



A review of microbial fuel cell prototypes, their efficacy in wastewater treatment and the contextual situation for Zimbabwe

Tafadzwa Portia Mahurede^{a,*}, Chido Hermes Chihobo^b, Beaven Utete^{c,d}, Phillip Taru^e

^a Chinhoyi University of Technology, Department of Wildlife Ecology and Conservation. P. Bag 7724, Chinhoyi, Zimbabwe

^b Chinhoyi University of Technology, Department of Fuels and Energy. P. Bag 7724, Chinhoyi, Zimbabwe

^c Chinhoyi University of Technology, Department of Freshwater and Fishery Sciences. P. Bag 7724, Chinhoyi, Zimbabwe

^d Fisheries and Wildlife Management Trust, Harare, P.O. Box Belvedere 390 BE, Zimbabwe

^e Chinhoyi University of Technology, Department of Geoinformatics and Environmental Conservation. P. Bag 7724, Chinhoyi, Zimbabwe

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ABSTRACT

Accelerated global human population growth and the corresponding increased urbanisation and industrialisation have resulted in increased manufacturing of goods, and production and loading of domestic and industrial wastewater overwhelming conventional wastewater treatment plants (CWTPs). The net result has been the release of untreated and partially treated domestic wastewater into water systems posing human health hazards and disturbing aquatic habitat integrity. Considering the severe challenges of wastewater treatment not only in Zimbabwe but in Africa and the world in general, it is prudent to assess the microbial fuel cells (MFCs) as an alternative wastewater treatment method for the CWTPs that have failed to operate efficiently. This purposive literature scoping review aimed to: (a) Examine the concept design and operational efficacy of microbial fuel cells (MFCs), (b) Examine the MFC operational system (c) Outline in brief the evolutionary history and assess the existent prototypes and (d) Establish the drivers and barriers for the uptake of microbial fuel cells (MFCs) from a global and local, Zimbabwe, context. Few prototypes have been utilized in real-world systems; with the majority of them being laboratory-scale based. Although MFCs are effective at treating wastewater, scaling them up is still difficult due to their low power generation. Nonetheless, MFCs' simultaneous wastewater treatment and power generation, low carbon footprint, and reduced sludge production are the main drivers behind their adoption. However, capital and maintenance costs and upscaling remain the major challenges in adopting MFC technology. If MFCs are to be used in developing nations like Zimbabwe, further studies should focus on low-cost materials that guarantee maximum power generation and effective wastewater treatment. To ensure effective wastewater treatment, MFCs should be compatible, and integrated with currently utilized sustainable wastewater treatment systems.

Introduction

Wastewater is defined as a suspension of water and waste from domestic and/or industrial activity including storm water runoff. Wastewater is mainly classified as domestic, industrial, agricultural and urban wastewater [1,2]. These types of wastewater affect discharge patterns and the chemical status of treated effluent [1]. The major contaminants in wastewater effluents are nutrients (nitrogen and phosphorus), hydrocarbons, organic matter, microbes, endocrine disruptors and heavy metals such as arsenic, cadmium, chromium, zinc, iron, nickel, lead and mercury [3–7].

Cross-cutting examples in literature reflected inherent challenges in

wastewater treatment in African countries ranging from poor maintenance of infrastructure, obsolete equipment, and increased waste loading due to accelerated industrialisation and urbanisation, and erratic supply of electricity [8–10] resulting in adverse effects to both human health and the environment [6]. Most heavy metals are toxic, more so at elevated concentrations, and pose a threat to human health, flora and fauna [11,12]. Pollution in water bodies has resulted in water related illnesses such as typhoid, cholera and pollution related deaths of fish abound in water systems of Zimbabwe [13–17]. The net result is a high rate of greenhouse gases release into the atmosphere ultimately resulting in global warming leading to climate change in the long-term whose effects tend to be severe for impoverished Sub-Saharan African

* Corresponding author.

E-mail address: tmahurede@cut.ac.zw (T.P. Mahurede).

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nations [18].

Nonetheless, there has been a continued use of Conventional Wastewater Treatment Plants (CWTP) for African nations with attendant challenges stated above. The largest volume of wastewater in Zimbabwe's cities and towns is treated using modified activated sludge systems with Biological Nutrient Removal and conventional biological trickling filter systems [19]. The advantages of this system is no chemicals are used, there is treatment of large amounts of wastewater and the sludge can be used for composting. However, it requires a number of tanks which greatly increases capital cost and detention times need strict monitoring and constant evaluation made for BOD and COD values [20]. CWTPs are energy intensive and require high electrical energy [9], and have major operating and maintenance costs rendering the use of CWTP very expensive for resource constrained municipal authorities in Zimbabwe. Consequently, there are intermittent breakdowns of the CWTP with authorities resorting to diverting untreated or partially treated wastewater or effluent directly into the streams and reservoirs [21–23].

Globally, water scarcity and the increasing demand for energy has resulted in the need to come up with climate smart alternative sources for wastewater treatment and electricity generation [24,25]. In contemporary studies, and in some practical use, there has been consideration (and use) of a relatively new environmentally friendly and sustainable electrochemical device for the treatment of wastewater known as a microbial fuel cell [26]. Microbial fuel cells (hereafter referred to as MFCs) are single or multi-chambered bioelectrical systems that convert chemical energy to electrical energy through catalytic reactions of bacteria [27]. The MFCs have found increasing consideration on a global scale with a rather slow uptake due to a raft of concerns on the energy generated and the wastewater treatment efficiency and initial set-up costs [28]. Factoring the dire challenges of wastewater treatment not only in Zimbabwe but Africa and the world in general, it is prudent to assess the MFCs as an alternative wastewater treatment method for the CWTPs that have failed to operate efficiently. This purposive literature scoping review aimed to: (a) Examine the concept design and

operational efficacy of microbial fuel cells (MFCs), (b) Examine the MFC operational system (c) Outline in brief the evolutionary history and assess the existent prototypes and (d) Establish the drivers and barriers for the uptake of microbial fuel cells (MFCs) from a global and local, Zimbabwe, context.

