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MINI-REVIEW

Gaseous pollutant treatment and electricity generation in microbial fuel cells (MFCs) utilising redox mediators

Evelyn · Yan Li · Aaron Marshall · Peter A. Gostomski

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Abstract Microbial fuel cell (MFC) is an emerging technology for sustainable energy generation and waste treatment. This paper reviews the potential of a gaseous substrate when it is combined with a mediator in an MFC to generate electricity and to treat toxic gaseous pollutants. Most MFCs for waste water treatment often cannot use mediator to enhance the electron transfer from the microbe to the anode because of the difficulty in recovering the expensive and potentially toxic compound. Combining gas feeds with mediators is possible since the soluble mediator would remain in the anode chamber as the gas passes through the reactor. In addition, this type of MFC is possible to be integrated into an anaerobic biofiltration system (BF-MFC), where the biofilter removes the gaseous contaminant and produces the reduced mediator and the MFC produces the electricity and recycles the reoxidised mediator. This paper also talks about the past research on gaseous feed MFCs, and reviews the mechanism and strategies of electron transfer in MFC using redox mediator. The advantages, process parameters and challenges of BF-MFC are discussed. This knowledge is very much required in the design and scale up of BF-MFC. This paper will be useful for those who work in the area of gaseous pollutant treatment and electricity generation.

Keywords Gaseous substrate · Mediator · Microbial fuel cell · Biofilter

List of symbols

k_0	Vibration frequency of motion of the nuclei (10^{13}/s)
β	Distance decay constant ($Å^{-1}$)
d	Interatomic distance between donor and acceptor (Å)
d_o	Close contact distance (a value of 3 Å)
λ	Marcus reorganisation energy (eV)
ΔG^0	Standard free energy change for the reaction (eV)
R	Gas constant
T	Absolute temperature (K)
S	Substrate/gaseous pollutant
RM_{ox}	Oxidised mediator
RM_{red}	Reduced mediator

1 Introduction

Global energy supply security and the need for generating efficient and clean energy have increased the interest in research related to alternative fuel and

Evelyn (✉)
Department of Chemical Engineering, University of Riau, Pekanbaru 28293, Indonesia
e-mail: eev12@uclive.ac.nz

Evelyn · Y. Li · A. Marshall · P. A. Gostomski
Department of Chemical and Process Engineering, University of Canterbury, Private Bag 4800, Christchurch 8041, New Zealand

energy systems. Among these alternative systems, microbial fuel cell (MFC) technology has been identified as one of the key energy technologies for the future since it can make electricity using any biodegradable materials, and it can also be modified to produce hydrogen, methane, hydrogen peroxide, and various chemicals such as acetate, glutamate, propionate and butanol (commonly referred as microbial electrolysis cells or MECs) (Bruce and Rabaey 2012). During a decade of MFC research, a considerable amount of publications have been produced and around forty patents have been registered (Yang et al. 2011). The maximum power densities reported using air-based cathode have reached over 1.0 kW/m^3 (reactor volume) or 2.77 W/m^2 (anode area) under optimum conditions, although these values are still lower than those produced by hydrogen fuel cells (Bruce and Rabaey 2012).

In microbial fuel cell, power generation in the form of electric current is created when electrons flow from the anode to the cathode. The current produced is calculated by measuring the voltage using a voltmeter or a potentiostat (Huang et al. 2013). The electrons in the anode are resulted from microbial utilisation of substrates under anaerobic conditions, and these electrons flow from the microbes to the anode surface whether directly or via a redox mediator (Fig. 1). Protons (which are also generated from the metabolism) diffuse through the solutions in the anode, and penetrate through a proton exchange membrane (PEM) to the cathode where they are combined with electrons and oxygen (widely accepted electron acceptor) to form water (Yang et al. 2011).

