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Bio-electrochemical system - a novel technology for metal recovery

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ABSTRACT

Metals like platinum, silver, nickel, cadmium, chromium, copper, zinc, gold etc. are released in the environment through the discharge of industrial wastewaters. Wastewater containing these metals poses severe health hazards to the human being and ecosystem, if discharged without proper treatment. Recovery of metals from the wastewater is one of the most sustainable approaches to reduce their discharge in the environment. Conventional technologies for metal recovery include coagulation-flocculation, chemical precipitation and membrane processes, but they are generally energy and chemical intensive. Disposal of hazardous sludge further aggravate the problem due to land requirement. To overcome the constraints of existing technology, bio-electrochemical technology provides a novel and alternative approach for metal recovery. Bio-electrochemical reactor converts chemical energy of organic compounds to electrical energy through catalytic reactions of microorganisms. Bio-electrochemical technology reduces metal ions into metal by accepting the electron in the cathode chamber generated through the oxidation of organic substrate in the anode chamber. This paper describes various facets of Bio-electrochemical system with special emphasis on its efficiency, optimization of process parameters, cost and the efficacy of various electrodes. The metal recovery efficiency of the bio-electrochemical technology varies depending upon the initial concentration of metal ions, substrate utilised, reaction time and

reactor configuration and found to vary from 70% to 99% depending upon the metal concentration, substrate utilised, reactor configuration and duration of the reactor. The distance between the electrodes also plays a major role. The studies revealed that minimizing the distance between electrodes enhances the performances of the system. Among different type of electrodes, graphite electrodes were the best in enhancing the performance of the system than aluminium, stainless steel and iron electrodes. The current density generation depends upon the microbial community in the anode chamber, type and concentration of substrate utilised. When acetate was utilized as substrate, current density generated was 0.8 mA/cm^2 using pre-acclimated microbial culture as inoculum whereas current density generated was 2.05 mA/cm^2 when Sodium fumarate was used as substrate with microbial inoculum of *Geobacter. Sulfurreducens*. The paper also highlights various drawbacks and constraints with focus on the application of this technology at field scale.

Keywords: Bio-electrochemical system, electrodes, metal recovery, substrate, current density

1. INTRODUCTION

Current century has led to industrial revolution for development purpose. This industrial revolution and other anthropogenic activities have led to increase in metal containing wastewater. A large amount of valuable metals such as platinum, silver, nickel, cadmium, chromium, copper, zinc, gold etc. are released in the wastewater from Industries. The metals in wastewater accumulate in living tissues of plants and animals once ingested. These metals cause dreadful diseases and have harmful effects on ecosystem (1). Renal dysfunction, Lung disease, Lung cancer, Bone defects (Osteomalacia, Osteoporosis), increased blood pressure , kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer, mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness and,

acute or chronic damage to the nervous system, epilepticus, liver, tremors, gingivitis, minor psychological changes characterized by pink hands and feet, spontaneous abortion, damage to nervous system, protoplasm poisoning are some of the shocking effects of metal on human physiology. To overcome this problem and to avoid excess and valuable metal loss in the environment; metal recovery is one of the most sustainable approaches.

Conventional technologies for metal recovery include coagulation-flocculation, chemical precipitation and membrane processes, but they are generally energy and chemical intensive. Conventional technologies face various drawbacks for utilisation. For chemical utilisation, its dosage needs to be monitored and fixed as per the amount of metals in the effluent which may vary due to process, production and working of that particular industry. Membrane utilisation for metal recovery is limited due to its high cost and blockage due to presences of organic matter in the wastewater. The cost of membrane use is recurring. Hazardous sludge is also generated due to chemical precipitation and its disposal further aggravates the problem due to its handling and land requirement. Skilled labour, its handling, safety disposal of hazardous sludge is troublesome process. To overcome the constraints of existing technology, bio-electrochemical technology provides a novel and alternative approach for metal recovery.

2. BIO-ELECTROCHEMICAL SYSTEM

Bio-electrochemical system (BES) is similar to microbial fuel cell (MFC) only without energy harvesting. It is a combination of biological and electrochemical method utilised for metal recovery. It usually consists of externally connecting cathode and anode electrodes (and optional membrane separator) and the circuit is completed with the help of wastewater. BES converts chemical energy of organic compound to electrical energy through catalytic breakdown of organic matter with the help of microorganisms. During the microbial oxidation of organic matter, electrons are released and are attached at the anode electrode thereby generating electric current between the cathode and anode. The metal ions present in the wastewater are reduced into metal by accepting the electron in the cathode chamber generated through the oxidation of organic substrate in the anode chamber (1, 2, 3, 4).