The concept design and operational efficacy of microbial fuel cells (MFCs)

A microbial fuel cell is a bioelectrical system that converts chemical energy to electrical energy through the catalytic reaction of microorganisms mostly bacteria [27]. The MFC consists of electrodes (anode and cathode), a separator or membrane, substrate (wastewater), microbes and an external circuit [29]. The major function of the MFC system is electricity generation and pollutant removal. The device can be single chambered, double chambered or stacked MFC (Fig. 1), with the most often used system being the double chambered MFCs [30]. According to Yaqoob, et al. [30] the dual chamber MFCs produce high power generation than single chamber MFC and thus, are more frequently used than the single chamber MFCs. However, Zuraidah, et al. [31] argues that single chamber MFCs have better performance than double chamber MFC. These confounding statements make it difficult to conclude on which MFC type outperforms the other since these experiments are done under different conditions, using different materials and the protocols used may be difficult to reproduce. This becomes a huge challenge when it comes to replicating these studies.

The Stacked MFC are MFCs connected in series or parallel [32]. Stacking increases power production/output [33,34]. The first attempt for MFC stacking was by Cohen in 1931 as he stacked 35 units of MFCs in series with an open circuit voltage of 35 V [35]. MFCs connected in series have increased voltage without increasing current, whilst MFCs connected in parallel improve power by increasing the current without increasing the voltage [33]. Due to the improved stability of redox potential across all cells, a series-parallel stack design system exhibits considerable COD removal and maximum power density [36].

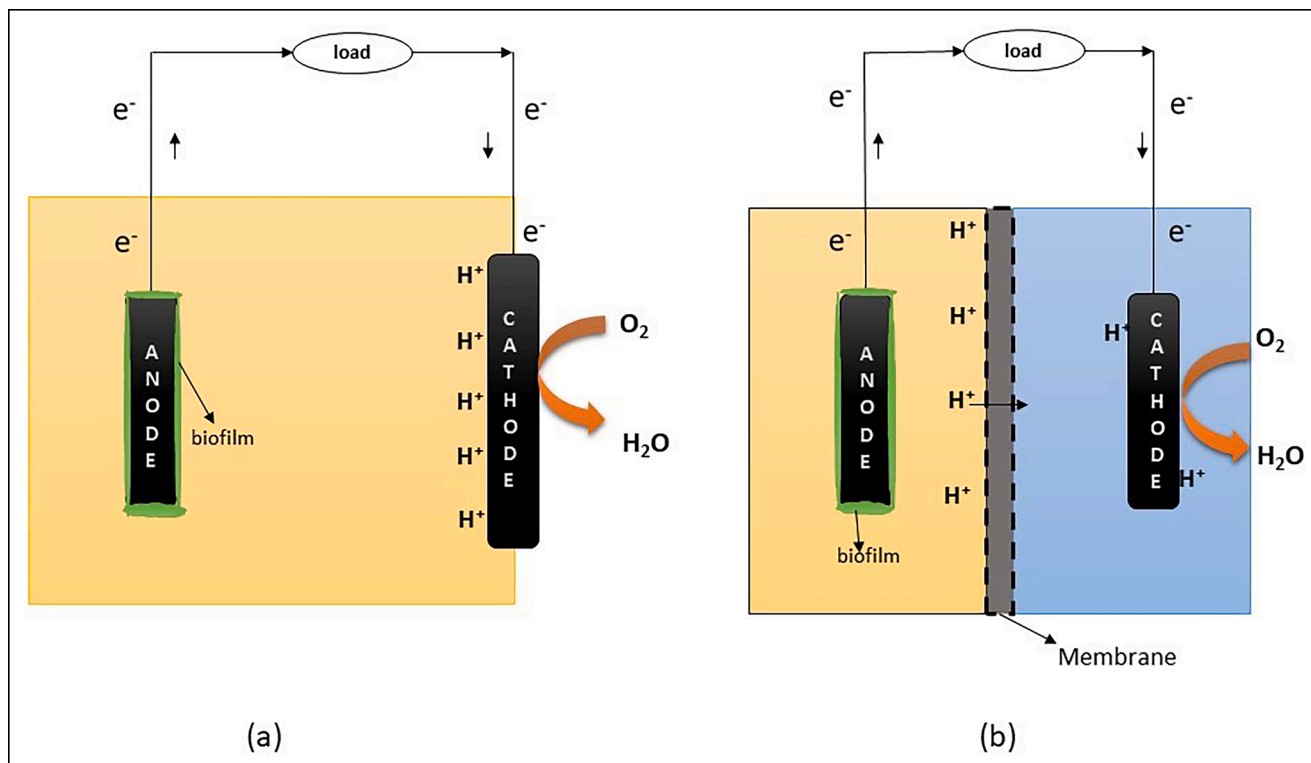


Fig. 1. A Schematic representation of (a) Single chamber MFC and (b) Double Chamber MFC.

MFC operational system

In principle MFCs consist of two electrodes an anode (fuel electrode) and cathode (oxidant) which are two halves of a spontaneous oxidation–reduction reaction. The anode is made up of a substance that is readily oxidised (releases electrons) while the cathode being a made of a substance that is readily reduced (accepts electrons) [37]. An electrically negative terminal releases electrons into an electrically positive terminal. All of the reaction's energy is released as heat when the anode and cathode are in close proximity. Therefore, the electrodes must be separated in such a way that electrons can flow from the anode to the cathode through an external load while still being in some sort of contact to enable the reaction to happen in order to take advantage of the available electrical energy [38]. To accomplish this, an electrolyte is used to separate the anode and cathode (substance that contains ions) [39]. The electrolyte contains ions but does not conduct electricity; as a result, preventing short circuiting between the anode and cathode.

Wastewater microorganisms oxidize biodegradable substrates to produce protons and electrons in the anode chamber, which are used to break down organic materials [40]. Cytochromes or redox-active proteins convey and collect the electrons produced by the metabolic activity of microbes on the anode's electrode surface before passing them to the cathode, where they interact with the electronic acceptor (for example, oxygen), through the electrical circuit (copper wire) [41]. Protons are transferred internally through the membrane at the cathode at the same time, forming a water molecule. An electrical potential difference is produced due to the difference in solution concentrations between the anode and cathode [42]. The difference in solution concentrations between the anode and the cathode results in a difference in electrical potential. The movement of electrons across the external electric circuit produces electrical power. In the cathode chamber, electrons combine with protons and oxygen to form an electron acceptor (such as oxygen or ferricyanide), which is subsequently reduced to produce water molecules amongst other possible outcomes [43].