Biodegradable substrate (or electron donor) plays a vital role determining electricity generation in the MFC (Liu et al. 2009). Various organic and inorganic substrates, mostly in the form of liquid or particulate/solid have been added to MFCs, and these also have been well reviewed in the literature (Pant et al. 2010). These substrates ranging from a simple and easily biodegradable compounds such as acetate and glucose to complex organic compounds contained in municipal and industrial wastewater, or in marine sediment (Fornero et al. 2010). The power produced by MFCs may vary, depending on the availability of the substrate and the capability of microorganisms to metabolize the substrate. However, it is also affected by many components involved in the MFC i.e. the anode, the cathode, the electrolyte, and the ion-exchange membrane (if used). Moreover, there are various influential factors to the performance of MFC such as temperature, pH, nutrients and fuel cell configuration. One of main challenges facing by MFC technology today is the low power output that limits their use in real applications (Zhang and He 2013). For this reason, microbial fuel cells utilise waste streams or low-value organic compounds are highly promising because they enable a combination between the recovery of energy and the treatment of waste stream (Zhang and He 2013; Zhang and Angelidaki 2012a; Sevda et al. 2013).

In the past decade, most applications of MFC research worldwide focussed on treating wastewater to produce electrical energy due to the energy-demanding process in conventional treatment (Li et al. 2011). Renewable gaseous substrates such as hydrogen and methanol are also potential electron donors for microbial cells. Microbes can obtain their metabolic energy by receiving electrons from the gaseous substrate, and transferring these electrons to a terminal electron acceptor i.e. oxygen (in aerobic respiration). When the electron acceptor is other than oxygen e.g. nitrate, certain anaerobic-respiring microbes are able to utilise electrons from the gaseous donor and transfer them to nitrate. Therefore, gaseous substrates can also be used to support the respiration of anodic microorganisms in MFC.

Industrial processes release a wide variety of toxic gaseous pollutants. Various physical, chemical and biological methods have been practiced in which the main goals are to minimize the toxic gaseous pollutants release to environment and to protect public health. Biological method such as biofiltration has been known as a cost-effective and sustainable approach to remove large air flows ($> 1{,}000\ m^3\ h^{-1}$) and low concentration ($< 1{,}000$ ppm) of toxic gaseous pollutants, with removal efficiency of nearly 100 % (De Clippeleir et al. 2012; Omri et al. 2011). Hydrocarbons (aliphatic, aromatic, chlorinated), VOC, BTEX, alcohols, amines, aldehydes, ketones, terpenes, esters, nitriles, and inorganic compounds are groups of gaseous pollutants that have been successfully treated using biofiltration (Ralebitso-Senior et al. 2012). These waste gases are rich-energy substances, providing alternative to the substrates used for electricity generation in MFCs. Accordingly, microbes that could grow, live, and reproduce by utilising these gaseous substrates are the potential microorganisms in the anode of MFCs.