The recovery of metals is dependent upon the redox potential of the metal ions to be recovered. The positive redox potential of the metal ion thermodynamically favours the reduction of metals ions present in the cathode chamber after production of electric current between the two electrodes of the BES. The metal ions having negative redox potential are thermodynamically not favourable to get reduced in the cathode chamber requires external electric supply. External supply is used, as electrons produced by microbial metabolism are not sufficient for reduction of metal ions. Such cell where external electricity is used to reduce metal ions to metal is called Microbial Electrolytic cell (MEC). Whereas in BES microbial electron production is sufficient to reduce metal ions to metal is referred to as MFC.

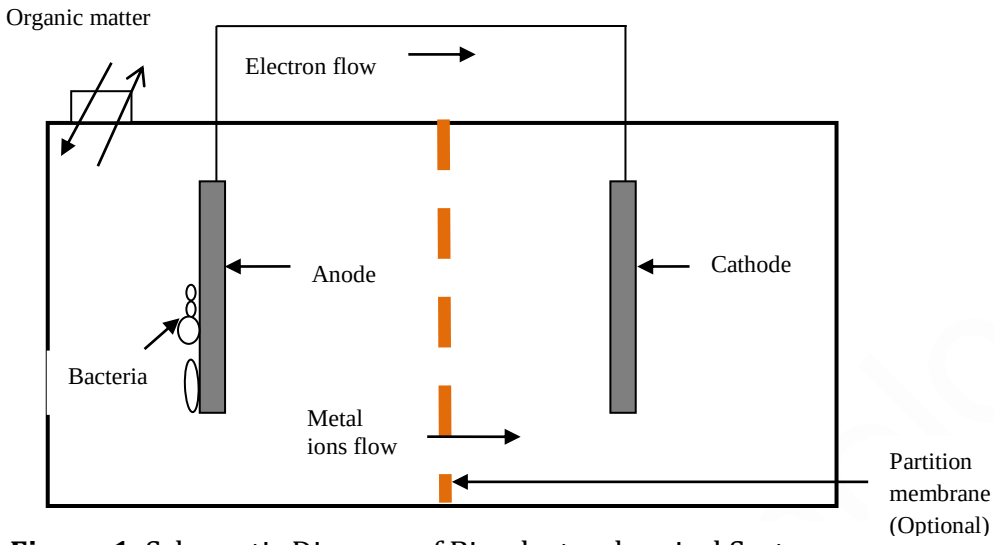

Figure 1. Schematic Diagram of Bio-electrochemical System

3. FACTORS AFFECTING BES PROCESS

The BES process depends on substrate and its concentration, operating conditions, microbial inoculum, types of electrodes used and configuration of the reactor. Substrate plays an important role in the BES. Substrate oxidation is going to decide the amount of electron production. The substrate can vary from pure compounds to complex mixtures of organic matter present in wastewater. Type of the substrate and its concentration is important process parameter in production of electron and thus the functioning of BES (5). Various substrates can be used for BES studies depending upon the nature and complexity of substrates observed in actual wastewater.

The metal recovery of the bio-electrochemical technology varies depending upon the operating conditions, initial concentration of metal ions, substrate utilised, reaction time and reactor configuration and found to vary from 70% to 99%. (6) The distance between the electrodes also plays a major role. Sangeetha T. proved that electrodes placed at a distance of 10 cm showed higher performance than those placed at 12- and 15-cm distance. Similarly Ghangrekar proved maximum power density of 10.9 and 10.13 mW/m2 was observed at lower spacing between the electrodes (20 cm) as compared to greater electrode spacing and for lesser surface area of the anode, respectively.(7, 8,9)These studies revealed that minimizing the distance between electrodes enhances the performances of the system. Among different type of electrodes, graphite electrodes were the best in enhancing the performance of the system than aluminium, stainless steel and iron electrodes (7).

Table 1 Recovery of metals using BES along with factors affecting it

S. No	Metal and its concentration (mg/L)	Substrate utilised	Concentration of Substrate	Configuration of BES Cell	Microbial Inoculum	Operating Conditions	Type of Electrode, its shape and surface Area	Recovery efficiency	Current density (mA/cm2) / maximum power/ Electric quantity	Reference
1	Copper Cu^{+2} 600 2000	Sodium Acetate	500 mg/L 1000 mg/L	Vertical column- 15 cm Anode chamber - 6000 mL Cathode chamber- 10,000 mL	Mixed Microbial Culture scrapping from anode of MFC for copper removal	pH-2, Temp – 25 ± 5 °C	Anode- Graphite felt (73 cmX 25 cmX 1 cm) Cathode- Graphite disks(dia 14 cm)	92% over 480 h 48% over 672 h	Max Power-0.585 mW Electric quantity- 8703 C at Cu^{+2} 600 mg/L	Hu-Chun Tao et al 2011(8)