Operation of MFC depends on factors such as pH, electrical resistance; the electrolyte used and dissolved Oxygen (DO) concentrations in the cathode [44,45]. Operation of MFCs in the absence of a separator results in decreased coulombic efficiency due to increased oxygen diffusion and substrate crossover [46]. At the anode, bacteria oxidise organic matter resulting in a loss of electrons and H^+ ions move through the PEM/separator into the cathode [37]. The protons passing through PEM/separator and electrons passing through the circuit then combine at the cathode in the presence of oxygen, thus, completing the circuit [25,47].

Microbial fuel cell components

The anode

The anode must have high compatibility, electronic conductivity, volumetric surface area and should be chemically stable to prevent corrosion and biofouling [48]. Biofouling results in reduced performance resulting in ineffective treatment of wastewater. A variety of materials can be used as anodes in MFCs but they each have their pros and cons. Metal anodes have been previously used because of chemical stability against bio corrosion and cost-effectiveness [49]; however, metals have low porosity levels and do not favour biofilm attachment. Thus, carbon based materials such as carbon cloths, fibers, papers and graphite fibers and brushes are used because of their high conductivity and stability and relatively low cost [50]. Anode materials play a pivotal role in influencing power generation by determining the actual accessible area for bacteria to adhere, electron transfer efficiencies and diffusion rates of metabolic byproducts [51]. The anode is responsible for bacterial growth, removal rate, electron generation, and the transformation to a cathode. That being said, the anode surface area should be rough to offer more bacterial adhesion at the anode so as to efficiently treat wastewater and electricity generation [52].

According to Yaqoob, et al. [52], carbon cloth is the mostly used carbon material. Carbon cloth has a large surface area but is chemically unstable causing fouling thereby reducing long-term stability of the anode electrode. Carbon mesh has reasonable cost and its open structure reduces biofouling [53]; however, it has low electrical conductivity and poor chemical stability which results in reduced MFC performance. Granular activated carbon is biocompatible and cost effective but it has a low electrical conductivity due to high porosity. This limits electron flow due to empty spaces present in the anode material and reduce electrochemical performance by reducing current output to enhance the bio-filtration process. Graphite based anodes have good biocompatibility, mechanical strength and a reasonable surface area which results in improved performance due to increased organic matter breakdown by bacteria at the anode. Rough graphite offers reasonable results in energy generation and pollutant removal efficiency [54]. However, they are costly and offer low conductivity and hence they have limited use in both single and double chamber MFCs.

Metal or metal oxide based anodes offer high electrical conductivity than carbon based materials because they can facilitate effective electron flow [55]. For example, Yamashita and Yokoyama [49] discovered that, a Molybdenum anode achieved a power density of 1296 mW/m². However, metal-based anodes are prone to corrosion in the long-term run, they do not have effective bacterial adhesion and are costly. Natural waste derived anodes are economically affordable, stable, they use recyclable materials (biomass waste), and they also offer good electrical conductivity [56]. Examples of natural waste derived anodes include fruit peels, shells and coffee wastes [56], biochar from sewage sludge [57] and wood [58]. Hung, et al. [59], studied renewable coffee water-based porous carbonized materials for anode and the MFC achieved power density of 3927 mW/m². Although this process is effective, much time is required to change waste materials into valuable materials to develop electrodes [60]. On a global scale, carbon based materials are mostly used as anode materials.

The cathode

The cathode is costly and challenging to design and maintain and has proven limiting in most MFC designs [61]. The cathode is regarded as a major performance limiting component for MFCs because it is the site for oxygen reduction reactions [62]. Thus, if the reaction does not take place power will not be produced. Efficient cathodes have a large active surface area and great catalytic capabilities for reduction reactions [63]. An MFC cathode can be made of biocatalysts (enzymes or microbes) for the oxygen reduction reaction, abiotic catalysts (carbonaceous materials such as activated carbon, carbon nanotubes and graphene) (Yuan, Hou et al. 2016). The air cathode is the most feasible cathode configuration because it increases oxygen acceptor surface area that greatly reduces energy consumption for wastewater treatment [64]. Platinum-based cathodes were previously used for their favourable reduction potential and outstanding electro catalytic activity but are being slowly dismissed due to high costs that proves to be a challenge when scaling up the MFCs for high end industrial purposes [65–67].

Carbon based materials are cost efficient, durable, stable and have a high surface area [65,67]. For example, carbon black and activated carbon have high surface area, excellent electron conductivity and they are cost effective. However, they have low catalytic ability. Graphene also has a large surface area, high conductivity and mechanical strength, but, it is expensive to manufacture [66]. Metals and metal based ORR catalysts can also be used as MFC cathodes. Metal oxides have high-cost effectiveness, environmentally friendly, simple preparation process and superior ORR electrocatalytic efficiency and excellent physiochemical properties. However, they offer poor electrical conductivity and high over potentials [68]. Biocatalysts e.g., microorganisms and enzymes are cheap, sustainable and resistant to biofouling. However, they are affected by an increase in pH, long term operation suffers from stability of the microbial community and biocatalysts may exhibit significantly lower ORR activity [66,68]. Overall, the cathode materials mostly used

on a global are platinum and carbon based materials. As previously mentioned platinum is expensive hence the need to come up with cost effective materials to use as MFC cathodes.

The membrane/separator

MFC membranes/separators allow the transport of protons and other cations to the cathode whilst avoiding the transfer of bacteria into the cathode and the transfer of oxygen from the cathode into the anode chamber [45,69,70]. Membranes are essential to ensure an efficient and stable operation of MFCs [71]. A good MFC membrane should be inexpensive, have low ionic resistance to make proton migration from the anode to the cathode easier, a non-porous microstructure to prevent oxygen transport and substrate crossover, and excellent biofouling resistance to preserve the membrane [72]. Drawbacks of separators include high internal resistance, biofouling, pH splitting, oxygen diffusion and substrate loss across the membrane [72]. These challenges result in high maintenance costs due to the need for frequent cleaning [73].

Separators are essential in the functioning of configurations with a small electrode spacing (such as flat-plate designs), however, they are optional in the case of large electrode spacing configurations [74]. Membranes include cation exchange membranes (CEM) for example Nafion [69], anion exchange membranes, nylon fibres, glass fibres, ceramics and natural rubber [75]. The proton exchange membrane is at times referred to as CEM because it allows the transfer of other cations such as Na^+ and NH_4^+ apart from the protons. This competition therefore inhibits proton transfer to the cathode inhibiting performance [44]. Nafion provides great performance for MFCs, however, it is expensive up to \$1400/m² (Roy, Marzorati et al. 2017). Sulphonated biochar PEM is affordable and its negative surface prevents biofouling on the membrane surface making it a suitable alternative [67].