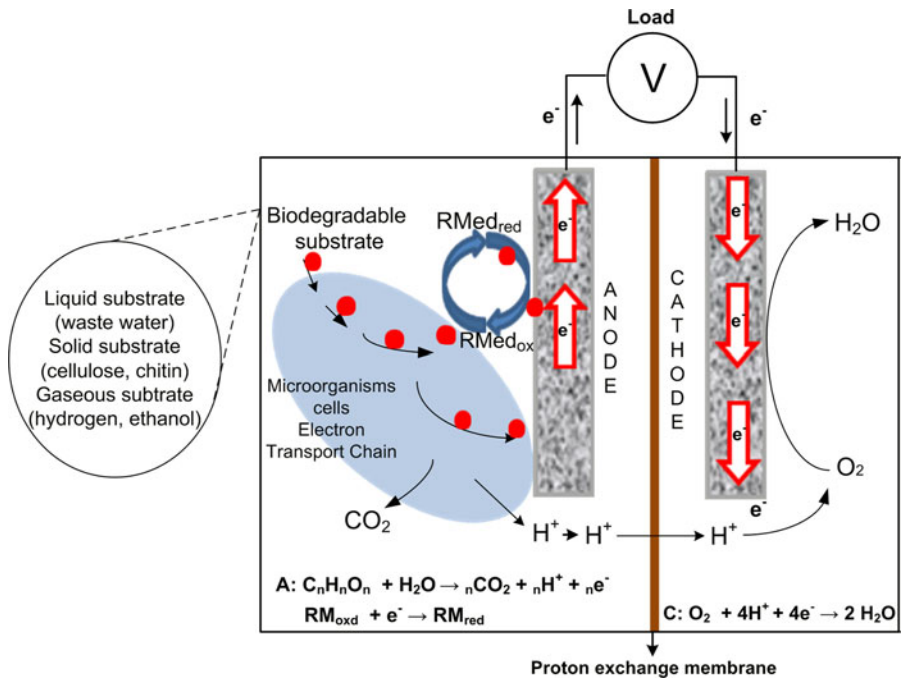

Fig. 1 Schematic diagram of typical microbial fuel cell

Externally supplied (*exogeneous*) mediator can be employed to enhance electron shuttle from bacterial cells to an electron acceptor. There have been accumulated evidence on anaerobic biodegradation organic and inorganic substrates utilising redox mediators over the past twenty years, such as for treating azo dyes and nitroaromatic pollutants present in waste water (Van der Zee and Cervantes 2009). There were increases in the efficiency of the biodegradation by utilising these redox mediators (Dos Santos et al. 2004; Van der Zee and Cervantes 2009). In several cases, redox mediators were required for the reactions to proceed (Van der Zee and Cervantes 2009). A number of redox mediators have been used in the anode of MFCs to facilitate electron transfer in order to reduce the activation energy (or the activation polarization, thus minimizing the potential losses) (Xie et al. 2011). It has been shown that the amount of energy obtained in the presence of redox mediator is higher than in its absence (Evelyn et al. 2012; Sun et al. 2013). Nonetheless, the use of redox mediators in MFCs for wastewater treatment can create significant drawbacks thus does not attract considerable interest amongst researchers interested in liquid phase wastewater treatment using MFC technology. In the preferred mode of operations i.e. continuous and fed-batch systems, the toxic and expensive redox mediators could accumulate to high concentrations when depleted-nutrient solution is replaced after each cycle (Logan 2008), and separating these mediators from the solution is difficult. As a result, much of the MFC works involves growing biofilms directly on the anode to facilitate electron transfer or using organisms that produce soluble electron carriers (Franks et al. 2010).

Gaseous fuels (i.e. gaseous pollutants) can be combined with redox mediators in an MFC since the soluble mediators would remain in the anode chamber as the gas flows through the reactor. The value of gaseous pollutants will increase if the degradation can be linked to the electricity generation through MFC. MFCs still cannot stand alone as the electricity generator due to the low power outputs (Bruce and Rabaey 2012), thus coupling of an MFC into a waste gas treatment system i.e. biofilter can be recommended. Increasing number and types of industries result in a more diverse and complex mixtures of air pollutants than before. Nowadays, industries in many countries are forced by legislations to limit toxic gaseous emissions (Nicell 2009; Hayes et al. 2006; Latos et al. 2010), and biofiltration is superior over various abatement technologies for controlling complex mixture of air pollutants (Ralebitso-Senior et al. 2012). The purpose of this review is to elucidate the

advantages, the process parameters involved, the challenges to face, and the industrial applications of integrating an MFC into a biofilter treating gaseous contaminants (BF-MFC). Prior to that, the past research on gaseous-feed MFCs, the possible mechanism of electron transfer utilising redox mediators enhancing the electron transfer in the anode, and the strategies to achieve a high performance of mediated MFCs are discussed.

2 Combination of gaseous feed and mediator in MFC

2.1 Past research on gaseous feed MFCs

It is not new with gaseous feeds as the fuel in an MFC. Van Hees (1965) pioneered the use of gaseous feed (i.e. methane) as the electron donor with *Pseudomonas methanica* suspension at the bioanode for electricity generation in an MFC. The microbial fuel cell produced the open circuit voltage of 0.5–0.6 V, but a very low current density i.e. 2.8 μA/cm^2 was generated. Addition of a redox mediator i.e. 1-naphtol 2-sulphonate indo 2,6-dichlorophenol had no effect on the open circuit voltage of the fuel cells therefore there was not any evidence on electricity generation by combining a gaseous substrate and a mediator in the MFC. There were no further researches on methane-fed MFCs for more than forty years were seen following this study, until methane-fed MFCs by Girguis and Reimer (2009) appeared but without any added mediator. The fuel cell utilized sediment inoculum with *Methylomonas methanica* was identified as one of the genera. The power production was examined by varying methane and oxygen flowrate, and the power generation decreased with methane and oxygen flux reduction. This study looks promising in terms of power generation i.e. 0.1 mW/cm^2.

