Microbial fuel cell: A green eco-friendly agent for tannery wastewater treatment and simultaneous bioelectricity/power generation

Christina Saran [a], Diane Purchase [b], Ganesh Dattatraya Saratale [c], Rijuta Ganesh Saratale [d], Luiz Fernando Romanholo Ferreira [e,f], Muhammad Bilal [g], Hafiz M.N. Iqbal [h], Chaudhery Mustansar Hussain [i], Sikandar I. Mulla [j], Ram Naresh Bharagava [a,*]

[a] *Laboratory of Bioremediation and Metagenomics Research (LBMR), Department of Environmental Microbiology (DEM), Babasaheb Bhimrao Ambedkar University (A Central University), Vidya Vihar, Raebareli Road, Lucknow, (U.P.), India, 226 025*

[b] *Department of Natural Sciences, Faculty of Science and Technology, Middlesex University, The Burroughs, Hendon, London, NW4 4BT, England, United Kingdom*

[c] *Department of Food Science and Biotechnology, Dongguk University, Seoul, Ilsandong-gu, Goyang-si, Gyeonggi-do, 10326, Republic of Korea*

[d] *Research Institute of Integrative Life Sciences, Dongguk University–Seoul, Ilsandong–gu, Goyang–si, Gyeonggido 10326, Republic of Korea*

[e] *Waste and Effluent Treatment Laboratory, Institute of Technology and Research (ITP), Tiradentes University, Farolandia, Aracaju, SE, 49032-490, Brazil*

[f] *Graduate Program in Process Engineering, Tiradentes University (UNIT), Av. Murilo Dantas, 300, Farolandia, 49032-490, Aracaju, Sergipe, Brazil*

[g] *Institute of Chemical Technology and Engineering, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, PL-60695 Poznan, Poland*

[h] *Tecnologico de Monterrey, School of Engineering and Sciences, Campus Monterrey, Ave. Eugenio Garza Sada 2501, Monterrey, N.L., CP 64849, Mexico*

[i] *Department of Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, NJ, 07102, USA*

[j] *Department of Biochemistry, School of Allied Health Sciences, REVA University, Bangalore, India*

*corresponding author: bharagavarnbbau11@gmail.com; ramnaresh_dem@bbau.ac.in

HIGHLIGHTS

- Tannery wastewater is the major source of Cr^{6+} contamination in the environment.
- Cr^{6+} is highly toxic to the environment, human, plants and microbes.
- Cr^{6+} can be reduced/detoxified effectively by microbial fuel cells.
- MFC is a bio-electrochemical device used in wastewater treatment with power generation.
- Different parameters can influence/ affect the reduction of Cr^{6+} and power generation

KEYWORDS - Tannery wastewater; Hexavalent chromium; Microbial fuel cells; Reduction; Power generation; Environmental sustainability

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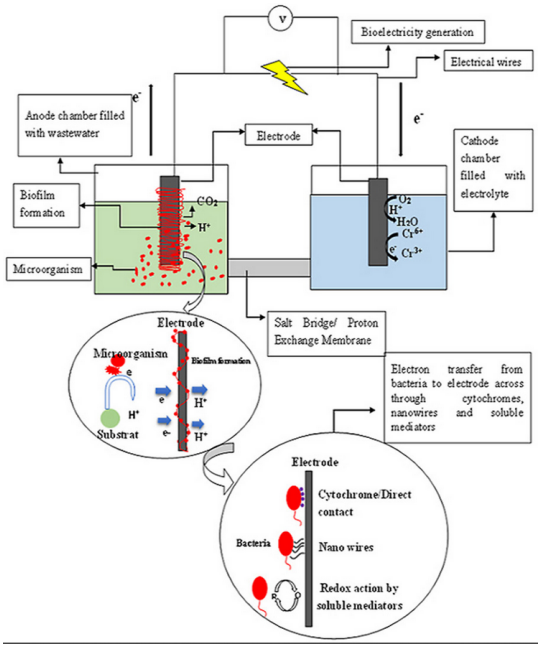
GRAPHICAL ABSTRACT



ABSTRACT

This review paper emphasised the origin of hexavalent chromium toxicity in tannery wastewater and its remediation using novel Microbial Fuel Cell (MFC) technology, including electroactive bacteria, which are known as exoelectrogens, to simultaneously treat wastewater and its action in the production of bioenergy and the mechanism of Cr^{6+} reduction. Also, there are various parameters like an electrode, pH, mode of operation, time of operation, and type of exchange membrane used for promising results shown in enhancing MFC production and remediation of Cr^{6+}. Destructive anthropological activities, such as leather-making and electroplating industries are key sources of hexavalent chromium contamination in aquatic repositories. When Cr^{6+} enters the food chain and enters the human body, it has the potential to cause cancer. MFC is a green innovation that generates energy economically through the reduction of toxic Cr^{6+} to less toxic Cr^{3+}. The organic substrates utilized at the anode of MFC act as electron (e^-) donors. This review also highlighted the utilization of cheap substrates to make MFCs more economically suitable and energy production at a minimum cost.

1. Introduction

Heavy metal pollution in the environment has expanded massively during the past few decades across the world (Lu et al., 2018). In addition to natural processes like biogeochemical cycles and volcanic eruptions that release metals into the environment, human activities like uncontrolled mechanical and metropolitan advancement also cause the unpredictable release of substantial metals into the ecosystem (Bárcena et al., 2017; Carolin et al., 2017). Consequently, stringent legislation is implemented to reduce the concentration of metals in the environment to a satisfactory limit (Dhal et al., 2013; Thatoi et al., 2014).

Industrial wastewaters are significant sources of ecological contamination as these contain high levels of organic pollutants, organic matter, phenolics, tannins and heavy metals. Many of the organic pollutants present in industrial wastewater are not fully degraded even after the secondary treatment process. These organic pollutants may promote the growth of pathogenic microorganisms, which could be discharged into the water bodies along with the wastewater to cause different diseases in the biota (Bharagava and Mishra, 2018).

The wastewater discharged from tannery industries is the major source of Cr^{6+} contamination into the environment and the cause of various health hazards if, not properly treated. In the tanning process, a huge amount of water and synthetic chemicals are used to convert the rawhide/skins into the finished leather and around 30–35 m^3 of wastewater is produced per ton of hide/skins processed. This presents two significant issues for tanneries: the accessibility of good quality water and the satisfactory treatment of such a huge volume of exceptionally contaminated wastewater. Tannery wastewater (TWW) is an alkaline, dull, earthy-coloured wastewater with high COD, BOD, TSS, TDS, chromium and sulfides values, and has a strong odour (Saxena et al., 2016). However, the attributes of TWW are highly variable depending on the practice of an individual tannery; the use of unrefined components and synthetic compounds, and the characteristics of tannery wastewater reported by various authors have been given in Table 1. Although, tannery industries play an important role in the national economy of many developing countries like India, China, Nigeria, Ethiopia, Pakistan and Bangladesh, yet these are known as the major source of environmental pollution (Saxena et al., 2016) as these produce a large volume of harmful wastewater. For example, in Nigeria (kano), about 2100 kg solid waste (per month in year 2005) was generated as a result of processing 1860 tons of hides and skins in 40 tannery industries located in Challawa (Gunwa et al., 2006; Oke et al., 2006). Ethiopia produces 17 tons of tannery wastewater per day (Mehari et al., 2015). In Bangladesh, 270 registered tanneries located in Hazaribagh produce 7.7 million litres of liquid waste and 88 million litres of solid waste in a day (Nur-E-Alam et al., 2020). In China, 788 tanneries used about 70–118 L of water to convert 1 kg of hides into finished leather and discharge ~60–100 L of wastewater per day (Zhou et al., 2012). In Pakistan, most of the tannery industries are located in Lahore (Kasur) and Sialkot, there are 700 registered tanneries that produce about 150 tons of solid waste and 264 registered tanneries that produce about 962, 335 million gallons (4.369 × 109 m_3/year) in these states, respectively (Butt et al., 2021). In India there are roughly 3000 tanneries, mainly situated in the provinces of Tamil Nadu, West Bengal, Uttar Pradesh, Andhra Pradesh, Bihar, Gujarat, and Maharashtra, producing in total around 1,75,000 m^3 wastewater each day. In Uttar Pradesh, around 444 active tanneries in Kanpur and Unnao areas produce 22.1 MLD of wastewater each day (Central pollution control board, 2013; Bharagava and Mishra, 2018).

Tannery wastewater causes toxicity to the environment and severe diseases to human and animals. In the environment, Cr^{6+} contamination affects the aquatic biota, microbes, and human and animals. First, we discussed the impact of chromium-contaminated water on aquatic biota as it can influence flora development and yield. The accumulation of harmful metals is biomagnified at various trophic levels through the food chain. Tannery wastewater causes phytotoxicity that influences different metabolic cycles e.g. reduce plant biomass due to a decrease in the rate of respiration and photosynthesis and impeding reproductive development through slow mitotic cell development. The accumulation is dependent upon the plant species, the bioavailability of metal, redox, pH, cations, dissolved oxygen, temperature and secretion of roots (Sharma et al., 2021). Second, we discussed about the impact of Cr^{6+} on microorganisms, which may be valuable or detrimental to their growth, depending on the chemical or physical nature and oxidation state of metal ions, changes in the morphology of Gram-positive and Gram-negative bacteria had been also observed. In resistant microorganisms, Cr^{6+} is reduced into Cr^{3+} with the aid of enzymatic or non-enzymatic actions. Cr_{6+} is the most toxic form of Cr as it quickly enters the cytoplasm causing oxidative harm to proteins and nucleic acids. In some microbes e.g. *Euglena gracilis*, Cr^{6+} can result in alteration in the cytoskeleton leading to the lack of motility of the organisms (Mishra and Bharagava, 2016).