A salt bridge is an economic alternative to highly priced proton exchange membranes in the construction of MFCs. It also acts as proton transfer channel from the anode to the cathode. However, it results in high internal resistance [76]. According to Mohamed, et al. [77], carbon membranes exhibit a higher performance than anion membranes due to their fast proton transfer and low resistance. Though ceramic separators have excellent applicability due to their high physical strength, rigid nature, low cost and the ability to withstand extreme conditions of alkalinity and acidity; however, they have increased internal resistance with long term operation [78,79]. An anion exchange membrane has high anion conductivity, however, it has relatively high ohmic resistance and biofilm growth during long term operation [80]. Glass fibres have high level of proton and low oxygen transfer and produces low ohmic resistance, however, they are non-biodegradable which might be an environmental risk [81]. Non-woven fabrics of polypropylene offer high power density, high proton diffusion, applicable for large scale and affordable material cost [46].

Microbes

In the anode chamber, microbes anaerobically oxidise organic matter in wastewater releasing protons, electrons and carbon dioxide. The protons pass through the anode chamber to the cathode chamber via the PEM, while electrons pass through the external circuit [82]. Microbes oxidise organic matter in wastewater producing electrons which are transported to the anode and protons to the solution [25]. In the biofilm, electrons are transferred through mediators, direct contact and/or nanowires produced by bacteria [25]. Microbes such as *Rhodospirillum rubrum*, *Geobacter sulfurreducens* and *Shewanella putrefaciens* do not require mediators, unlike *Saccharomyces cerevisiae* and *Escherichia coli* require mediators for electron transfer [81,83,84].

In direct electron transfer, metal reducing bacteria such as *Geobacter sulfurreducens*, *Rhodospirillum rubrum* and *Shewanella putrefaciens* use insoluble electron acceptors such as Fe (III) Oxide to transfer electrons to the external circuit, whilst mediator electronic transfer is facilitated by redox mediators. Different substrates influence the type of bacteria

which in turn affects performance [85], thus, a mixture of bio-waste can result in more electricity generation [86]. Bacteria can survive under extreme conditions of pH, temperature and salinity [87]. Bacteria are self-replicating, thus, can be able to sustain MFCs. Microbes can be present as single and mixed cultures. Mixed cultures produce more power as opposed to single cultures due to the diversity of the bacteria in the solution. Examples of microbes found in wastewater include *Clostridium*, *Geobacter*, and *Shewanella* [45].

Mixed cultures have nutrient adaptability, stress resistance, they are readily available in the environment and offer the best performance, whilst, pure cultures produce low power generation than that of mixed cultures [81,84,88]. *Geobacter sulfurreducens* is the predominant genus on the anode with good power generation and high coulombic efficiency. However, it is not suitable for actual application in the environment because of its limited metabolic diversity and flexibility [83,84,89]. *E. coli* is highly abundant in wastewater but it requires mediators and produces current after long acclimation times [81,90].

Wastewater type

Wastewater is the main substrate in microbial fuel cells and it provides both microbes and organic matter required for giving off electrons. The most dominant pollutants in municipal/domestic wastewater are organic matter, microbes, BOD, different hydrocarbons including pharmaceuticals and detergents, suspended solid, range of heavy metals and coliforms [2]. These pollutants can be used in electricity generation, however, municipal wastewater has lower BOD concentrations yielding low energy densities and it is difficult to maintain stable power production [91–93]. Industrial wastewater constitutes wastewater from industrial processing plants such as petrochemical, coffee processing, acid mine drainage, tannery effluent, milk parlour, slaughter house, steel making, pulp and paper, oil field, floriculture, textile and agro-food wastewaters. The main characteristics of industrial effluent are its high organic load and COD, high acidity or alkalinity, colour, turbidity, nutrient load, TSS, salts, colloids and specific toxic contaminants [2]. Industrial wastewater is high strength wastewater but may lack microbes depending on the type of effluent. For example, there are challenges in finding appropriate bacterial community that is capable of utilizing the mixture of dyes in dye wastewater [91,94]. Agricultural wastewater from different farming operations produces effluent streams that require prior treatment before being discharged to environment. Pollutants in agricultural wastewater include organic and biodegradable load, excess concentrations of nutrients and some pesticides and herbicides [2]. Agricultural wastewater is high strength wastewater, it has better efficiency because of methanogenic inhibitors and natural presence of electron transferring mediators e.g., lignin. However, other agricultural wastewater types such as swine wastewater produce volatile acids produced during fermentation of substrates [92,95,96]. Synthetic wastewater is easy to control in terms of loading strength, pH and conductivity [94].

MFC system modifications for higher power generation

The selection of material to be used as electrode is crucial for power generation in an MFC with regards to electron transfer, electrochemical properties and microbial adhesion. Material cost must be reduced and power densities maximized for MFCs to be applied in the field. Despite the differences in the criteria for material selection for anode and cathode, both should have high surface area, electrochemical properties, material stability and cost effectiveness and biocompatibility [97,98]. Increasing the effective surface area reduces internal resistance and enhances electrode kinetics by providing more reactions sites. High electrical conductivity and low interfacial impedance, facilitates effective flow of electrons through the circuit. The electrode material should be stable and durable in order to provide long term performance with minimum fouling or degradation. Moreover, electrode material should be cost effective, accessible and sustainable, for economic viability of the

technology at large scale [98]. Anode materials should be highly biocompatible to enable efficient biofilm formation by bacterial adhesion thereby increasing overall MFC performance [98]. The anode material should also be environmentally friendly in order to minimize the

carbon footprint during its production.