However methanotrophic bacteria have been known for the need of oxygen in the metabolism. On the contrary, microbial fuel cell requires the anode typically to be maintained under anaerobic conditions thus not limiting the power generation (Nevin et al. 2011). In addition, electricity generation with methane in anaerobic environment is thought less feasible compared to hydrogen or methanol due to a high activation polarization with methane as the fuel (Lewis 1966). Studies by scientific community showed that anaerobic methane oxidation (AOM) is possible with sulphate, nitrate, manganese (birnessite) and iron (ferrihydrite) as the electron acceptor, but this reaction is believed to occur only in the deep sea using consortium microorganisms (Boetius et al. 2000; Raghoebarsing et al. 2006; Beal et al. 2009). Subsequent evidence also indicates that the AOM is an enzymatic reversal of methanogenesis from carbon dioxide using the nickel containing methyl-coenzyme M reductase (MCR), but MCR operating in the back reaction have been rarely found (Scheller et al. 2010). Another study showed AOM could proceed with nitrite as the terminal electron acceptor under strictly anaerobic condition, nevertheless 'a new intra aerobic' pathway of nitrite reduction to dinitrogen and oxygen was found (Ettwig et al. 2010). None of the AOM studies exhibited pure cultures and all attempts to the isolation have failed so far. The AOM studies suggest that methanotrophs are able to use a wide variety of oxidants. Theoretically, methanotrophs should be able to use perhaps ferricyanide to oxidize methane anaerobically since there is a high driving force for electrons to flow i.e. $E_{ocell} = 0.6$ V (Eq. 3). The possible gaseous reaction with electrons and protons generation at the anode and electrons consumption at the cathode is shown in Eq. 1 and 2, respectively. Yet, ferricyanide is not a sustainable oxidant for real application of MFCs (Alzate-Gaviria 2011), and MFCs with methane as the donor competes with methanogenesis (Yang et al. 2011). To conclude, the feasibility of methane-fed MFCs needs to be carefully investigated and evaluated.

$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^- \quad E_o = -0.24\ V \tag{1}$$

$$8FeCN_6^{3-} + 8e^- \rightarrow 8FeCN_6^{4-} \quad E_o = 0.36\ V \tag{2}$$

$$CH_4 + 8FeCN_6^{3-} + 2H_2O \rightarrow 8FeCN_6^{4-} + CO_2 + 8H^+ \quad E_o = 0.60\ V \tag{3}$$

There were several other publications with gaseous feeds as the energy source in MFCs. These include electricity generation from carbon monoxide (unwanted product in syngas) and alcohols i.e. ethanol and methanol (Mehta et al. 2010; Kim et al. 2007b). The electricity was successfully generated, however the magnitude of power densities are still not adequate for powering low electronic devices. Coupling the MFC to ethanol-containing wastewater treatment was suggested by Kim et al. (2007b), and such system has been

reported in literatures (Cai et al. 2010; Kazemi et al. 2010).

None of the gaseous-based MFCs have included redox mediators to enhance electron transfer in the anode. This consideration prompted Evelyn et al. (2012) to investigate the power production of an ethanol-fed MFC utilising various redox mediators in the anode chamber. The addition of mediators in the MFCs enhances the power density by almost ten times compared to mediatorless MFCs, and the power density was double when the mediator concentration was increased from 0.2 mM to 1 mM (Evelyn et al. 2012). The maximum power density of 0.16 mW/cm^2 was achieved using 1 mM *N*,*N*,*N*′*N*′-tetramethyl-*p*-phenylenediamine (TMPD) as the best selected mediator, which is higher than the methane-fed MFCs by Girguis and Reimer (2009), and more than three times higher than ethanol-fed MFC by Kim et al. (2007b) i.e. 0.05 mW/cm^2. Nevertheless, this value is still lower than acetate-fed MFC i.e. 0.27 mW/cm^2 (Xing et al. 2008). Although different cell configurations were used, the results suggest that electricity production was improved with the facilitation of electron transfer.