Table 1
Characteristics of tannery wastewater reported by various authors

parameters	Soaking	Unhairing laming	Bating deliming	Pickling	Chrome Tanning	Re-tanning	References
pH	7.7	11.9	8.6	3.6	–	5	Tunay et al. (1995)
	10	13	11	4	3.2	10	Cassano et al. (2001)
BOD	5000	20,000	4000	100	250	15,000	Cassano et al. (2001)
	11,000	45,000	9000	–	4000	15,000	Dixit et al. (2015)
COD	6000	–	–	1000	3000	–	Sundarapandiyan et al. (2010)
	11,800	40,000	7000	800	400	75,000	Cassano et al. (2001)
	33,000	122,000	20,000	–	11,000	40,000	Dixit et al. (2015)
	31,000	58,000	5325	2900	–	4365	Tunay et al. (1995)
TSS	40,000	–	–	30,000	70,000	–	Sundarapandiyan et al. (2010)
	6700	25,000	10,000	–	–	–	Cassano et al. (2001)
	17,000	97,000	2000	–	10,000	11,000	Dixit et al. (2015)
TDS	33,000	–	–	29,000	67,000	–	Sundarapandiyan et al. (2010)
Cr	–	–	–	–	4100	3000	Cassano et al. (2001)
					5000	2000	Dixit et al. (2015)
S^{2-}	700	3300	250	–	–	–	Sundarapandiyan et al. (2010)
	2000	2000	26,000	–	55,000	25,000	Dixit et al. (2015)

(BOD= Biochemical oxygen demand, COD= Chemical oxygen demand, TSS = Total Suspended solid, TDS = Total dissolved solid, Cr = Chromium, S^{2-}= Sulfides).
[Note: The wastewater volume data that are given in the above table are in cubic meters per ton (m^3/ton)].

Second, we discussed about the impact of Cr^{6+} on microorganisms, which may be valuable or detrimental to their growth, depending on the chemical or physical nature and oxidation state of metal ions, changes in the morphology of Gram-positive and Gram-negative bacteria had been also observed. In resistant microorganisms, Cr^{6+} is reduced into Cr^{3+} with the aid of enzymatic or non-enzymatic actions. Cr^{6+} is the most toxic form of Cr as it quickly enters the cytoplasm causing oxidative harm to proteins and nucleic acids. In some microbes e.g. *Euglena gracilis*, Cr^{6+} can result in alteration in the cytoskeleton leading to the lack of motility of the organisms (Mishra and Bharagava, 2016).

Third, we discussed the impact on human and animals, persistent exposure to tannery labours for five months to fourteen years poses a high-risk factor for the development of infections related to hereditary harm. Harmful tannery effluents containing a high level of chromium, hydrogen sulphide, lead, zinc, cadmium and formaldehyde also have transitory impacts like dizziness, migraine, and irritations of the eyes, skin or lungs etc. (Chandra et al., 2011). Damage to the liver, kidney or sensory organs was recorded because of the absence of

oxygen and long-term ailment like asthma, ulcers, bronchitis, hereditary deformities and dermatitis in humans were also observed (Tadesse et al., 2017). In server cases, Cr^{6+} can also cause skin aggravation, eardrum perforation, nasal irritation, ulceration and lung carcinoma in people and animals, and disabling fetal improvement in mammals (Chandra et al., 2011). Because of the aforementioned environmental and health hazards, metal-loaded wastewater must be treated adequately before being released into the environment. A number of treatment methodologies have been reported to treat metal-loaded wastewater effectively (Mishra and Bharagava, 2016; Wang et al., 2008). However, these traditional methods (physico-chemical method e.g. adsorption, coagulation/flocculation and biological methods e.g. micro-organisms, enzymatic etc.) are costly at large scale and detrimental to the ecosystem because of their high energy demand and generation of sludge as a secondary pollutant. Hence, an economic and environment-friendly approach is needed to treat wastewater containing metals (Wang et al., 2008). Microbial Fuel Cells (MFCs) can be a promising approach for wastewater treatment with the generation of value-added products. An MFC is typically comprised of cathode and anode chambers where the cathode is usually abiotic while the anode contains electrochemically-dynamic microbes. A proton exchange membrane (PEM) separates these two chambers from each other (Wang et al., 2008; Liu et al., 2020).

MFCs are also known as the bio-electrochemical framework, according to Rozendal et al. (2009) it is the best-in-class innovation in the treatment of metal-polluted wastewater. The microbial consortia in the anodic chamber of MFCs are equipped to survive in conditions containing high levels of external stressors. Additionally, exceptionally receptive species, for example, •OOH, •OH and so forth, are generated by means of a two-electron pathway in the cathodic chamber (Rozendal et al., 2009). It makes MFCs good treatment candidates to treat tannery wastewater via utilizing the organic matter (Fig. 1) and production of responsive oxygen species (ROS) or starting a Fenton-like cycle (Jain and He, 2018). MFC has been shown to yield up to 1600 mW/m^2 (Li et al., 2008), 1540 mW/m^2 (Gupta et al., 2017) and 1221.94 mW/m^2 (Li et al., 2018) in three separate research. This review paper provides a comprehensive study of MFCs design, their applications and challenges that need to be addressed in order to promote this eco-friendly and sustainable technology for industrial wastewater treatment and bioenergy production that can benefit the environment as well as human welfare.

2. Microbial fuel cells (MFCs): the design principles, types and their characteristic features

2.1. Principle of MFC

MFC technology is a new form of renewable technology which it removes organic materials, inorganic pollutants and generates bioelectricity. In an MFC, the anode and cathode chamber remain connected by a proton exchange membrane/salt bridge. These two chambers have their respective electrode which depends on their conductivity. Microorganisms exist in an anode chamber where they utilize the organic compounds e.g. glucose (C6H12O6) or any other substrate (wastewater) to act as an electron (e^-) donor (Table 2). The breakdown of these natural compounds produces electrons as well as protons and the electrons are transported to the cathode through an outside circuit from the anode, where they are received by electron acceptors to

generate bioelectricity (Uddin et al., 2021). The protons are transferred from the electrolyte through a proton exchange membrane to the cathode chamber. The electrons and protons interact with e^- acceptors at the cathode to produce harmless by-products and bioelectricity.

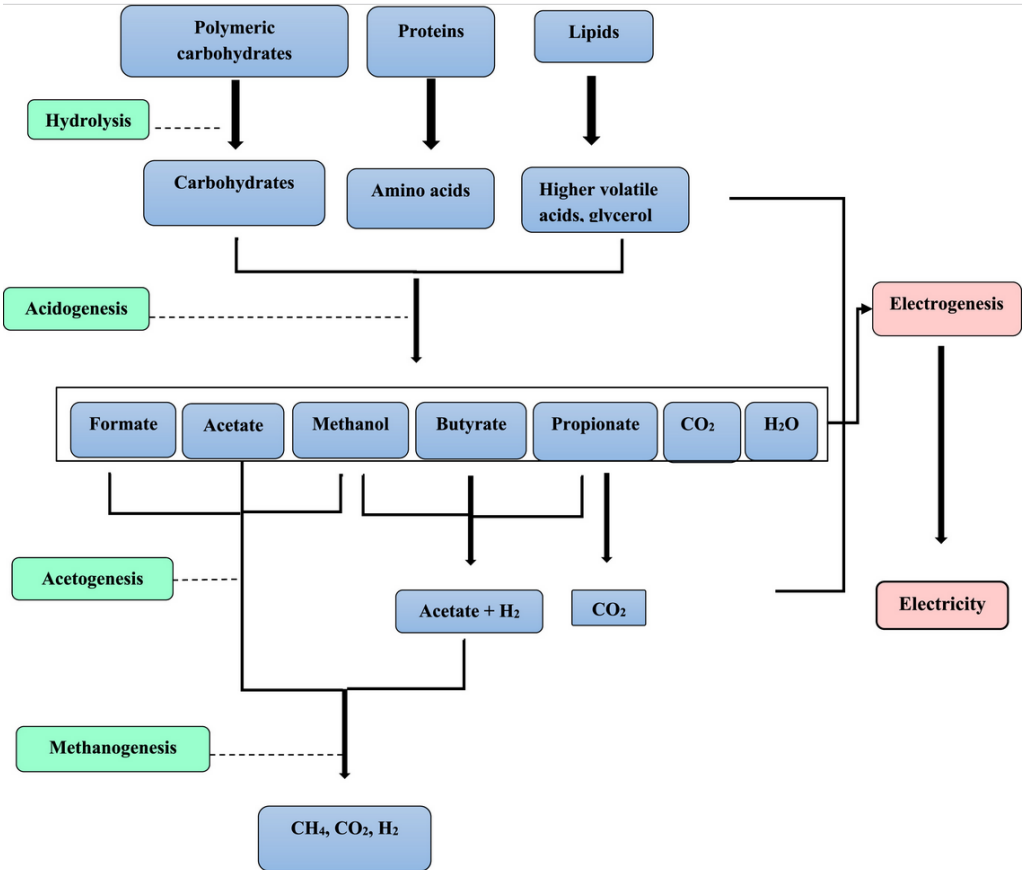


Fig. 1 A general mechanism of organic matter degradation.

