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Review

Metals removal and recovery in bioelectrochemical systems: A review

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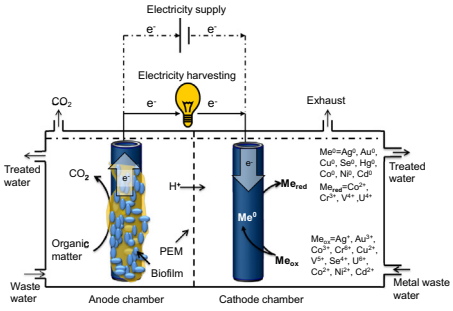
HIGHLIGHTS

- Bioelectrochemical systems are promising for recovering metal from waste streams.
- Bioelectrochemical removal of metal ions was reviewed and summarized.
- Studies should focus on metal recovery from metallurgical waste streams and leachates.
- Long term operation of bioelectrochemical systems for metal recovery is needed.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal laden wastes and contamination pose a threat to ecosystem well being and human health. Metal containing waste streams are also a valuable resource for recovery of precious and scarce elements. Although biological methods are inexpensive and effective for treating metal wastewaters and *in situ* bioremediation of metal(loid) contamination, little progress has been made towards metal(loid) recovery. Bioelectrochemical systems are emerging as a new technology platform for removal and recovery of metal ions from metallurgical wastes, process streams and wastewaters. Biodegradation of organic matter by electroactive biofilms at the anode has been successfully coupled to cathodic reduction of metal ions. Until now, leaching of Co(II) from $LiCoO_2$ particles, and removal of metal ions i.e. Co(III/II), Cr(VI), Cu(II), Hg(II), Ag(I), Se(IV), and Cd(II) from aqueous solutions has been demonstrated. This article reviews the state of art research of bioelectrochemical systems for removal and recovery of metal(loid) ions and pertaining removal mechanisms.

1. Introduction

Availability and supply of raw materials such as metal(loid)s can greatly influence the economy (in terms of exports and job creation) of many countries (Hennebel et al., 2015). Since the reserves of raw materials are finite, unequally distributed in the world and rapidly dwindling due to urbanization, high standard of living and the world population explosion, scarcity of critical raw materials is expected in the coming years. In the case of critical metals, the scarcity is perceived as an increased risk faced by the industry and characterized by the price volatility. To avoid the risk of price volatility and to stockpile raw materials for future generations, there is a need to identify secondary sources and to develop suitable technologies for their recovery. In this context,

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metallurgical wastes and process streams could be potential alternative sources for resource recovery, but the economics of metal recovery from such wastes needs re-estimation due to increased prices of certain metals over the years (Hennebel et al., 2015). Metal laden waste streams are generated in various anthropogenic activities such as mining, metallurgical operations, burning fossil fuels, cement production, electroplating, leather tanning, manufacturing plastics, fertilizers, pesticides, anticorrosive agents, Ni–Cd batteries, paints, pigments, dyes and photovoltaic devices (Fu and Wang, 2011). The concentrations of certain metal(loid)s are abundant in metallurgical wastes and process streams. The concentrations of metal ions in wastewaters are usually quite low, often in the range of μg to mg/L (Wang and Ren, 2014). Therefore, the treatment methods should not only be efficient in removing metals from dilute streams but also be able to treat large volumes of waters and concentrate the metal(loid)s in sufficient amounts. Despite the challenges in recovering metals, there is a need to develop cost effective methods for removing metal ions from large volumes of metal laden wastewaters generated in various industries to comply with the discharge limits and to avoid environmental pollution.

Metal contamination of natural resources is a health hazard and an environmental concern because metals are not biodegraded unlike organic pollutants and many metals can transfer across trophic levels and accumulate in the biota. Also, the presence of heavy metal ions in wastewaters is a concern. Some metal ions such as As, Pb, Hg, Cd, Cr, Cu, Ni and Zn are commonly encountered in wastewaters (Fu and Wang, 2011). Although many metal ions are essential trace elements in the metabolism of living organisms, they cause acute and chronic toxicity at higher concentrations. Due to potential toxic and carcinogenic effects, as many as 13 metals i.e. Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn are included in the US EPA priority pollutants list (US EPA). Therefore, stringent limits have been adopted for discharge of various metal ions in wastewaters to avoid environmental contamination.