Anode modification carbon nanotube (CNTs) and conductive polymers (CPs) provide a large specific surface area, extremely high conductivity, mechanical flexibility, reduced cellular toxicity and improved

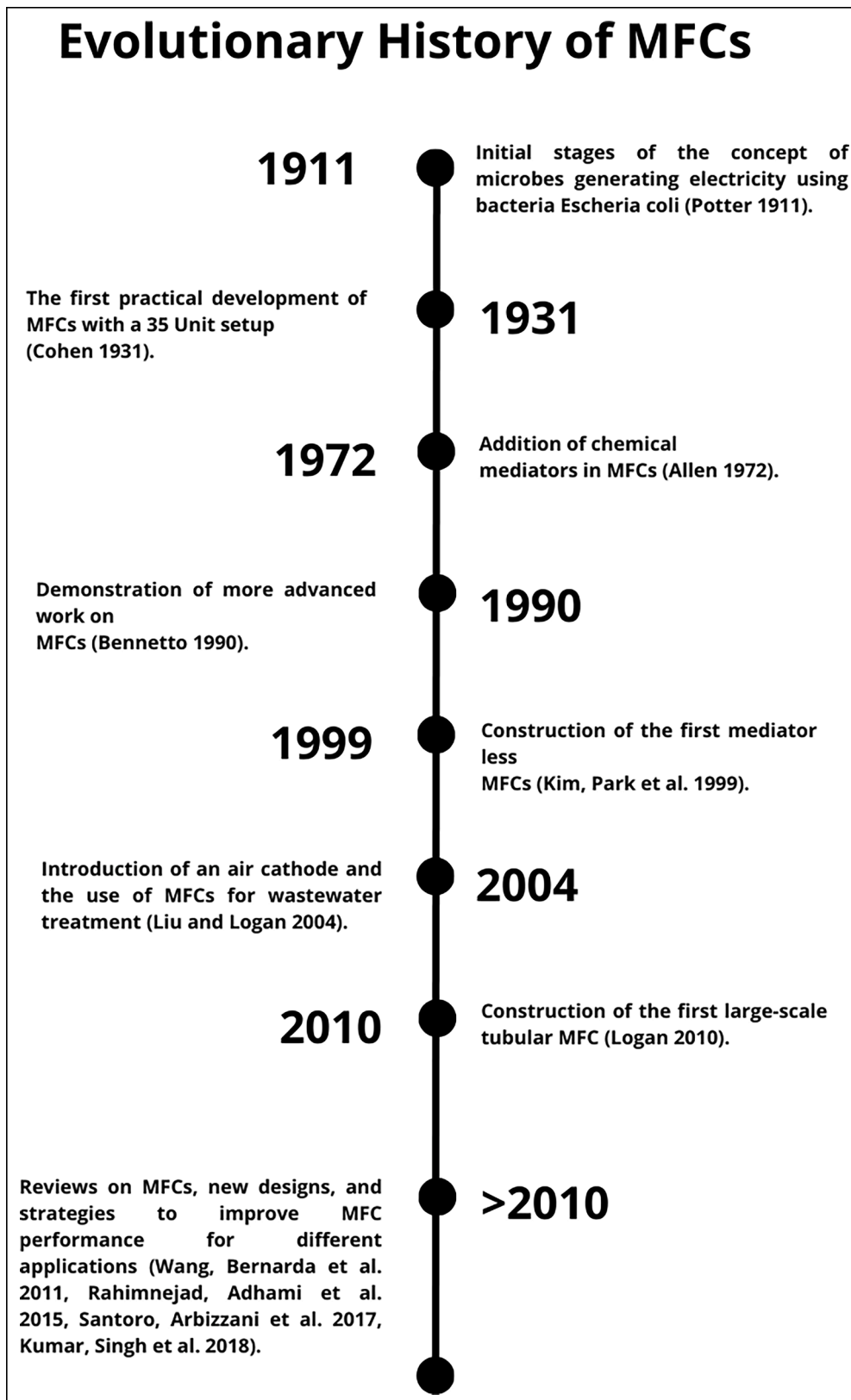


Fig. 2. Evolutionary history of Microbial fuel cells.

electrocatalytic activity [97,99]. Graphene modified electrodes also offer large specific surface area, high electronic conductivity and good biocompatibility [100]. Modification using metal or metal oxides provide a high rate of redox reaction and electrical conductivity [56]. However, metals are costly making them a poor alternative especially if scaling up is to be considered. Metal oxides for example, MnO_2 , FeO_2 and Fe_2O_3 have structural stability, they are cost effective, nontoxic and good biocompatibility [97]. Electrodes can also be modified by using natural materials such as biomass wastes. This is an advantage because the electrodes are made from recyclable materials, they are readily available and stable, cost-effective and eco-friendly nature [56]. Microbial bio-cathodes can act as modified cathodes. They use microorganisms as the electrocatalytic agents for oxygen reduction reactions. Bio-cathodes have many advantages such as self-regeneration; low cost; sustainability and great activity at neutral pH. However, bio-cathodes have disadvantages such as low power generation and

dependency of the performance on an illumination [99]. The use of waste materials to construct modified electrodes for MFCs would be more significant and interesting in terms of cost efficiency and sustainability.

Evolutionary history of MFCs

MFC technology has evolved over many years (see Fig. 2) with the first experimental realisation of electricity generation by bacteria in 1911 [101]. Subsequent research focused on the practical use of MFCs, however, these required the use of mediators [35,102]. These mediators MFCs were toxic (causing fouling) which then resulted in the construction of the first mediator less MFCs in 1999 [103]. To further improve the performance of the MFCs, there was the introduction of new designs/prototypes and the use of MFCs in treating real wastewater [61, 104]. From 2010 to date, a considerable amount of literature has been

Table 1

Examples of microbial fuel cell prototypes, materials used, type of wastewater, power produced and wastewater treatment efficiency.