2.2. The electron transfer mechanisms

The interaction of electrons from microbes to an electrode is critical for MFC activity as shown in (Fig. 2). The two cases where the electrons are transferred to an extracellular solid substrate can take place either by indirect contact between the cell surface and solid substrate or indirectly by means of exogenous and endogenous mediators present in the substrate (Debabov, 2008).

2.2.1. Direct electron transfer

Debabov (2008) observed that the "electrons should arrive at the external layer of the cell for their direct transfer between microbes and electrodes (or metal oxide particles). Especially high amassing of a c-type cytochrome in *Shewanella putrefaciens* MR-1 external membrane over the span of anaerobic growth" (Debabov, 2008). At the point when microorganisms begin colonizing the outside surface of an anode to frame a biofilm, they adhere to the anode surface and move straightforwardly to cytochrome without the involvement of diffusional redox species. This type of electron movement has been observed in *Geobacter* species or in mixed cultures (Huang et al., 2011). Microbes develop a biofilm on electrodes and facilitate e^- transfer where the microbial layer in direct contact with the electrode participates in the transport of electrons (Schröder, 2007).

Table 2
Microbes reported by various workers capable for the reduction of hexavalent chromium with simultaneous bioelectricity generation.

Microorganism for removal of Cr^{6+}	Substrate or inoculum sources	Working volume	Operation time/days	Cr^{6+} removal efficiency	MFCs Performance		Reference
					Voltage	Current	
Mixed consortia	Anaerobic sludge	0.014l (14 ml) anode chamber 0.028l (28 ml) cathode chamber	6 months	80.4% 95.6 ± 0.8% 97.9 ± 0.8% 99.4 ± 0.2%	– 432 ± 4.6 mV 451 ± 19.1 mV 327 ± 6.8 mV		Wang et al., 2020
Microbial consortium	anaerobic sludge	25 ml	240 h	75.4 ± 1.9%	748.9 ± 25.1 mV	2462.5 ± 23.1 mA m^{-2}	Zhang et al., 2012
Mixed consortia	Synthetic water	30 ml	32 h	100%	880 ± 14 mV		Liu et al., 2020
Mixed consortia	Synthetic water + red soil	60 ml	13.5 h	90.9%	480.2 mV	2460 mA/m^2 Current density	Ren et al., 2018
Bacillus cereus ATCC14579	LB broth	70 ml	20 h	50.6 ± 1.8%	600 mV		Wu et al., 2018
Ochrobactrum anthropic YC152	LB broth	170 ml	27 days	98.5–100%	268 ± 2.8 mV	0.00099 μA	Wang et al., 2016
Bacilli	Anaerobic sludge	200 ml	24 h	97.7%			Wang et al., 2010
Trichococcus pasteurii and Pseudomonas aeruginosa,	anaerobic culture enriched from an anaerobic digester.	230 ml	45 days.	99%	0.365 V	123.4 mA/m^2 current density	Tandukar et al., 2009
Mixed consortia	Anaerobic sludge	250 ml	7 days	99.85%	517 mV		Gangadharan and Nambi (2015)
Limnococcus limnectius and leptolynbya	BG-11 medium	250 ml	14 days	58%			Sen et al., 2017
Anaerobic microbial consortia	Domestic wastewater	250 ml	174 h	92.65%	910 mV	0.079 mA/cm^2 Current density	Wang et al., 2008
Mixed consortia	Domestic wastewater	250 ml	150 h	74.6–100%	560 mV		Wang et al., 2008
Mixed consortia	Contaminated soil	300 ml	210 h	100%	420 mV		Huang et al., 2010
Bacteria isolated from lab	Synthetic Medium	340 ml	72 h	100%	1190 mV		Li et al., 2018
Pseudomonas stutzeri KU708859 Acinetobacter baumanii KU708860	Bushnell Hass (BH)	500 ml	72 h	96%		30 mA/cm^2 current density	Kuppusamy et al., 2017
Mixed consortia	anaerobic sludge (10% v/v) from lake sediments	510 ml	26 h	97%	−1.0 to +1.5 V		Li et al., 2009
Bacillus cereus	Activated sludge	700 ml	30days			10.38 mA	Mathuriya (2014)
Proteobacteria, cyanobacteria, Bacteriodetes		1000 ml	12 h	99%			Habibul et al., 2016
Moheibacter, Nitrobacter, Truepera	Anaerobic sludge	1200 ml	12 days	90%	300 mV	447 μA	Beretta et al., 2020
Mixed consortia	Industrial wastewater	1400 ml	18 days	95% 86%	931 mV (4 mg/l) 700mv (8 mg/l)		Sophia and Saikant (2016)
Mixed consortia	Activated sludge	25l	60days	93%	588.2 mV	3.79 mA	Mu et al., 2020

2.2.2. Indirect electron transfer

To expand the electron movement and consequently improve the efficiency of MFCs, external chemicals known as mediators can be added to the system. An indirect transfer using a mediator is also known as mediated electron transfer (MET), wherein the mediator works as an electron transport within the microorganism and the final electron acceptor. These mediators can be either endogenous or exogenous (Song et al., 2019; Babanova et al., 2011). Endogenous mediators are produced by the actual microbes with no external support. Chemicals like flavins (Yang et al., 2012a, b), sulfate-sulfide, pyocyanin can be created by *Pseudomonas* and *Shewanella* as endogenous mediators (Yang et al., 2012a, b).

2.3. Microorganism's mechanisms

There is considerable communication among microbes within the biofilm on the electrodes in an MFC. The biofilm influences the oxidation-reduction response in MFC chambers. In an anode chamber, the biofilm surface influences the substrate degradation and e^- creation; subsequently, this regulates the interactions of heavy metals present in the wastewater, electrode potential and the electrical energy produced in the MFC. The limitation on the transfer of electrons in or out of the cell is generally governed by the oxidization state of the e transporters in microbes (Logan et al., 2007). In addition, the distinctive extracellular mechanisms in biofilm

generate H_2O_2 and protons close to the cell surface. However, the dynamic growth or development of biofilms on the anodic electrode can lead to the overall inner resistance of the MFCs (Sindhuja et al., 2018).

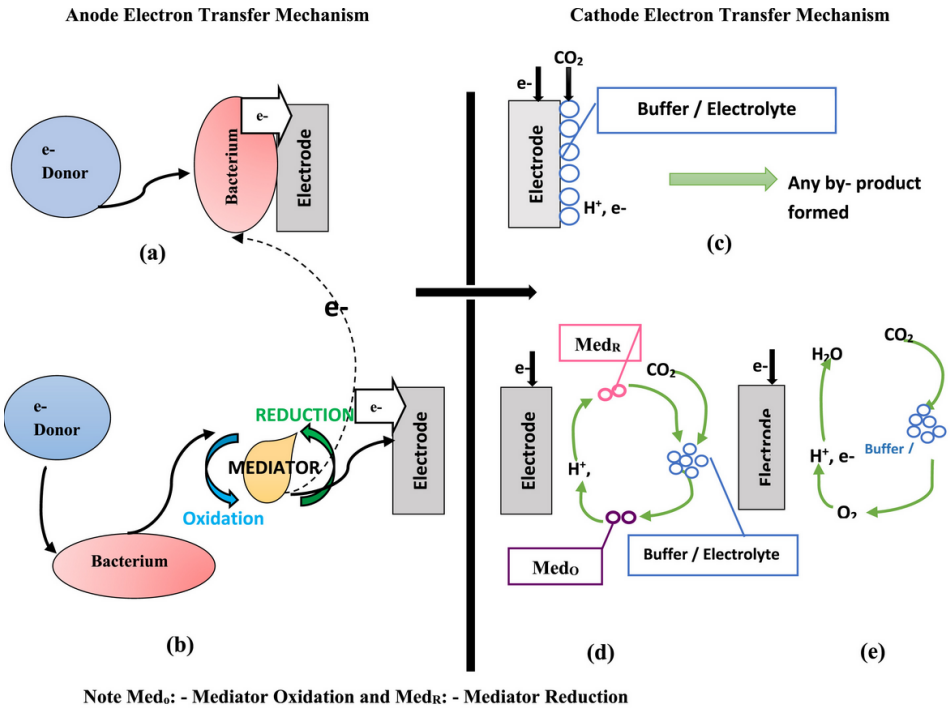


Fig. 2. Electron transfer mechanism (a) shows direction of electron flow from bacterium to the electrode; (b) electron transfer from metabolic product redox reaction; (c) direct electron transfer from cathode to electrolyte; (d) mediator (metabolic products) assisted electron transfer; (e) reduction of in-situ generated oxygen.

2.3.1. Biofilm formation

Because of the negative surface charge, the positive charge of the anode attracts microbes to its surface (Uddin et al., 2021) as shown in (Fig. 3), where microbes build up a biofilm (Gangadharan and Nambi, 2015). The anode biofilm produced by exoelectrogenic microorganisms such as *Geobacter sulfurreducens* is a thick polymeric substance where electron transfer takes place in MFC (Nevin et al., 2008). But the biofilm thickness had been shown to reduce bioenergy production in an MFC using stainless steel mesh or graphite plate as an electrode (Uddin et al., 2021). Previous research on studying Cr^{6+} in MFC focused mainly on biofilms and their organic carbon reduction.