The most recent study on gaseous-fed MFCs showed a strain of genetically engineered *G. sulfurreducens* capable of generating current utilising hydrogen as the sole electron donor without any added carbon source (ASM 2013). This research confirms that gaseous substrate is an attractive alternative for use as the substrate in MFCs. Various *Geobacter* and *Shewanella* spp. have become the most studied bacteria in MFC technology due to their capability of transferring electrons directly to the anode electrode (often called exoelectrogenic bacteria), and the MFCs are believed to have more potential for commercial applications than mediated MFCs. The mechanism of electron transfer from these bacteria onto the anode of an MFC is found using several ways: cytochrome on the outer-cell membrane; biofilm containing cytochrome; conductive *nanowires* or *pili*; or self-produced electron shuttles (*endogenous* mediators) i.e. flavins, pyocyanin and phenazines (Bond et al. 2012; Reguera et al. 2005; Marsili et al. 2008; Pham et al. 2008; Gomes et al. 2011; Okamoto et al. 2013). Microbial fuel cells utilising exoelectrogenic bacteria are not in the scope of this present review.

2.2 Mechanism and requirements electron transfer with redox mediators

Mechanisms for transferring of electrons from substrate to microbes, to redox mediators, and to the surface of the electrode have been widely studied in MFCs due to the use of microbes in this technology. Energy-rich substances, in this case gaseous pollutants, supply electrons for the microbial metabolism and provide metabolic energy for the microbes in the form of ATP. The electron transfer in the metabolism progresses through a series of biological reductive systems in electron transport chain/ETC (i.e. NAD^+, FAD, dehydrogenase, ubiquinone, coenzyme Q or cytochrome) prior transferring these electrons to the electron acceptor i.e. redox mediator at the anode. Electron mediators are chemical molecules which can enter the bacterial cells and get reduced (because of accepting electrons) before being reoxidised (because of transferring these electrons) to an electron acceptor or to an anode electrode of microbial fuel cell. Redox mediator is often added (*exogeneous* or *artificial*) to promote the electron transfer as most microbes do not exchange electrons directly with electrode. By oxidizing gaseous pollutants, each microorganism has certain ability to work with a redox mediator in the absence of oxygen, which can be seen basically by observing the color change of the redox mediator (Bidoia et al. 2010). A number of chemical compounds have been investigated for use as the mediator in MFCs, these include various dyes such as neutral red and methylene blue, and inorganic compound such as potassium ferricyanide (Scott and Murano 2007; Park and Zeikus 2000; Emde et al. 1989). The mechanisms of electron transfer using *exogenous* mediators, as well as its difference with *endogeneous* mediators are described in Fig. 2. The biological degradation of gaseous pollutants utilising redox mediator in the anode of MFCs is given by the following equation,

$$\text{Gaseous pollutants} + RM_{ox} + nH_2O \rightarrow RM_{red} + nCO_2 + nH^+ + ne^- \quad (4)$$

Some general characteristics of an ideal redox mediator for an efficient electron transport have been described in several reviews (Van der Zee and Cervantes 2009; Rabaey and Verstraete 2005; Katz et al. 2003). These include the ease of entering

bacterial cell membrane to collect the electrons from the reductive species inside microorganisms, and the ease of the reduced form to pass the electrons onto the anode electrode. In other words, it should not be adsorbed on bacterial cells and also electrode surface. Redox mediator should also have a high solubility and stability in the growth solution. The oxidised and reduced form of the mediator also must not inhibit other metabolic processes. Furthermore, the kinetics of oxidation of the microbially reduced mediator at the electrode surface should be fast, and vice versa (reversible).