MFC Type	Anode Material	Cathode Material	Membrane/ separator	Type of wastewater	Electricity generation	Pollutant removal	Reference
Single chamber MFC	Graphite fibre brush	Binder-free coating of N, P co-doped carbon ORR catalyst onto a graphite fibre brush current collector rotating three-dimensional air-cathode	Anion exchange membrane	50 mM phosphate buffer solution with pH 7.0 was used as an electrolyte solution	879 ± 16 mW/m ²	-	[62]
Two chambered MFC	Carbon brush	Carbon cloth with gas diffusion layers	Anion exchange membrane	Sludge with anolyte	4.25 W/m ²	silver metal recovery efficiencies as high as $99.91 \pm 0.00\%$	[107]
Dynamic membrane MFC	Tubular shape carbon felt	Activated carbon fibre felts connected to the circuit by graphite rods	Nylon mesh used as a dynamic membrane supporting layer connected to the circuit by graphite rods	Inoculated using granular anaerobic wastewater sludge, fed a synthetic medium containing glucose, NaHCO_3 , NH_4Cl , NaH_2PO_4 , and NaCl	1923 mW/m ³	-	[80]
Stack of 12 vertically arranged constructed wetlands coupled with MFCs	Granular graphite layer with a rectangular graphite rod as current collector	Granular graphite layer with a rectangular graphite rod as discharging of electrons	-	Synthetic wastewater (grey water)	30.85 mW/m ³	$\text{NH}_4\text{-N}$ 90.4%, $\text{NO}_3\text{-N}$ 86.9% COD 98.5%	[109]
Single chamber MFCs	Graphite fibre brushes	Fe-N-C catalyst on AC with stainless steel mesh current collector	Hydrophobic PVDF membrane diffusion layer	Sodium acetate dissolved in a 50 mM phosphate buffer solution amended with 12.5 mL L^{-1} minerals and 5 mL L^{-1} vitamins	2.4 ± 0.1 W/m ²	-	[114]
Two chambered MFC	Platinum rod	Platinum rod	PEM made from sulphonated biochar	Synthetic wastewater with sucrose as a carbon source	0.278 Wl ⁻¹	-	[115]
Single chamber MFC	Graphite fibres distributed along two twisted wires of titanium	Graphite paper	Membraneless	20% of municipal wastewater and 80% of a synthetic solution containing sodium acetate as the source of carbon	9.2 mW/m ²	80% organic matter degradation	[111]
Air cathode microbial fuel cells	Carbon felt	Carbon cloth with a diffusive layer	Proton exchange membrane	sodium acetate, phosphate buffer solution, vitamins and trace minerals	458.85 mW/m ³	-	[116]
Earthen pot MFCs	Stainless steel mesh	Graphite plate	Earthen pot acted as PEM	Synthetic wastewater with sucrose as carbon source Inoculated with anaerobic sludge	24.32 mW/m ²	-	[113]
Double chamber microbial fuel cells	Zinc	Copper	Proton exchange membrane (salt bridge)	Organic waste of avocado	566.80 ± 13.48 mW/cm ²	-	[117]
H type double chamber MFC	Anode enriched with microorganisms	-	Nafion 117 membrane	Whey	1800 ± 120 W/m ²	90 days (92.8% tCOD)	[118]

published on MFC operation, design and performance. However, the application of MFC in real-world systems and scaling up still remains a challenge with most studies being laboratory based. It would be interesting to assess the functioning of MFCs in real systems.

Microbial fuel cells (MFCs) prototypes

Several MFC prototypes have been proposed in an attempt to efficiently treat wastewater and increase their power output. The studies are also focused on developing cost effective yet high performing MFCs with potential for scalability. Some of the prototypes are shown in Table 1. According to Aziz, et al. [105], the two chambered H-shape with a proton exchange membrane is mostly used. Nevertheless, single chambered MFC are mostly being used because of their reduced internal resistance, cutting membrane/separator costs and direct diffusion of air to the cathode [106]. A rotating graphite fibre brush air cathode was tested against a non-rotating static air cathode and produced a power output of $879 \pm 16 \text{ mW/m}^2$ and $486 \pm 11 \text{ mW/m}^2$. Rotating cathode increased catalytic sites for oxygen reduction reaction and improved oxygen diffusion. This therefore increases performance, simplifies reactor design and allows it to be integrated into existing wastewater treatment facilities [62]. Chen, et al. [62] suggested a passive rotation of the air-cathode purely by wastewater movement. However, wastewater movement might not have much power to propel the movement of the cathode efficiently enough to cause a reaction.

A cost-effective microbial fuel cell (MFC) system was developed in order to recover silver metal from silver ion containing wastewaters. Maximum power density was 4 W/m^2 [107]. Graphene; a building block of graphite attracted a lot of attention in 2004 due to its extraordinary properties of increased surface area, high conductivity and mechanical strength and low cost resources [108]. It shuttles current at high rates than carbon nanotubes. However, scalable industrial production of graphene remains a challenge since graphene materials are prepared by sophisticated laboratory scale synthesis techniques [108]. This really negatively affects Sub Saharan African countries as some lack such sophisticated equipment to produce the material.

Tamta, et al. [109], designed a new MFC system made up of a stack of 12 vertically arranged constructed wetlands coupled with MFCs. The COD removal increased gradually with decreasing external resistance reaching 98.5% at 0.08Ω , $\text{NH}_4\text{-N}$ removal efficiency was 90.4% at $15 \text{ k}\Omega$ and 86.9% for $\text{NO}_3\text{-N}$ at $0.08 \text{ k}\Omega$. The maximum power density for the system reached was 30.85 mW/m^3 at $15 \text{ k}\Omega$. The advantage of this setup is, through the coupling of the two methods of wastewater treatment, there was a combination of their benefits such as low cost of construction, lesser land footprint, operation, wastewater treatment and electricity generation and maintenance. Through the study, it was also discovered that a low external resistance results in the growth and metabolism of microorganisms and nutrient removal. However, even with the integration of the methods (constructed wetlands and MFCs) and stacking; electricity generation still remained quite low. Microalgae based MFCs are an efficient system for removing nitrogen, phosphorus and carbon dioxide from wastewater and bioelectricity production. However, its challenge is in oxygen cross over [110]. There is therefore need to select algal strains that are suitable for use in both the anode and cathode compartments.

Buitrón and Cervantes-Astorga [111]; tested a low-cost single chamber MFC with a graphite cathode catalyst. It generated a power density of 9.2 mW/m^2 and degraded 80% of fed organic matter ($367 \text{ mgO}_2\text{L}^{-1}$) with an internal resistance of 8.530Ω . This MFC produced 1.52 times more power density than the platinum catalysed cell. Zhang, et al. [112]; designed a flexible and low cost polypyrrole nanotubes membrane as an anode for electricity generation in MFC. It had a high surface area improving bacteria interaction at the anode. The polypyrrole MFC had a maximum power density of 612 mW/m^2 . Behera and Ghangrekar [113], constructed earthen pot MFCs with the pot as the anode chamber. From synthetic wastewater, a power density of 24.32

mW/m^2 was achieved using a 3 cm wall thickness MFC. Though a low cost MFC was able to outperform the platinum catalysed cell, its power output was still quite low. Most of the MFC prototypes have different configurations, use different materials and operate under different operational parameters making it difficult to compare them. Moreso, some of the experiments did not use real wastewater as the substrate which makes it difficult to conclude whether they will be efficient in treating wastewater or not.