2.3.2. Role of microbes in MFCs

Comparable investigation with graphite electrodes in a dairy wastewater sediment interface observed an open circuit voltage (OCV) of ~800 mV with current and power density of 68×10^{-6} $mAcm^{-2}$ and 53×10^{-6} $mWcm^{-2}$, respectively (Saravanan et al., 2010). Artificial wastewater in an MFC containing *Saccharomyces cerevisiae* showed a maximum OCV generation ~760 mV. A few studies have shown that MFCs working in a mixed culture generate higher levels of bioenergy than pure culture (Logan and Regan, 2006; Schneider et al., 2016). Most

studies concluded that it would be more pragmatic to utilize mixed cultures rather than pure cultures (Chaturvedi and Verma, 2016; Logan, 2008; Oliveira et al., 2013). Nevertheless, it should be viewed with caution as the reactors setup varied in different studies to preclude a meaningful comparison.

Jafary et al. (2011) used natural red and ferricyanide as moderators and achieved the power and current density of ~33 mWm^{-2} and 97 mAm^{-2}, respectively. However, ferricyanide is not recovered or regenerated which leads to high running cost. Azo dyes with their double-bond nitrogen may offer a cheaper and effective alternative (Verma et al., 2021).

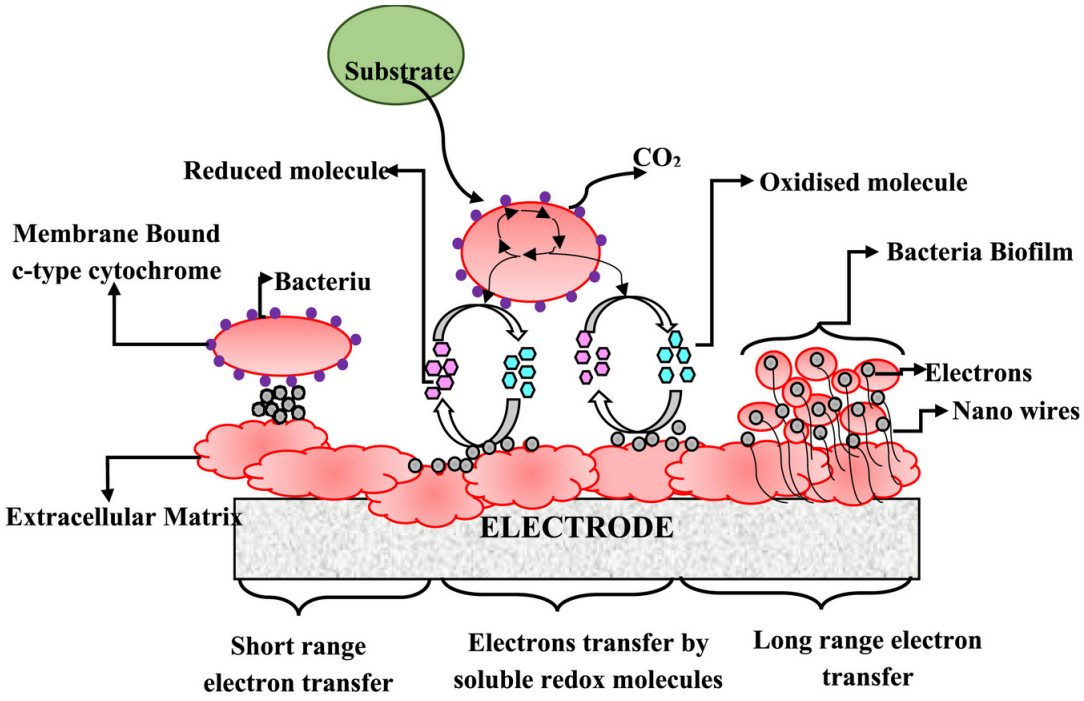


Fig. 3. Biofilm formation on anodic chamber electrode.

2.4. Different designs and types of MFCs

MFCs can be classified based on their nature, different designs, working principles and construction. The following section provides information on the most popular types of MFCs employed by industries to treat their effluents.

2.4.1. Single-chambered MFCs (SCMFCs)

A single-chambered MFC is a basic anode compartment used for protons without a specific cathode compartment. Its structure is similar to that of a permeable cathode. This kind of MFC is composed of a single compartment that houses anode and cathode chambers. The anode is located near the isolated proton exchange membrane. The goal is to minimize the dispersing of the component. In a Single Chamber MFC, microbial debasement and converse section of O_2 from cathode to anode are common technical issues. However, a Single Chamber MFC has a relatively simple cost requirement, as it has one anodic compartment with no additional need for aeration in a cathodic compartment (Singh et al., 2016). *2.4.2. Double/dual chamber MFCs* A double-chamber MFC is the most common design, it comprises a single chamber (can be of various

designs) is utilized as the anode and the opposite as a cathode that remains separated by H^+/cation exchange membrane (PEM/CEM) or also known as a salt bridge. A double/dual chamber MFC can be of an assortment of shapes; for example, a U-shape with the cathode in one arm of the chamber and anode in another arm. Both electrodes remain separated by an ion-selective membrane/proton exchange membrane that allows only protons to go through. Another regular design utilizes a simple H-shaped chamber with an anode and cathode on either side of the arm separated by a proton exchange membrane (PEM) (Lepage et al., 2014). As a rule, in a double-chambered MFC, the medium (substrate/ nutrient medium) in the anode is utilized by microbes to create bio-energy. The double/dual compartment MFC is frequently worked in batch mode. The catholyte can characterize the design of the MFC; e.g., if the air is utilized in the cathode as an e^- acceptor, the MFCs can be classified as double/ dual-compartment air-cathode MFC. Such MFCs may demonstrate significance to create power in remote detecting areas.

2.4.3. Up-flow MFC

The up-flow is cylinder-shaped MFCs. The cathode chamber is situated at the top and the anode chamber is at the base. Both compartments are connected by a film of glass wool and glass beads. The substrate is fed at the lower part of the anode, then moves upward toward the cathode and leaves at the top at an angle to ensure good activity of the fuel cell. In this design, there is no differentiation between anolyte and catholyte as it does not have any actual partition. Upflow MFCs have good potential for wastewater treatment and they can be easily scaled up compared to other designs (Okabe, 2020). Nonetheless, the major disadvantage of up-flow MFC is the energy expenses to siphon the substrate. So, the main function of an up-flow MFC is wastewater treatment rather than energy production. These sorts of MFCs are generally utilized in fundamental exploration and the studies suggested that power densities are low because of the high internal resistance.

2.4.4. Stacked MFCs

In stacked MFCs, the output of MFC is improved by multiplying the individual power or current output of a series of MFCs. In most cases, a single MFC can produce the greatest open-circuit voltage (OCV) of 0.8 V (Ramya and Kumar, 2022). This method involves stacking a number of MFCs units in parallel or series association. In addition, if the stacked MFCs are connected to the same cell, the overall voltage may not increase since the individual cell voltages are not being increased. This is because the parallel associated stack MFCs can generate more current than the series stacked ones. In parallel stacked multi-purpose units, a higher biochemical response rate is achieved than in-series units. This will increase the productivity of wastewater treatment plants by reducing the COD consumption. An effective examination of six multi-state batteries (MFCs) showed that they can produce a volumetric power density of over 60 W/m_3 and can be associated in parallel with copper wires (Aelterman et al., 2006). In stacked MFCs, various Columbic efficiency could be accomplished through connecting the cells in different configurations. A high rate of Columbic efficiency could be achieved with MFCs working in parallel. For example, a parallel design delivers 78% Columbic efficiency compared to 12% from those stacked in series (Shaikh et al., 2021). Voltage reversal is a significant limitation in stack MFC to accomplish higher voltage. The voltage inversion results from the exhaustion of substrate in the cell, highlighting the reduced capacity of microbes to create higher voltage.

2.4.5. Hybrid combination of MFCs

There have been reports of improved Cr_{6+} removal efficiency using a hybrid system that combines MFC with other waste treatment techniques such as adsorption, photocatalyst and electrocatalyst (Hidayat et al., 2022). The removal efficiency was enhanced up to 90.96% by combining MFC with the adsorption approach, which simultaneously converts Cr^{6+} into Cr^{3+} and adsorbs Cr^{3+} onto zeolite (Hejazi et al., 2019). Additionally, the MFC and adsorption techniques combined to produce a high-power density of 2.5 mW/m^2 (Rachman et al., 2018). The soil and groundwater that have been contaminated with Cr^{6+} can be cleaned effectively by using this hybrid MFC-adsorption system. It has also been reported that the hybrid MFC-adsorption system can be used to treat heavy metals other than Cr. It has been demonstrated that using tubular MFCs with porous adsorbents, like granular activated carbon (GAC), increases electricity production. The highest power density 74 ± 6 mW/m^3 was produced by MFC combined with the adsorption system. The GAC-MFC adsorption hybrid system (GAMFC) removed 95% of the waste and produced 110 W/m_2 (Hejazi et al., 2019).

Using semiconductor materials as MFC cathode allows for the integration of bio-electrochemical MFC with the photoelectrochemical system. To enhance electron transfer in photoelectrochemical cells (PEC), semiconductor photocatalysts have been thoroughly researched. The separation of the photogenerated electron-hole pairs at the electrode interface initiates a catalytic reaction under light irradiation, which boosts the external current flow. Even though titanium dioxide (TiO_2) nanotubes only absorbed UV photons when used as photoelectrodes in the MFC-PEC system, the maximum current was enhanced by 14.2% (Tong et al., 2022). Higher Cr^{6+} elimination efficiency was achieved by photocatalytic-MFC configuration's improved energy carrier separation. The complexity of reactor design and long-term stability has limited the use of such integration, despite the fact that it provides significant advantages as a potential solution for wastewater treatment (Hidayat et al., 2022).