S. No	Metal and its concentration (mg/L)	Substrate utilised	Concentration of Substrate	Configuration of BES Cell	Microbial Inoculum	Operating Conditions	Type of Electrode, its shape and surface Area	Recovery efficiency	Current density (mA/cm2) / maximum power/ Electric quantity	Reference
2	Copper Cu^{+2} as in $Cu(NH_3)_4^{2+}$) -350	Sodium Acetate	1000 mg/L	Anode chamber - 125 mL (5 cm X 5 cm X 5 cm) Cathode chamber- 62.5 mL (5 cm X 2.5 cm X 5 cm)	Mixed Microbial Culture scrapping from anode of MFC (Tao et.al 2011 10)	pH-3 & 9 Temp – 35°C	Anode- graphite felt (5 cm X 4.5 cm X 1.0 cm thickness) Cathode- Graphite plate (5 cm X 4.5 cm X 1.0 cm thickness)	96% within 12 h at pH 9 84% within 8 h at pH 3	Max Power density- 0.20W/ m^2 at current density- 0.74 A/m^2	Li-Juan Zhang et al 2012 (9)
3	Copper -200	Glucose	5000 mg/L	Anode & Cathode chamber - 1000 mL	100 mL anaerobic sludge collected from anaerobic digester at Wastewater treatment plant	Temp-35 °C	Anode- Graphite Plates(14 cm X 10.5 cm X 0.5 cm thickness) Cathode- graphite plates (6 cm X 4.5 cm)	99%	Max power density generation-339 mW/m^3 at initial con of 6412.5± 26.7 mg/L	Hu-Chun Tao et al 2011(11)
4	Silver 50 ppm to 200ppm	Sodium Acetate	1000 mg/L	Each chamber volume -112 effective volume 100 mL (7 cm X 4 cm X 4 cm)	50 mL sludge (Wang et. al. 2011)	pH-7	Anode- carbon brush (L-2.5 cm, dia- 2.5 cm) Cathode- carbon cloth with surface area-2.2 m^2 (1.7 cm X 1.3 cm)	99.91% to 98.26	Max power-4.25 mW/m^3 Max current density- 5.67 A/m^2 at 1000 ppm initial silver conc.	Chansoo Choi et. al. 2011 (12)
5	Cu^{+2} -800 pb^{+2} - 400 Cd^{+2} -800 Zn^{+2} - 300	Sodium Acetate	20 mM	Anode & cathode chamber- (3 cm X 3 cm X 10 cm)	Aerobic and Anaerobic Sludge	Catholyte - pH-2	Anode- Carbon Felt (8 cm X 3.7 cm X 0.2 cm) attached to 9 cm long , 0.5 cm dia. graphite rod Cathode- 4 cm long, 0.81 mm dia Titanium wire	Metals were deposited	---	Modin, Oskar, et al
6	Chromium 80 mg/L	Sodium Acetate	----	H-type MFCs were constructed with two borosilicate glass bottles separated by a PEM. Volume-230 mL each chamber	Culture from anaerobic digester and cathode inoculum- mixture of denitrifying and anaerobic mixed cultures enriched in the presence of Cr(VI)	pH-7	Anode and cathode - Graphite plate electrodes of similar size (5.4 cm × 2.5 cm × 0.6 cm	Recovered fast till 80 mg/L	Max current and power densities obtained -123.4 A/m2 and 55.5 mW/m2, respectively, at 63 mg/L Cr(VI) conc.	Tandukar, Madan, et al.

4. CONSTRAINTS OF BES

The activity of biocatalysts, electron transfer between the bacteria and the anode, internal resistance and potential difference between both the electrodes are the main limiting factors of BES (18). The proper working and functioning of microbial metabolism

is clearly not understood in BES. The role of microbial communities and their activity are not clearly understood. There exists a lack of information about the structure of the microbial communities and the roles of the members of each community in the catalysis. Along with this, limited electrochemical COD removal efficiency is one of the major disadvantages of BES. Maintenance and material costs of BES are significantly high. Based on the material costs, it is estimated that – assuming the costs of 4000 euros per m3 of the electrode compartment; the costs of 1 kW power output per m3 anode produced by an MFC are higher by a factor of approx. 10 compared to the equivalent production costs for conventional processes. (18). BES reactors sophisticated arrangement of electrical wires and connections makes the whole BES more troublesome. A high internal resistance causes a considerable potential drop due to ohmic losses in the BES (19). So by using low material costs as well as low operational costs BES can be used for recovery of metals.

5. CONCLUSION

BES is upcoming, novel technology and has great potential for recovering metals from wastes and aqueous streams. More studies should be considered on the converting this technology into application on a large scale. More study on bacterial consortia and its development can be done for production of large no of exo-electrons, thereby increasing the efficiency of BES. Reactor configuration can also be modified as per requirement so as to minimize the cost required for its application.

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