Several physical, chemical and biological treatment methods have been developed for removing metal ions from water and wastewaters. Fu and Wang (2011) have provided a comprehensive review of physical and chemical methods for removing heavy metal ions from wastewaters. Microorganisms are well known to interact with a broad range of metals, metalloids and radionuclides, thereby influencing the mobility of metal(loid)s and radionuclides in natural and engineered environments (Francis and Nancharaiah, 2015). The mechanisms of metal removal by microorganisms include, but are not limited to biosorption, bioaccumulation, bioreduction and biomineralization. Microbial transformation of certain metal(loid)s and radionuclides is a useful strategy in *in situ* bioremediation efforts and for their removal from contaminated waters and wastewaters (Francis and Nancharaiah, 2015). However, more efforts are being made to develop innovative methods to recover metal(loid)s in order to make the treatment cost effective and sustainable (Wang and Ren, 2014).

In this context, bioelectrochemical systems (BES) often used in the literature to represent both microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) have emerged as a method of choice because they not only couple the treatment of organic wastewaters with that of metal laden wastewaters, but also offer a possibility to recover the metals. In fact, the evaluation of BES for removing metal ions from wastewaters has prominently begun less than a decade ago (Li et al., 2008). Since then, the utility of BES for removing various metal ions such as Ag(I), Au(III), Co(II), Cd(II), Cr(VI), Cu(II), Hg(II), Pb(II), Se(IV), V(V), U(VI), and Zn(II) has been reported. This review provides a brief introduction to BES and the state of art research performed on metal removal and recovery in both MFCs and MECs.

2. Bioelectrochemical systems

Electricity generation during oxidation of organic matter by microorganisms has been known since 1910, when M.C. Potter made first observations on glucose oxidation coupled to simultaneous production of 0.3–0.5 V electricity using baker's yeast, *Saccharomyces cerevisiae*. This research topic has actually gained momentum only after the 1990s and since then seminal work has been carried out to improve the power output as well as to expand MFC applications to address other societal problems. MFCs are electrochemical hybrid systems that integrate microbial and electrochemical processes to release reducing equivalents from organic matter and convert chemical energy to electrical energy through a cascade of redox reactions mediated by microbial metabolism (Venkata Mohan et al., 2014a,b). The MFCs and other BES are being intensively pursued in both basic and applied research as a futuristic and sustainable platform specifically for harnessing energy and generating value added bio-products along with simultaneous contaminant remediation (ElMekawy et al., 2014, 2015). The microbial metabolism is linked via electron donating or accepting conditions through the external electrodes (anode and cathode), which facilitate development of a potential difference leading to bioelectrogenic activity. The research both in basic and applied fronts on MFCs and other BES has been intensified in the last decade due to its inherent ability to produce sustainable energy from renewable organic waste (Logan, 2010; Venkata Mohan et al., 2008). The power production of BES in the order of 10–100 W/m^3 is still small compared to energy recovered in other anaerobic treatment technologies (i.e. anaerobic digestion) despite remarkable improvements in the design and electrode materials made during the last decade.

Microbially catalyzed electrochemical mechanisms occurring in BES provide an inherent advantage for diverse applications in the arena of energy conservation, value-added product synthesis and waste remediation. The reducing equivalents (e^- and H^+) generated as a result of biodegradation of organic matter can be utilized towards harnessing of power by MFC, waste remediation by bioelectrochemical treatment (BET), microbial electrosynthesis of various value added products and H_2 production in MECs (Patil et al., 2015; Schröder et al., 2015; Modestra et al., 2015; Venkata Mohan et al., 2014a,b). All these systems, along with other BES configurations not described here, share similarities on the anode but differ in cathode reactions. The terms such as BES, microbial electrochemical technology (MET) or BET are increasingly and interchangeably referred in the literature to cover all the configurations (Patil et al., 2015; Schröder et al., 2015; Modestra et al., 2015). In MFC, chemical energy available in the organic matter is converted to electricity using the innate biodegradation capability of anaerobic microorganisms. The biodegradable organic matter available in the wastewater is oxidized by the microbial community, growing in a biofilm on the anode, into CO_2, electrons and protons (Fig. 1a). CO_2 and protons are released into the solution, while the microbial community conducts the electrons to the solid electron acceptor, the anode. These electrons then travel via an external circuit to the cathode, where they are finally accepted by oxygen to form water in combination with the protons available in the solution. By transferring electrons to the anode, bacteria harvest energy through anaerobic respiration.

In BES, microbial communities need to use either a solid electron acceptor (bioanode) or an electron donor (biocathode) as part of their metabolism (Fig. 1b). However, it is likely that microorganisms that receive electrons from the solid electron donor (cathode) may not gain energy (Rosenbaum et al., 2011). Bacteria face a serious challenge to either transfer or accept electrons from, respectively, a solid terminal electron acceptor (TEA) or solid electron