To improve power density and reduce Cr^{6+}, MFC can also be integrated with an electrocatalyst. Due to its large surface area, excellent catalytic characteristics, low cost, biocompatibility, and non-toxicity, tungsten oxide (WO_3) is thoroughly researched as anode in MFC. Additionally, the WO_3 particle surface increased bacterial colonisation and biofilm formation (Read et al., 2010; Pham et al., 2009). As demonstrated by Das and Ghangrekar (2020) and Varanasi et al. (2016), tungsten oxide can produce a maximum power of 0.16 mW/cm^2 when used as an electrocatalyst in MFC.

2.4.6. Miscellaneous design

New designs have been developed to overcome the challenges associated with above mentioned MFCs. Min and Logan (2004) developed flat-plate MFCs (FPMFC) to decrease the Ohmic obstruction by providing more inter-electrode dividing space. The anode and the cathode comprised of flat-plates (each plate with an extended surface area of 225 cm^2). A Nafion membrane was put between two plates. This reactor produced 56 mW/m^2 of power density by using domestic wastewater as substrate and a reduction of COD (58%) was accomplished by the study. Different substrates like acetic acid, starch, and glucose generated less power output than solid cube reactor, probably as a result of the too firmly joined electrodes, and O_2 may tolerate the membrane to

microbes within the anode chamber, subsequently influencing the development of microbial community (Patil et al., 2011).

2.4.6.1. Photosynthetic Algae MFCs (PAMFCs).

Angioni et al. (2018) reported microalgae have "incredible photosynthetic proficiency and need a lesser amount of water than terrestrial crops to be developed". Nearly all algal strain has exceptionally high lipid content up to half of their dry weight. Depending on the types of microalgal strains, several significant optional metabolites with health and nourishing benefits can also be obtained in the photobioreactors (Yadav et al., 2020). For example, lipids, unsaturated fats and other high economic value metabolites including carotenoids, sugars, proteins, super-food, animal feed, polyhydroxyalkanoates (progressed plastics for smart packaging) could be obtained from the microalgal culture. The ability of microalgae produces biofuel whilst removing pollutants simultaneously is also an added advantage (Chisti, 2007; Suganya et al., 2016). There are various advances in the production of microalgal biomass based on heterotrophic or photoautotrophic development (Brennan and Owende, 2010). Among these microalgae as in-situ oxygen producers can advance the bio-electrochemical responses in MFCs. In an MFC, carbon dioxide is produced at the anode as a result of organic substrate oxidation (for example in wastewater), while O_2 is needed at the cathode to accept H_+ transported from the anodic chamber and free e^- from external circuits. In the presence of light, photosynthesis takes place in cathode chamber resulting in the generation of CO_2 and biomass production. Power or electricity might be created and gathered at the cost of natural substrate disintegration. The algal culture is developed in the cathode compartment and O_2 is produced by the photosynthetic cycle. Hence, these systems are called as photosynthetic Alga MFCs (PAMFCs) (Rosenbaum et al., 2010). The general flow chain reactions are as follows (Lee et al., 2015; Pandit and Das, 2015):

(i) Oxidation [Half reaction at anode]: Organics $CO_2 + H^+ + e^-$
(ii) Reduction [Half reaction at cathode]: $2O_2 + 4H^+ + 4e^- \; 2H_2O$
(iii) Complete electrochemical reaction:
  (a) Organic + O_2 CO_2+H_2O + Bioelectricity
  (b) CO_2+H_2O + Light Biomass + O_2

Several geometrical designs have been reported in literature: tubular, coupled, single-chambered sediment and dual-chambered PAMFCs. These designs may involve the algae in either anode or cathode, and the presence of a chemical and biological mediator for electron transfer. Among all of these geometrical designs, dual-chambers are the most popular because it has several advantages: treatment and purification of wastewater from different sources, growth of functional microalgae and generation of bioenergy (Angioni et al., 2018). PAMFCs property relies upon parameters such as the intensity of light, the state of anode material utilized like brush or plane, electrode distance and species of microalgae. *Scenedesmus, Chlamydomonas reinharditi, Chlorella vulgaris* were found to be ideal for the remediation of wastewater in PAMFCs (Gajda et al., 2015; Kondaveeti et al., 2014; Liu et al., 2013).

2.4.6.2. Microbial desalination cell (MDCs).

Microbial desalination cell is another green innovative approach which can be used to treat ocean water and brackish for water desalination, H_2 production, solidity evacuation and groundwater remediation. Microbial desalination cells (MDCs) are used to obtain desalinated water from saline water and in wastewater treatment in a single-chamber reactor. MFC incorporates positive and negative electrodes and specific or selective proton-exchange membranes, the aerobic and anaerobic environment at the particular electrodes is created by a marginal circuit. The distinction between MFC and MDC is that the latter does not require microorganisms as an intermediary source; it depends on the interior sludge which is electro-dynamic (Sophia et al., 2016). The wastewater comprising the natural organic matter enters the anodic side where biofilm is formed because of the expansion of microorganisms and power is generated (Sevda et al., 2015). The biofilm adheres to the anode surface and starts bio-catalysis measured by oxidizing bio-pollutants present in wastewater to deliver H^+ and e^-. This directed e^- is captured by an anode through an external circuit. The positive chamber of MDC is either oxygen-consuming or anaerobic. The MDC produces bioelectricity because of a potential difference across the anode and cathode chambers. The emphatically charged particles traffic to the cathode by a particular cationic membrane, where it joins with electrons and oxygen species to produce clean water (Sophia et al., 2016).

3. Applications of MFCs

3.1. Bioremediation of soil and sediment

MFC shows numerous advantages as a remediation technology such as accelerated decontamination, self-supported activity in eco-friendly manner (Li and Yu, 2015; Wang et al., 2012). Many studies have shown their potential in the remediation of refractory organics and heavy metal contaminated sites. Mohan et al. (2008) used MFCs in the remediation of petroleum sludge whereas Sherafatmand and Ng (2015) utilized sediment MFC in the remediation of naphthalene and acenaphthene. Other natural contaminants for example phenol and pesticides are also reported to be degraded efficiently by MFCs (Huang et al., 2011; Cao et al., 2015). Wang et al. (2016) also found MFCs effective in the remediation of chromium-contaminated soils. The contaminants removal from soil by MFCs demonstrated that MFCs can be a novel sediment or soil bioremediation innovation.

3.2. Bioremediation of tannery wastewater

The use of MFCs in wastewater treatment was first considered in the early 1990s (Habermann and Pommer, 1991). MFC is a promising approach that can be used in the treatment of municipal as well as industrial wastewater (He et al., 2017). Steady flow and single-chambered MFCs and membranes-less MFCs are used in the treatment of wastewater. Corbella and Puigagut (2018) used wetlands as MFCs for the effective treatment of domestic wastewater.

For a proficient treatment system, high operational stability and less material expenses are effective qualities. MFCs have been tested at a field scale with another treatment unit to treat wastewater in remote regions (Ramya and Kumar, 2022). Up to 90% of COD can be eliminated sometimes and Columbic effectiveness as high as 80% and up to 228 mW/m^2 power had been achieved (Ramya and Kumar, 2022).

The bioremediation of tannery wastewater by using MFCs is a bioelectrochemical as well as the conventional approach to removing and recovery of heavy metals and simultaneously bioelectricity generation. As shown in Table 2 which was focused on different types of microbial consortiums used. Also, Table 3 shows various types of MFCs on the basis of design help to remediate the metal.

Ryu et al. (2011) showed that Cr^{6+} reducing microorganisms could be applied to remediate Cr-contaminated sludge in a double chamber MFC. Habibul et al. (2016) reported ~ 99% reduction of Cr_{6+} where only a small quantity of soluble Cr^{3+} remained in plant-MFC and most Cr^{3+} get precipitated in the form of $Cr(OH)_3(s)$ or was adsorbed onto the electrodes. Different natural and inorganic compounds play an important role in Cr^{6+} reduction and power generation in double-chambered MFCs (Liew et al., 2014; Singh et al., 2016). The oxidation potential of Cr^{6+} is 1.33 V, which is higher than that of O_2 (1.23 V). Cr^{6+} is a preferred oxidant over O_2. Cr^{6+} is a more appropriate electron acceptor than $[K_3Fe(CN)_6]$ (Pandit et al., 2011). In double-chambered MFCs, the enhanced inoculum showed more removal of Cr^{6+} from tannery wastewater (Kaushik and Singh, 2020).

Table 3
Effect of different parameters on the reduction of hexavalent chromium as well as bioenergy production.