Drivers and barriers for the uptake of MFCs in the world and Africa

Drivers for the uptake of MFCs in the world and Africa

Wastewater treatment

MFCs are capable of nutrient removal of high strength wastewaters making it a great competitor against other WWTS [91]. Microbial fuel cells are also efficient in heavy metal removal, thus can help solve the issue of biomagnification and bioaccumulation in waters that receive treated water using other sources of wastewater treatment [119]. Microbial fuel cells are adaptable to decentralised wastewater treatment making them applicable to any area even those that lack electricity [120]. The treatment process results in the production of lower sludge volumes reducing sludge handling costs. Microorganisms present in the wastewater can self-generate meaning there is no need to periodically place bacteria in the MFCs [121].

Electricity generation

Coupled with WWT, MFCs produce electricity. MFCs utilise waste as fuel and have low chemical requirements thus making them cost effective once operation commences [122]. Wastewater contains more energy than the energy used to treat it. This energy is therefore converted to electricity during the breakdown of organic matter by bacteria. The process operates at ambient temperatures and does not require energy for aeration [30].

Climate smart and environmentally friendly

The MFC WWT process has a low carbon footprint making it a very sustainable and environmentally friendly solution. The treated wastewater/effluent can be used for water reclamation especially in areas where water scarcity is a problem [123], for example irrigation, recreational activities, industrial and urban reuse. The drivers and barriers for the uptake of MFCs are highlighted in Fig. 3.

Barriers and contextual issues in the uptake and use of MFCs in Africa

High cost

Like any technology, microbial fuel cells come with their share of challenges. Reducing material costs remains a challenge in microbial fuel cell construction [28]. Most materials used in MFC construction such as Nafion membranes and platinum electrodes are expensive [92, 124–127]. Additionally, the electrodes and PEM need be replaced every five years of MFC operation, adding a total extended maintenance cost to the already expensive reducing materials [45]. If the capital costs of MFCs outweigh those of conventional activated sludge, conventional activated sludge might as well remain in use more so for impoverished developing countries in Africa.

Unstable performance

Another disadvantage of MFC is that it has a low energy harvesting efficiency whilst treating real wastewater and has unstable performance long-term (anode and membrane biofouling) [128]. Microbial fuel cells have low pollutant degradation rates and poor performance with actual wastewater in real systems [91], thus making them an inefficient wastewater treatment system. They have long hydraulic retention times meaning that larger reactor volumes are required which add to the

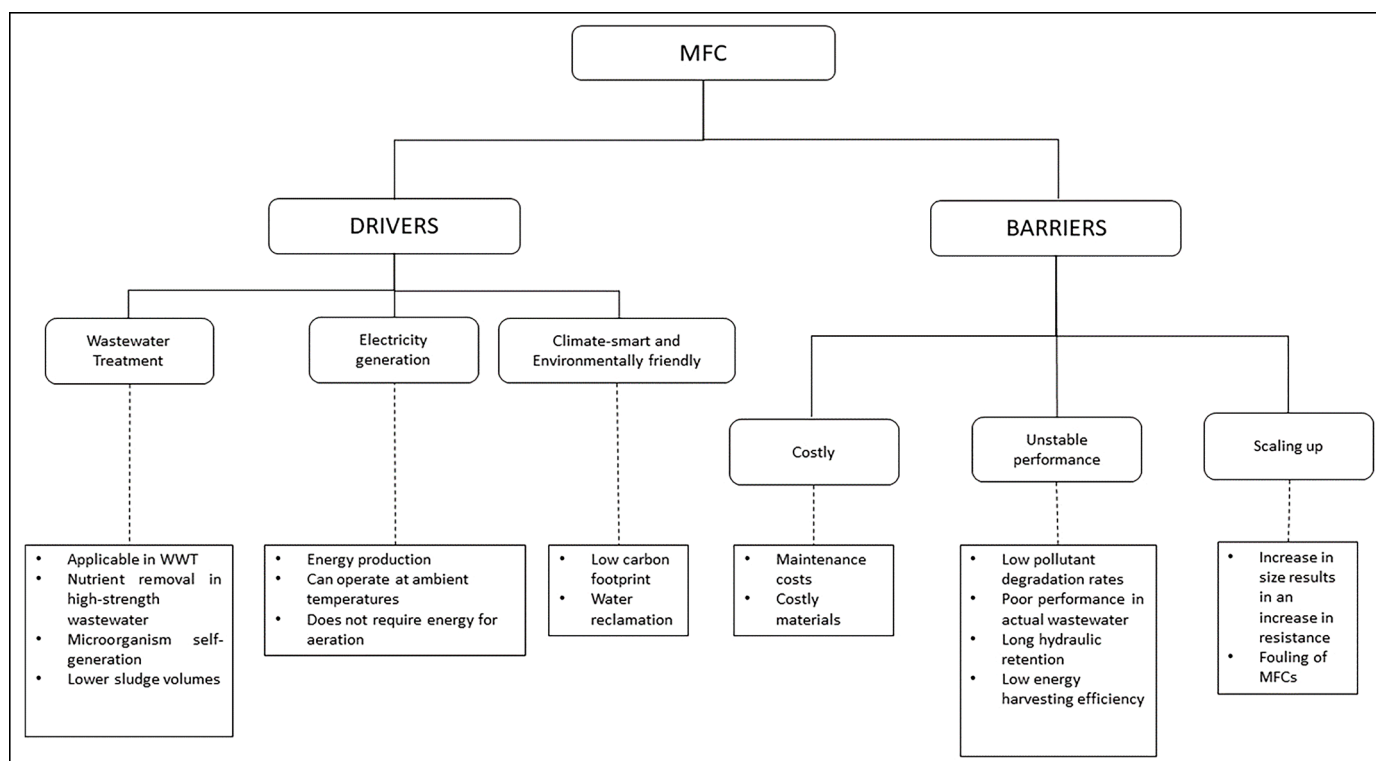


Fig. 3. Drivers and barriers for MFC uptake of MFCs.

capital and maintenance costs [91]. It is also unclear if the MFC WWT process can remove impurities such as grease and microplastics in wastewater. This therefore becomes a limiting factor in implementing MFCs in impoverished countries such as Zimbabwe. Most MFC studies focus on power generation rather than the actual treatment of wastewater making it difficult to conclude on whether MFCs are efficient at pollution reduction at a broader scale.