Ideally, the standard redox potential (E_o) of a mediator is between the two half reactions, the oxidation of electron donor and the reduction of electron-withdrawing compounds. The E_o should also be more positive than the last redox active species inside microorganisms to make it adequately reduced, although few cases performed remarkably different (Van der Zee and Cervantes 2009). However, it should not be too far or too close to the terminal electron acceptor at the cathode in order to maximize the cell potential (thus the power production), since the maximum MFC cell potential will be the difference between redox potential of the mediator and the terminal electron acceptor at the cathode (Fig. 3). Barriere (2010) suggested the potential difference of 0.05–0.1 V between the mediator and the redox enzyme to provide a fast electron transfer. For example, if the bacterial last redox enzyme in the electron transport chain is *cytochrome c* (+0.22 V vs NHE), therefore theoretically N-TMPD (+0.278 V vs NHE) is the more potential redox mediator compared to potassium ferricyanide (+0.360 V vs NHE). The mediator will be reduced quite fast by bacteria and will yield the MFC cell voltage of 0.54 V compared to 0.46 V with potassium ferricyanide as the redox mediator (assuming oxygen is used as the final electron acceptor).

Marcus and Sutin (1985) suggested an electron transfer rate constant (k_{ET}) to describe the characteristic of an ideal redox mediator and several ways for the good performance of electron transfer (high current density). According to the theory, a redox mediator should have a high k_{ET} value with the last redox active site within bacterial cells (Eq. 5), and this can be obtained: by using a (soluble) low molecular weight mediator; by increasing the distance of

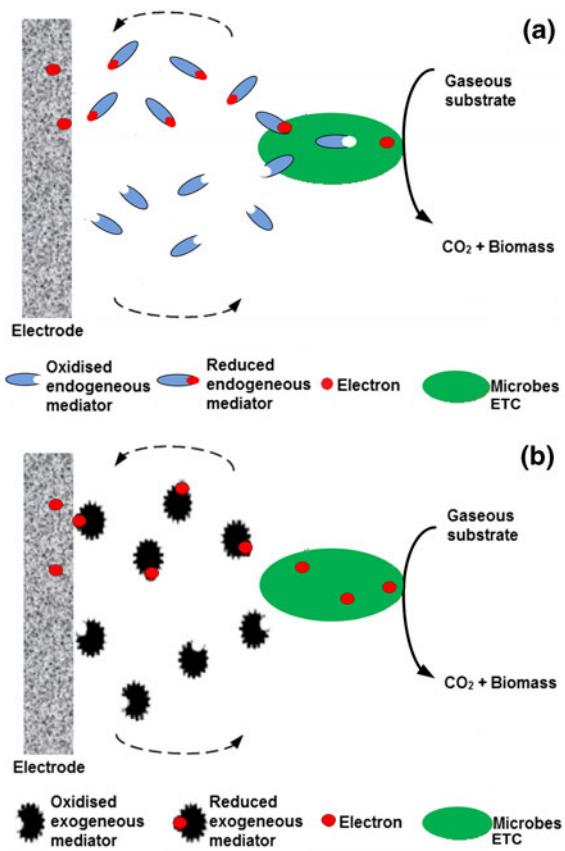

Fig. 2 Schematic representation of electron transfer mechanism between bacteria and an electrode via: **a** endogeneous mediators, and **b** exogeneous mediators (modified from Sabatier 2010)

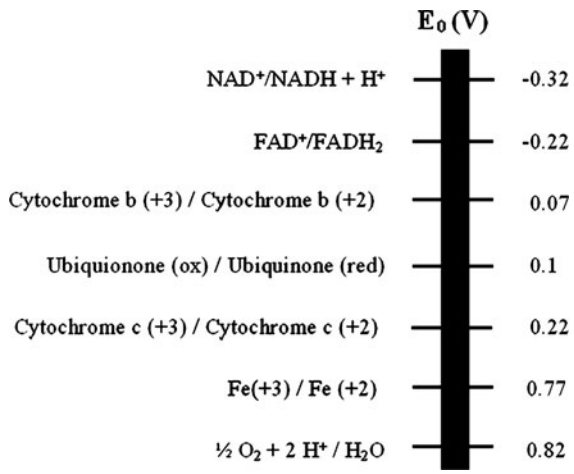

Fig. 3 Standard redox potential (pH 7, 25 °C, vs NHE) of some electron transport chain molecules (Schaetzle et al. 2008)