Electrode material		pH	Temp. (°C)	Mode of operation	Time of Operation	Membrane/salt bridge	Total energy/ power density (mW/m^2)	Cr^{6+} removal efficiency	References
Anode	Cathode								
Graphite felt	Graphite felt	7.0	30	Fed-Batch	20 h	Nafion 117	31.8 ± 1.06	50.6 ± 1.8%	Wu et al., 2018
Carbon cloth	Carbon cloth	2.0	–	Anode- fed-batch Cathode-batch	168 h	Nafion 117	767.01	99.85%	Gangadharan and Nambi (2015)
Graphite cylinder	Graphite cylinder	7.4 ± 0.1	18 ± 1	Fed-batch	12 days	Nafion 117		90%	Beretta et al., 2020
Carbon paper	Carbon paper	6–7	35	Fed- batch	27 days	Nafion 117	89.1 ± 1.2	98.5–100%	Wang et al., 2016
Graphite plate	Graphite plate	4	–	Fed-batch	–	Membrane coated with 5%H2o2	135.5	13.8%	Samsudeen et al., 2017
Stainless steel	Stainless steel	7	–	Fed- batch	60 days	Granular activated carbon	426.8	96%	Mu et al., 2020
Plain carbon cloth	Carbon cloth with MnO2	2	30	Fed- batch	32 h	Nafion 117	1429 ± 83	100%	Liu et al., 2020
Graphite plate	Graphite plate	7.5	22–26	Batch	210 h	Nafion 117	2400 ± 0.1	99.23%	Huang et al., 2010
Graphite sheet	Graphite sheet	5.62 ± 0.3	–	Fed- batch	18days	1%KCl with 5% agar	89 ± 3 69.5 ± 2.1	95% (4 mg/l) 86% (8 mg/l)	Sophia and Saikant (2016)
Graphite felt	Graphite felt	2	35 ± 0.5	Fed- batch	7months	TiO2/Fe2O3	1302	90.9%	Ren et al., 2018
Graphite brush	Carbon cloth	2.89 ± 0.09	28	Batch	24 h	Nafion 117 (PEM)	19.6	80.4	Wang et al., 2020
		2.46 ± 0.02	28	Batch	24 h	Ultrex CMI -7000 (CEM)	338	95.6 ± 0.8	
		2.49 ± 0.01	28	Batch	24 h	Ultrex AMI- 7001 (AEM)	431.8	97.9 ± 0.8	
		2.21 ± 0.02	28	Batch	24 h	Neosepta BP-1 (BPM)	320	99.4 ± 0.2	
Carbon felt	Carbon cloth/ carbon brush	2	–	Fed-batch	72 h	Nafion 117 with 30% H2O2	1221.91	100	Li et al., 2018
Graphite plate	Graphite plate	2	25 ± 2	Fed- batch	174 h	Nafion 117	150	92.65	Wang et al., 2008
Carbon paper	graphite	7	30	Fed- batch	30days	Glass with nafion 117			Mathuriya (2014)
graphite plates	graphite plates	7	25 ± 2	Fed-batch	150 h	Nafion 117	150 mW/m^2	74.6–100%	Wang et al., 2008
graphite plate	natural rutile-coated polished graphite	6.5 (±0.2)	22	Batch	26 h	Nafion 117	–	97%	Li et al., 2009
carbon fiber felt	carbon fiber felt	from 7.00 to 6.27 ±0.09		Batch	240 h	Nafion 117	970.2 ± 20.6 mW m^{-2}	75.4 ± 1.9%	Zhang et al., 2012
Graphite plate	Graphite plate	7	22–24	Batch	45 days	Nafion 117	55.5 mW/m^2	99%	Tandukar et al., 2009

3.2.1. Mechanism of hexavalent chromium reduction

Bacteria reduce Cr^{6+} by indirect (chemical) or direct (enzymatic) methods. In the indirect/chemical method of Cr_{6+} reduction, compounds like sulphite, thiosulphate, cysteine and glutathione are involved whereas in direct/enzymatic reduction of Cr_{6+}, different types of soluble and membrane-bound reductase enzymes present in aerobic, anaerobic and facultative bacteria are involved (Joutey et al., 2015). A detailed mechanism of Cr_{6+}reduction is shown in (Fig. 4). In aerobic reduction, bacteria reduce Cr_{6+} in presence of oxygen in two to three steps. Initially, Cr_{6+} is reduced to the short-lived intermitted Cr_{5+} or Cr_{6+} before being further reduced into thermodynamically stable end product Cr_{3+}. Cr_{5+} undergoes one electron redox cycle to regenerate Cr_{6+} by donating electrons to oxygen. This process produces ROS (reactive oxygen species) that is easily combined with DNA protein complex. However, it is unclear whether the reduction of Cr_{5+} to Cr_{4+} and Cr_{4+} to Cr_{3+} is spontaneous or enzyme-mediated (Cheung and Gu, 2007). In the anaerobic method, Cr_{6+} could serve as a terminal electron acceptor in the respiratory chain for a large range of electron donors, which include fats, protein, carbohydrates, hydrogen, NADPH and endogenous electron reserves. Both soluble and membrane-associated enzymes mediate the Cr_{6+} reduction process under anaerobic conditions (Cheung and Gu, 2007).

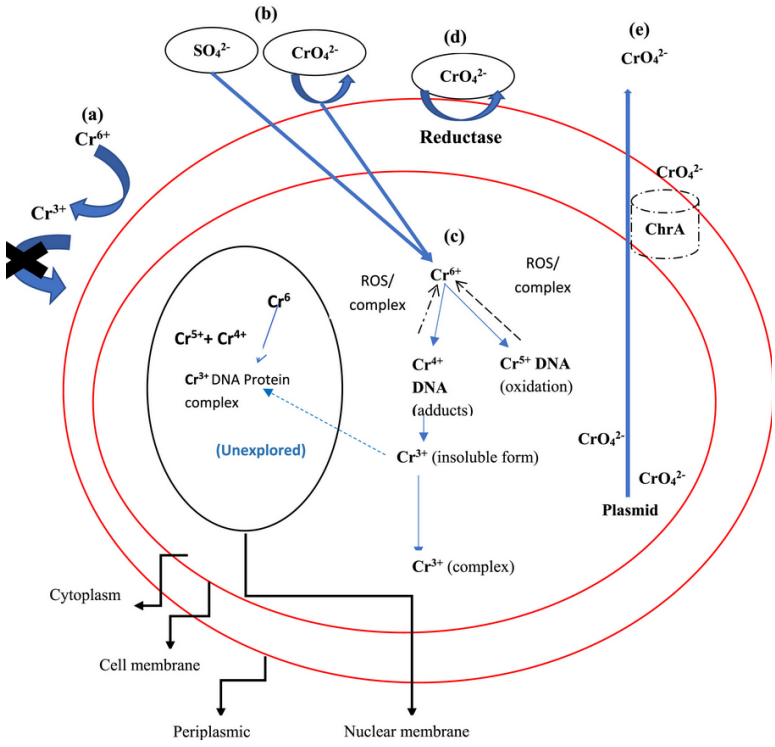


Fig. 4. It shows the mechanism of Cr^{6+} removal **(a)** Extracellular reduction of Cr^{6+} to Cr^{3+} in which metal form do not cross the membrane; **(b)** Sulphate uptake pathway which used by chromate to enter the cell; **(c)** Intracellular Cr^{6+} to Cr^{3+} reduction may generate reactive oxygen species (ROS) and oxidative stress that causes protein and DNA damage; **(d)** Membrane-bound chromate reductase; **(e)** Plasmid determined resistances to chromate ions in *Pseudomonas*.

In the indirect method, sulphate and iron-reducing bacteria are important for anaerobic microbial communities. The reduction of Cr_{6+} by biogenic iron and sulfate-reducing bacteria generates 100 times faster than chromium-reducing bacteria. Sulfate-reducing bacteria produce hydrogen sulphide which helps as a Cr^{6+} reductant which involves (a) reduction of sulphide, (b) reduction of chromate by sulphide and (c) precipitation of Cr^{6+} by sulfide. The reduction of Cr^{6+} by iron occurs when iron-reducing bacteria reduces Fe^{3+} to Fe^{2+} which in turn reduces Cr^{6+} to Cr^{3+} (Somasundaram et al., 2011). Extracellular Cr^{6+} reduction is valuable to the organisms because cell does not need a transport mechanism to carry chromate and dichromate into the cell and later export to Cr^{3+} into the medium. Both Cr^{6+} and Cr^{3+} react easily with DNA, the presence of which could result in DNA damage and an increased rate of mutation. Extracellular reduction of Cr^{6+} protects the cell from DNA damage. It might be the reason that certain bacterial species have adopted the extracellular Cr_{6+} reduction process for existence in Cr_{6+} contaminated environments (Joutey et al., 2015). Membrane-bound reduction of Cr_{6+} in which Cr_{6+} acts as an electron acceptor in a process mediated by membrane-bound Cr^{6+} reductase, which is active in respiratory chains involving cytochromes (Joutey et al., 2015). In intracellular reduction of Cr^{6+}, it has been established that specific Cr^{6+} reducing enzymes (reductase) exist inside Cr^{6+} reducing bacterial cells, and several components of the cell protoplasm also reduce Cr^{6+}. It is predictable that the cytoplasm fraction of disrupted cells from most organisms will reduce Cr^{6+}. Such a reduction process is not energy-consuming but will directly affect the cell, since most of the intracellular proteins catalyse a one-electron reduction from Cr^{6+} to Cr^{5+}. When this occurs, harmful reactive oxygen species (ROS) are generated that cause damage to DNA. Some hexavalent chromate reductases were found to be localised in the cytoplasmic fraction of numerous chromium-resistant bacteria e.g., *Bacillus cereus* (Iftikharet al., 2007) and *Pannonibacter phragmitetus LSSE-09* (Xu et al., 2012). In contrast, some bacteria like *Pseudomonas putida* displayed chromate reductase activity that was mainly associated with both the supernatant and cytosolic fractions of bacterial cells (Garg et al., 2013).