Scaling up

Scaling up of MFC technology remains a challenge especially in the selection of materials, such as separators and electrodes. During MFC operation electrode poisoning during wastewater treatment, pH alleviation in the anode and cathode chambers, aeration for catholyte reduction, and nitrogen purging for maintaining a large anaerobic system still remain a challenge [129]. Increasing MFC size directly causes increased electrode distance resulting in high internal resistance ultimately leading to decreased power output [44]. Miniaturisation of MFC when scaling up is therefore advantageous as it allows high surface area to volume ratio, short electrode distance and fast response time thus producing better performance than macro sized MFCs [51]. However, miniaturisation may not really make sense when treating large volumes of wastewater as it might prove to be costly, it can take up space and the time for wastewater treatment becomes prolonged. Consequently, if MFCs are to be applied in real settings, future studies should emphasize on increasing MFC size without affecting its performance.

Microbial fuel cells in Africa

According to Striebig [130], many developing countries in Africa, Latin America and parts of Asia have unreliable electrical sources and little access to clean water. Thus, MFCs can be an effective technology in providing even low power electricity to charge phones and power light emitting diode (LED) lights. Microbial fuel cells are still in their infant stages in developing countries due to complexities of simplifying the design and cost of materials [131]. According to Ash, et al. [132] MFCs can be used to generate electricity for low power devices such as LED

bulbs to be used in emergency cases particularly in Africa where the majority of the people have no access to electricity.

Though South Africa has large coal reserves, it has recognised the need to diversify its energy mix [133]. This need for diversification is also now being realised by other countries due to the ever-increasing demand for energy in their countries. A study by Stafford, et al. [134] in South Africa evaluated the applicability of various technologies for energy recovery from wastewater. Microbial fuel cells were found to be suitable for use with low concentration organics in wastewater and its direct conversion to electricity. However, MFCs were found to be capital intensive, with a wide variability of COD removal in terms of wastewater type and the fact that it is still in its developmental stages presents a high-risk investment opportunity that can only be realised with the aid of high capital from governments and other interested parties. At present, this appears to be a far-fetched aim for highly impoverished African countries grappling with provision of basic human needs such as clean water, health, shelter and food.

In Tanzania, MFCs were used as biosensors in the monitoring of faecal pollution in groundwater. Microbial fuel sensors provided low cost and low maintenance whilst ensuring ground water quality [135]. However, this study focused mostly on environmental remediation and less on the electricity generation capacity of the MFC. Another study by [136], focused on the feasibility of MFCs in Tanzania through technical analysis and interviews with Tanzanian locals for cultural feasibility. The MFC operated with diluted manure and achieved a power density of 16.1 mW/m² and a 93% reduction in faecal coliforms. From the interviews, the locals seemed interested in the new technology provided it was safe and clean.

Microbial fuel cells in Zimbabwe

In Zimbabwe, there is little and/or anecdotal information on the use of Microbial fuel cells for wastewater treatment and electricity generation. This is a huge gap warranting studies on microbial fuel cells in the country. From the few available literature, it appears MFCs adoption in Zimbabwe and Africa is moving at a very slow pace requiring the need

for more research that focuses on low-cost fabrication of MFCs such that they can be implemented by low-income communities in Zimbabwe. Major challenges remain in meeting SDG 6 Clean Water and Sanitation and SDG 7 Affordable and Clean Energy [137]. Therefore, the use of MFCs in Zimbabwe is timely and necessary in order to meet the country's Vision 2030 and Sustainable Development Goals (SDGs). The MFCs will result in improved sanitation through the treatment of wastewater and affordable and clean energy through the generation of electricity. Though the power generated from MFCs is quite low, it can be used for lighting and charging phones since the country is facing huge power cuts due to load shedding.

The economic state of Zimbabwe is a big setback in the development of MFCs in the country. Using the international poverty line at USD \$1.90 per person per day, Zimbabwe ranks as 150 over 189 countries [138]. Thus, if the capital costs of MFCs outweigh the operation and maintenance of conventional wastewater treatment systems; conventional wastewater treatment systems might as well remain in use. If MFCs are to be implemented in Zimbabwe, there is definitely need to use cost effective yet efficient materials which can be accessible even to low income households. This is to ensure that there is country wide access to the technology even using the simplest designs and materials. From the review, it is clear that carbon based materials, natural waste derived materials (biochar), biocatalysts and ceramics offer cheap alternatives to the otherwise expensive materials whilst producing favourable power and efficient wastewater treatment. Future studies should therefore focus on modifying these low cost materials to produce higher power generation coupled with efficient wastewater treatment.

Conclusion, contemporary paradigms and recommendations for the future of MFCs

This scoping literature review though not exhaustive aimed to: (a) Examine the concept design and operational efficacy of microbial fuel cells (MFCs), (b) Examine the MFC operational system (c) Outline in brief the evolutionary history and assess the existent prototypes and (d) Establish the drivers and barriers for the uptake of microbial fuel cells (MFCs) from a global and local, Zimbabwe, context. For the existent MFC prototypes our literature examination reflected that most anodes and cathodes are made from carbonaceous material, the separators used are mainly made from Nafion and SMFC and DCMFC are the mostly used designs. Scoping through the evolutionary history of the development of the MFCs from the initial prototype by Potter in 1911 and first practical development by Cohen in 1931 most studies on MFCs were reported/published from 2004 to date. Assessment of the operational efficacy of the existent MFC prototypes indicated that although MFCs can generate electricity and treat wastewater, the power generated is very low and the treatment system is not applicable in real world settings mainly due to their small sizes and materials used. From the available literature on MFCs it appears the main drivers for the uptake of this technology, mostly for affluent developed nations, comprise the ability to simultaneously treat wastewater and generate electricity, heavy metal removal, lower sludge volumes and low carbon footprint. This simply stems from their ability to afford the high-cost anodes/cathodes. This is however, a challenge for African countries including Zimbabwe as they cannot afford these materials and the MFCs require high maintenance costs.

If MFCs are to be implemented in Zimbabwe, there is definitely need to use cost effective but efficient materials which can be accessible even to low income households. Carbon based materials, natural waste derived materials, biocatalysts and ceramics can be implemented in MFCs in Zimbabwe due to their cost effectiveness whilst producing favourable power and efficient wastewater treatment. For future studies and practical uptake of MFCs it is recommended that low-cost materials that ensure maximum power generation and efficient wastewater treatment are to be investigated before they are to be adopted in Zimbabwe. Further research should also be done to investigate the large-scale use of MFCs in real wastewater systems. MFC experiments should

also compare different MFC configurations under the same conditions so as to not have biased results. From this review, it is clear that MFCs cannot be used in isolation; hence, they should be integrated with other existing sustainable wastewater treatment systems and renewable sources of electricity generation.

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

Data will be made available on request.

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