turk. J. Biol. 31 (3), 161–166.

Rahman, M.F., Shukor, M.Y., Suhaili, Z., Mustafa, S., Shamaan, N.A., Syed, M.A., 2009. Reduction of Mo(VI) by the bacterium *Serratia* sp. strain DRY5. J. Environ. Biol. 30 (1), 65–72.

Raskin, I., Kumar, P.N., Dushenkov, S., Salt, D.E., 1994. Bioconcentration of heavy metals by plants. Curr. Opin. Biotechnol. 5 (3), 285.

Reith, F., Etschmann, B., Grosse, C., Moors, H., Benotmane, M.A., Monsieurs, P., Grass, G., Doonan, C., Vogt, S., Lai, B., Martinez-Criado, G., George, G.N., Nies, D.H., Mergeay, M., Pring, A., Southam, G., Brugger, J., 2009. Mechanisms of gold biomineralization in the bacterium *Cupriavidus metallidurans*. Proc. Natl. Acad. Sci. USA 106 (42), 17757–17762.

Ritchie, S.M.C., Kissick, K.E., Bachas, L.G., Sikdar, S.K., Parikh, C., Bhattacharyya, D., 2001. Polycysteine and other polyamino acid functionalized microfiltration membranes for heavy metal capture. Environ. Sci. Technol. 35 (15), 3252–3258.

Shugaba, A., Buba, F., Kolo, B.G., Nok, A.J., Ameh, D.A., Lori, J.A., 2012. Uptake and reduction of hexavalent chromium by *Aspergillus niger* and *Aspergillus parasiticus*. J. Pet. Environ. Biotechnol. 3 (3), 119–126.

Shukor, M.Y., Rahman, M.F., Suhaili, Z., Shamaan, N.A., Syed, M.A., 2010. Hexavalent molybdenum reduction to Mo-blue by *Acinetobacter calcoaceticus*. Folia Microbiol. 55 (2), 137–143.

Suzuki, Y., Kelly, S.D., Kemner, K.M., Banfield, J.F., 2003. Microbial populations stimulated for hexavalent uranium reduction in uranium mine sediment. Appl. Environ. Microbiol. 69 (3), 1337–1346.

Tandukar, M., Huber, S.J., Onodera, T., Pavlostathis, S.G., 2009. Biological chromium (VI) reduction in the cathode of a microbial fuel cell. Environ. Sci. Technol. 43 (21), 8159–8165.

Tao, H., Li, W., Liang, M., Xu, N., Ni, J., Wu, W., 2011a. A membrane-free baffled microbial fuel cell for cathodic reduction of Cu(II) with electricity generation. Bioresour. Technol. 102, 4774–4778.

Tao, H., Liang, M., Li, W., Zhang, L., Ni, J., Wu, W., 2011b. Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell. J. Hazard Mater. 189 (1–2), 186–192.

Tao, H., Zhang, L., Gao, Z., Wu, W., 2011c. Copper reduction in a pilot-scale membrane-free bioelectrochemical reactor. Bioresour. Technol. 102, 10334–10339.

Tao, H., Gao, Z., Ding, H., Xu, N., Wu, W., 2012. Recovery of silver from silver(I)-containing solutions in bioelectrochemical reactors. Bioresour. Technol. 111, 92–97.

Tariq, S.R., Shah, M.H., Shaheen, N., Khalique, A., Manzoor, S., Jaffar, M., 2005. Multivariate analysis of selected metals in tannery effluents and related soil. J. Hazard Mater. 122 (1–2), 17–22.

Tomei, F.A., Barton, L.L., Lemanski, C.L., Zocco, T.G., Fink, N.H., Sillerud, L.O., 1995. Transformation of selenate and selenite to elemental selenium by *Desulfovibrio desulfuricans*. J. Ind. Microbiol. Biotechnol. 14 (3–4), 329–336.

Varga, D.d.l., Díaz, M.A., Ruiz, I., Soto, M., 2013. Heavy metal removal in an UASB-CW system treating municipal wastewater. Chemosphere 93 (7), 1317–1323.

Veglio, F., Beolchini, F., 1997. Removal of metals by biosorption: a review. Hydrometallurgy 44 (3), 301–316.

Viti, C., Pace, A., Giovannetti, L., 2003. Characterization of Cr(VI)-resistant bacteria isolated from chromium-contaminated soil by tannery activity. Curr. Microbiol. 46 (1), 1–5.

Wang, J., Chen, C., 2009. Biosorbents for heavy metals removal and their future. Biotechnol. Adv. 27 (2), 195–226.

Wang, H., Ren, Z.J., 2013. A comprehensive review of microbial electrochemical systems as a platform technology. Biotechnol. Adv. 31 (8), 1796–1807.

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 (11), 1959–1966.

Wang, Z., Lim, B., Lu, H., Fan, J., Choi, C., 2010. Cathodic reduction of Cu^{2+} and electric power generation using a microbial fuel cell. Bull. Korean Chem. Soc. 31 (7), 2025–2030.

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 (10), 6304–6307.

Xue, A., Shen, Z., Zhao, B., Zhao, H., 2013. Arsenite removal from aqueous solution by a microbial fuel cell-zerovalent iron hybrid process. J. Hazard Mater. 261, 621–627.

Yabe, M.J.S., Oliverira, E.d, 2003. Heavy metals removal in industrial effluents by sequential adsorbent treatment. Adv. Environ. Res. 7 (2), 263–272.

Yates, M.D., Cusick, R.D., Logan, B.E., 2013. Extracellular palladium nanoparticle production using *Geobacter sulfurreducens*. ACS Sustain. Chem. Eng. 1 (9), 1165–1171.

Zhang, F., He, Z., 2013. A cooperative microbial fuel cell system for waste treatment and energy recovery. Environ. Technol. 34 (13–16), 1905–1913.

Zhang, B., Zhao, H., Shi, C., Zhou, S., 2009. Simultaneous removal of sulfide and organics with vanadium(V) reduction in microbial fuel cells. J. Chem. Technol. Biotechnol. 84 (12), 1780–1786.

Zhang, B., Feng, C., Ni, J., Zhang, J., Huang, W., 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.