3.3. Bio-hydrogen production

MFCs can also be used to produce hydrogen rather than power generation and the produced hydrogen can be aggregated for later applications (Du et al., 2007). Under normal conditions, the protons generated by the anode are relocated to the cathode to consolidate with oxygen to form water. The generation of hydrogen from protons and electrons delivered by MFCs metabolism is thermodynamically unpromising. According to Liu et al. (2005), MFCs can generate ~8–9 molH_2/mol glucose as compared to 4 mol H_2/mol glucose in conventional fermentation. For the generation of hydrogen gas in a typical MFC, the anodic potential should be expanded with an extra voltage of ~0.23 V or more. In the cathode chamber, oxygen ought to be eliminated to create an anaerobic environment for biohydrogen production, to avoid using oxygen as the terminal electron receptor. Hydrogen produced by MFC can be stored for later application, thus, providing a sustainable hydrogen source to support a hydrogen economy.

Although hydrogen has been indicated as a clean fuel, hydrogen creation actually requires a few fuels source. Water is known to be a common decision of hydrogen source, but water electrolysis is energy-demanding and costly. The energy cost exceeds the energy produced using hydrogen as a fuel (Liu et al., 2005). Hydrogen creation by high-temperature treatment of fossil fuel derivatives is the least expensive convention practice.

Hydrogen production by MFCs using organic waste could offer an eco-friendlier approach. In such devices, the anaerobic conditions are kept up in the cathode chamber and an extra voltage of ~0.25 V is applied to the cathode. Under such conditions, the protons are reduced to form hydrogen in the cathode (Liu et al., 2005). Such adjusted MFCs are named bio-electrochemically assisted microbial reactors (BEAMR) (Liu et al., 2005).

Despite the fact that BEAMRs require energy for hydrogen creation, the energy costs are not excessive (about 20% of the energy in the resulting hydrogen fuel). For instance, hydrogen creation in a BEAMR working on acetate is ~2.9 mol/mol (the hypothetical yield is 4.0 mol/ mol), and energy necessities are comparable to consuming ~0.5 mol of hydrogen (Logan and Regan, 2006). Different wastewater, solvents and natural substrates can be utilized as fuel for BEAMRs to reduce the running cost further.

The power needed for hydrogen creation in BEAMRs can be acquired from hydrogen-controlled fuel cells; these are the most effective device, with over 60% transformation obtained from hydrogen oxidation. Bacterial catalysts have been effectively utilized in hydrogen energy units to replace costly platinum (Kiely et al., 2011).

3.4. MFCs as biosensors

MFCs can be applied as biosensors for pollution examination, in situ observation and control (Feng et al., 2013). The MFC-based sensors are profitable as they have long-term stability and can be used persistently for online monitoring. The MFC biosensor does not require transducers (Sun et al., 2015). It has been applied to monitor the sludge condition in real time. As substrate degradation is emphatically identified with power generation. Khater et al. (2015) assessed the active sludge and metabolic pathway action utilizing MFCs. Furthermore, MFCs can serve in various capacities Along with the gas flow meter and pH meter in an anaerobic reactor because of the linear relationship with proton concentration, the volume of gas, and gas stream rate (Liu et al., 2014).

4. Factors affecting the efficiency of MFCs

Currently, the level of bioenergy generated by an MFC is limited. In order to bring this eco-friendly and sustainable technology to wide acceptance and application, the process needs to be optimised and scaled up effectively. A number of operational aspects need to be improved and challenges overcome.

4.1. The electrode material

Using the appropriate material for the anode or cathode can offer a number of improvements, for example, amplifying power generation, increasing coulombic productivity, limiting expense, or making adaptable architecture. For the cathode, the major requisite is the function of a catalyst; here, attention is to replace the valuable metal catalyst with non-valuable ones and other transition metals. For MFC's electrode, the pore size should not be too small (about 400 nm) to avoid clogging (Bose et al., 2018a,b; Logan et al., 2015). Considering the reactor plants for various purposes identified with wastewater treatment for example trickling channels or biofilm reactors, these are normally described by an ordinary surface area of 100 m^2m^3 (Bose et al., 2018a,b; Ross et al., 2015). This will not prevent biofilm formation but permit adequate airflow in a bioreactor. The arrangement of electrodes in MFCs assumes a pivotal part in the power creation limit (Bose et al., 2018a,b).

4.2. Cathode

On cathode, reaction of e^-, H^+ and O_2 happen at a catalytic agent during a tri-stage response. For the cathode to work adequately, the catalyst must have a conductive surface. The constituents predominantly used as a cathode are graphite granules, carbon (fabric, paper) graphite, woven graphite and brushes (Chaturvedi and Verma, 2016). For a large portion of research, platinum (Pt) remains the most common catalytic agent. The challenge with Pt-covered metal electrodes is primarily the oxide layer of platinum development on the outside of Pt, which decreases the movement of the electrode in additional time. Various resources for example solid manganese oxide (MnO_2) based cathodes and brushes of stainless steel have been studied for pragmatic applications as submerged biosensors (Bose et al., 2018a,b; Logan, 2008). Studies have shown that activated carbon can be a promising new alternative to platinum. A study revealed that it can be utilized as a covering over a carbon cathode. This arrangement is similar to that of PTFE (polytetrafluoroethylene) in that it is an oxygen-reducing catalyst. It can be utilized with dilute acid and is ideal for wastewater treatment. PVDF (Polyvinylidene fluoride) has a water pressure obstruction of ~1.2 m (Bose et al., 2018a,b; Li et al., 2017). Ferricyanide $[Fe(CN)_6]^{-3}$ has also been used as a mediator in a number of studies to improve power generation (Bose et al., 2020; Penteado et al., 2017; Zain et al., 2015). By using ferricyanide in the cathode, Bose et al. (2018a,b) and Penteado et al. (2017) were able to amplify power density and generated 1.5–1.8 times more power than a platinum-based carbon cathode double-chambered MFCs with a Nafion-117 membrane. Future studies can be carried out to explore the use of fluid catalysts. The utilization of catalysts binder is likewise significant as this permits the exchange of H^+, e^-, and O_2. Other improvements could include utilizing an air cathode, with a membrane (Nafion-117) (Zhang et al., 2015) at the opposite side of the cathode, using a hydrophobic covering could be functional to build framework productivity. Another basic part of cathode implementation is the existence of a cation exchange membrane (CEM). On the cathode side, a few gasses should be kept up (CO_2, N_2, O_2, CH_4) development which will rely upon the working conditions. Ferricyanide can expand and has a decent electron-tolerating limit. However, the use of synthetic mediators would add to energy costs in the event that they become part of the wastewater treatment measures.

4.3. Anode

The ideal anode should be non-destructive and electrically conductive with high porosity and more surface area, not susceptible to biofouling, cheap, effectively accessible and versatile in size. The microorganisms could move e^- to the anode through chemical mediators, nanowires or in direct contact (Bose et al., 2018a,b). Stainless steel meets many of these requirements for being a suitable anode material, but it has low power creation. Bose et al. (2018a,b) examined MnO (manganese oxide) plating on a graphite terminal and were able to deliver ~790 mWm^{-2} with an intricate lactate mediator. Logan and Regan (2006) used FeO (ferrous oxide) and Ni (nickel) covering on a graphite plate to produce 1.7–2.2 times more energy than ordinary graphite anodes (105 mWm^{-2} thought about 20 mWm^{-2}). Kim et al. (2016) examined stainless steel, tungsten (W), or titanium (Ti) anodes incorporated with ferric oxide (Fe_2O_3) or aluminium oxide (Al_2O_3), but they found the combination delivered low power density than carbon paper. Conductive polymers like polyvinyl chloride (PVC) showed low power

generation (99.4 ± 1.9 mV) (Kim et al., 2016). Therefore, more study is required for improved force densities and material steadiness.

4.4. Effect of pH

Microbe development is influenced by pH, the concentration of the substance, transmembrane potential or membrane voltage, H_+ development, as well as biofilm arrangement. Acidification/fermentation at the anode can reduce microbial action and influence biofilm stability and functions. Most research showed that pH 6–9 is suitable for the development and activity of biofilms from pH-neutral wastewater (Oliveira et al., 2013; Mani et al., 2017). The pH values vary in two compartments of an MFC and pH is a significant factor in power generation by an MFC. Mani et al. (2017) observed an increase in power density and cell voltage with a diminished pH polarity. By neutralising the impact of pH using a chemical buffer it was shown to improve voltage stability (Cheng et al., 2011; Bose et al., 2018a,b) and biofilm accomplishment (Oliveira et al., 2013). The impact of pH is more prominent in a single-chamber system. Carbon dioxide can be utilized in the cathode as it joins with hydroxide ions to make carbonate or bicarbonate buffer catholyte framework (Bose et al., 2018a,b).

4.5. Effect of temperature

Temperature is a significant parameter for COD reduction and bioenergy creation. Both power density and in an MFC, COD increases with an increase in temperature, which could be connected through a permeable membrane and microbial metabolism (Lopez et al., 2016). Various microorganisms have diverse optimal temperature ranges for biofilm development. System kinetic energy will determine the rate of substrate usage by microorganisms. Parameters like activation energy, arrangement conductivity alongside ‘‘electrode potential and Gibbs free energy will affect mass transfer and thermodynamics (Bose et al., 2018a,b). Microbe species could change in accordance with the change in temperature during biofilm development. Logan (2008) recommended an MFC start-up temperature between 30 and 45 °C.

4.6. Effect of aeration

In the cathode chamber, oxygen might contend with metal oxidation status (e.g., affect the reduction in hexavalent chromium content (Uddin et al., 2021; Kumar et al., 2018). Liu et al. (2011) discovered that H_2O_2 could be delivered by bypassing air in a cathode to enhance the reduction of Cr^{6+}. Conversely, the development of biofilms on the cathode surface might restrict metal reaction and reduce aggregate energy production. In the presence of oxygen, the heterotrophic microbes might break down the organic matter leading to an increase in Cr_{6+} reduction with more electricity generation (Behera et al., 2010).

4.7. Effect of membrane/salt bridge

The membrane is utilized in a dual-compartment MFC to separate liquid (wastewater) within the anode and liquid (catholyte) in the cathode chamber. H_+ is transferred from the anode to the cathode through a membrane. The permeability of the membrane is an important design factor. The constraint of the membrane is cost and biofouling. For example, Nafion (Dupont Co., Wilmington, Delaware, USA) can cost up to \$1400/m^2 while a basic CEM costs ~\$80/m^2 (CMI-7000, Layer International, Inc., Ringwood, New Jersey, USA) (Bose et al., 2018a,b).

Nafion-117 has the advantage as it has high conductivity (0.2 Scm^{-1}), mechanical and thermal stability, it's an equivalent weight of 1100 g and 0.007 inches of thickness. But the high cost will prevent widespread usage and upscaling.

Other materials tried as membrane substitution in MFC such as incorporating ultrafiltration (UF) membrane and salt-bridge frameworks fabricated from agar and immersed salt of K or Na (Zain et al., 2015). However, such a system shows high inner resistance consequently that restricts power production. High permeability to gases adds its constraints and these could be degraded by alkali metals at room temperature and pressure. The equivalent weight of Nafion-117 is characterized as the heaviness of Nafion (in terms of atomic mass) per sulfonic acid gathering (Zain et al., 2015). A study compares other types of membranes: Anion Exchange Membranes, cation exchange membranes and Bipolar Membranes to Nafion-117. The polymer design of CMI-7000 is gel polystyrene cross-linked with divinylbenzene with a sulfonic acid functional group. CMI-7000 membrane incorporates a covered woven fabric for stability, making a rigid nature that was not observed in the Nafion-117 layers i.e., for the better result, they use different types of exchange membranes which show better results than Nafion-117.

In several studies using Nafion-117 with carbon paper as an electrode, cellulosic waste, a microbial consortium of *Clostridium acetobutylicum* and *Clostridium thermohydrosulfuricum*, (Mathuriya and Sharma, 2010) found that an initial current of 6.35 and 7.31 mA was generated; respectively. A similar MEA arrangement was also used to treat wastewater from distilleries, dairies, municipal, and tannery industries (Mathuriya and Sharma, 2010) where the current generation is as high as 14.92 mA and the COD removal rate is 90.23%. Graphite electrodes were utilized in single-chambered MFCs which generated a peak power of 18 mWm^{-2}. In MEA incorporated with a Nafion-117 membrane with eight graphite electrodes as anode and an air cathode (Pandey et al., 2016), where the film was treated with 30% hydrogen peroxide, deionized water and 0.5 M sulfuric acid, a voltage of 0.32 V was generated between the terminals, with some susceptibility in normal energy generation. In another study, whey degradation utilizing *E. coli* obtained an open-circuit voltage (OCV) of around 751 mV (Nasirahmadi and Safekordi, 2011). The investigation utilized iron (III) chloride as a catholyte and MEA counted in graphite electrode with a Nafion-117 membrane. When autoclaved and centrifuged humic acid was utilized as mediator, the current produced is approximately 320 μW and 1190 μA, respectively (Mathuriya and Sharma, 2010). Research on wastewater, using available substrates like sucrose and glucose have typically shown high efficiency in removing COD from distillery wastewater in a non-mediator MFC, created near 11 mA of current at pH 7.

Investigations also included Nafion-117 film, and carbon paper as electrodes in MEA (Mathuriya and Sharma, 2010).

4.8. Effect of time of operation

MFCs power yield can be amplified by using a cylindrical or cube-shaped container that can be stacked and connected in series to produce more power at the same time. Liu et al. (2008) utilized MFCs having air cathode showed that bioenergy generation was not affected by an increase in the working volume. A digital control was

also used in a study connecting four MFCs to produce a voltage ~1.26 V. This system had the option to regulate substrate flow, electrical stacking and temperature (Boghani et al., 2017). When reactor exhibitions are evaluated with regard to time, residence time distribution (RTD) plays a significant role in determining the blending qualities during a reactor; the knowledge of RTD can be applied in a mathematical model to predict and improves reactor performance. As shown in Table 3, it is summarised the way that different factors affect the reduction of Cr_{6+} as well as bioelectricity production.

5. Future perspectives

MFCs have both pros and cons with respect to their applications in the field. The pros/advantages of an MFC are its capacities to convert biochemical energy into electrical energy through natural microbial actions. It can produce as opposed to consumed energy from oxidation of natural waste substances and under specific situations inorganic carbon (Do et al., 2018). The disadvantages include high operational expenses and low power yield, and this must be overcome in order to commercialize MFCs for wastewater treatment. Overall, the set-up cost is higher than that of the conventional activated sludge treatment frameworks for domestic wastewater because of its design and treatment. The significant level of capital expenditures in MFC is principally brought about by the utilization of costly anode materials like current authority, catalyst and separator materials. The power generated by cells probably would not be sufficient to run a sensor or a transmitter consistently. This is the fundamental issue with using an MFC. It can be treated by increasing the electrode surface area and or utilizing a reasonable power management program; for example, using an ultra-capacitor for energy storage. The other limit of MFCs is that they are not efficient at low temperatures due to a reduction in microbial activities at low temperatures.

Currently, using conventional carbon-based materials incurs high capital expense. Analysts showed that improvement of minimal effort, high-current-yield, carbon-rich anode materials would be a way forward. An MFC with a tubular membrane cathode has a larger surface area that enhances the mass transfer rate within the cathode to improve energy generation (Zuo et al., 2007). The decrease in ohmic loss was accomplished with a decrease in the distance between electrodes (Huang and Logan, 2008; Liu et al., 2008; Logan et al., 2007).

The utilization of carbon nanofiber-based electrodes scattered with initiated alumina/nickel nanoparticles enhances Cr_{6+} reduction in MFCs. The nanoparticles of actuated alumina improved the electrical conductivity of electrodes in the cathode; the reduction of toxic Cr^{6+} is catalyzed by the nickel nanoparticles (Gupta et al., 2017). Bio-waste with environmental effects has been utilized as substrates in MFCs that bring the total decrease in Cr^{6+} and generate 396.7 mW/m^2 electricity (Sindhuja et al., 2018). Recent technological developments incorporated the utilization of graphene bio-cathodes (Song et al., 2016), and bipolar membrane (BPM-MFC) (Kim et al., 2017) where electrochemically active microbes and electricigens were detected using fluorescent probes (Markandya et al., 2017) on the biotic anode (Li et al., 2018). The microbial cellulose was utilized as a starch polymer to increase the conductivity by oxidative polymerization with aniline (Loloei et al., 2017). Polyaniline, carbon left is utilized as a capacitive bio-anode (Wang et al., 2018) and LCD screen waste is treated in carbon-fabric electrode-based MFCs (Gangadharan and Nambi, 2017). To keep up the high-power generation and stable execution in field applications of this innovation remains a challenge. A few analysts have tentatively

accomplished a 100% reduction in Cr^{6+} (Uddin et al., 2021) broad exploration is needed to build up a similar degree of execution in large-scale operations.

6. Conclusion

MFCs are eco-friendly and cost-effective agents that can be used to treat industrial effluents, such as hexavalent chromium from a tannery, and simultaneously produce current. Nonetheless, broad research is as yet expected to predict the genuine energy generation capability of a full-scale framework on the grounds that numerous factors affect energy production during a pilot or full-scale MFC. Anaerobic treatment and MFCs are eco-friendly and sustainable agents effective in wastewater treatment with energy generation. To overcome MFC's limitations and commercialize these, it is important to coordinate MFCs with the wastewater treatment process. This combination can significantly increase the treatment efficiency of MFCs and has the capacity to be self-sustained and a net energy producer.

Credit author statement

Christina Saran: Conceptualization, Drafting, Writing and Revision of article, Validation, Data Curation, Editing, Revision, Visualization & final approval of the version to be submitted. **Diane Purchase:** Editing and Language improvement & final approval of the version to be submitted. **Ganesh Dattatraya Saratale:** Review, Editing & final approval of the version to be submitted. **Rijuta Ganesh Saratale:** Editing, Language improvement & final approval of the version to be submitted. **Luiz Fernando R. Ferreira:** Revision & final approval of the version to be submitted. **Muhammad Bilal:** Review & final approval of the version to be submitted. **Hafiz M.N. Iqbal:** Review & final approval of the version to be submitted. **Chaudhery Mustansar Hussain:** Language improvement & final approval of the version to be submitted. **Sikandar I. Mulla:** Revision & final approval of the version to be submitted. **Ram Naresh Bharagava:** Supervision, Conceptualization, Draft preparation, Editing, Revision, Review, Finalization & final approval of the version to be submitted, Resource management.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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