potential between the mediator and the redox reaction centre; and by utilising a fast self-exchange mediator. It is clear that the methods suggested are aiming to achieve an easy penetration to bacterial cell membrane, to provide enough driving force for electron transfer, and to ensure reversibility of the redox mediator used (the latter can be checked using voltammetry). This equation has been applied in many enzyme-electrode model interactions for its application in biosensors, although few cases have shown deviations due to influence other factors such as pH and the ionic strength of the growth medium (Monica 2002; Kavanagh and Leech 2013). In addition, many factors involved in the electron transfer process such as biological redox species and terminal electron acceptors may also affect the rate of electron transfer (or the current production). Interactions between substrates, microbes, redox mediators, and final electron acceptors must be assessed case by case to find the optimal condition for electron transfer.

$$k_{ET} = k_0 \exp(-\beta(d - d_0)) \exp - \left(\frac{(\Delta G^0 + \lambda)^2)}{4RT\lambda} \right) \quad (5)$$

2.3 Strategies to achieve a high performance in a mediated MFC

The open circuit voltage (OCV) in an MFC is the difference between the equilibrium potential of cathode and anode (E_e cathode and E_e anode) (Fig. 4a, b). E_e anode in a mediated MFC is defined initially by the written standard redox potential of the oxidised mediator used, but finally by the equilibrium potential of the reduced mediator in the electrolyte solution since a shift in the E_e value is commonly observed (Sund et al. 2007). At OCV, when no current being drawn from the MFC, the cell voltage is at a maximum. As current is produced, the cell voltage (ΔE) is determined by OCV lowered with overpotentials ($\Sigma\eta^{anode}$ and $\Sigma\eta^{cathode}$), and ohmic losses ($I\Sigma R_\Omega$) of the fuel cell (Fig. 4a, b). The plot of the cell voltage as a function of the current density production is termed polarization curve, and the power density is obtained by multiplying the cell voltage and the generated electrical current ($P = VI$). The optimal cell voltage (ΔE_{opt}) and current (i_{opt}) were derived from the point of maximum power density (Fig. 4b).

The power density decreases to a zero value when the mediator reaches its limited mass transport current on the anode surface, or when catholyte also reaches the mass transfer limitation at the cathode (i_{LIM}), commonly referred as concentration overpotentials. Both can be seen by a steep increase of the anode potential or a steep decrease of the cathode potential. Evelyn et al. (2012) observed power generation in the mediated MFCs were limited MFCs by the anodic mass transport current. Therefore, to ensure high performance of a mediated MFC (treating gaseous pollutants) as well as to summarize the ideal characteristics of a redox mediator, several strategies are available:

1. Maximizing the cell voltage (ΔE), this can be obtained by:
   - Choosing a mediator with a low redox potential value, e.g. mediator C in Fig. 4c (i.e. −0.3 V), having at least 0.05 V potential difference between the mediator and the last redox active site within bacterial cells (Barriere 2010), but not too low or too negative that makes it hard to be reduced by the microbes.
   - Choosing an oxidant which has a high redox potential value such as permanganate. However, in real applications, using permanganate is not sustainable and practical instead of oxygen cathode (He and Angenent 2006), therefore selection of a mediator plays a vital role in mediated MFCs.
2. Maximizing the mass transport limiting current of the mediator (assuming cathode is not a limiting factor), this can be achieved by:
   - Using a high (and an optimal) concentration of the mediator which will give a high (limited) mass transport current, i_{LIM} (mediator D in Fig. 4c). Mediator B in the same figure has a lower redox potential by 0.05 V compared to mediator D, but it reaches i_{LIM} faster. Mediator C may give the best performance since it can provide the lowest redox potential (thus a high cell voltage can be obtained), and it still gives a high i_{LIM}. Mediator A has the worst performance among all the redox mediators.
   - Using a mediator which has a fast electron transfer (reversible), and has a high solubility

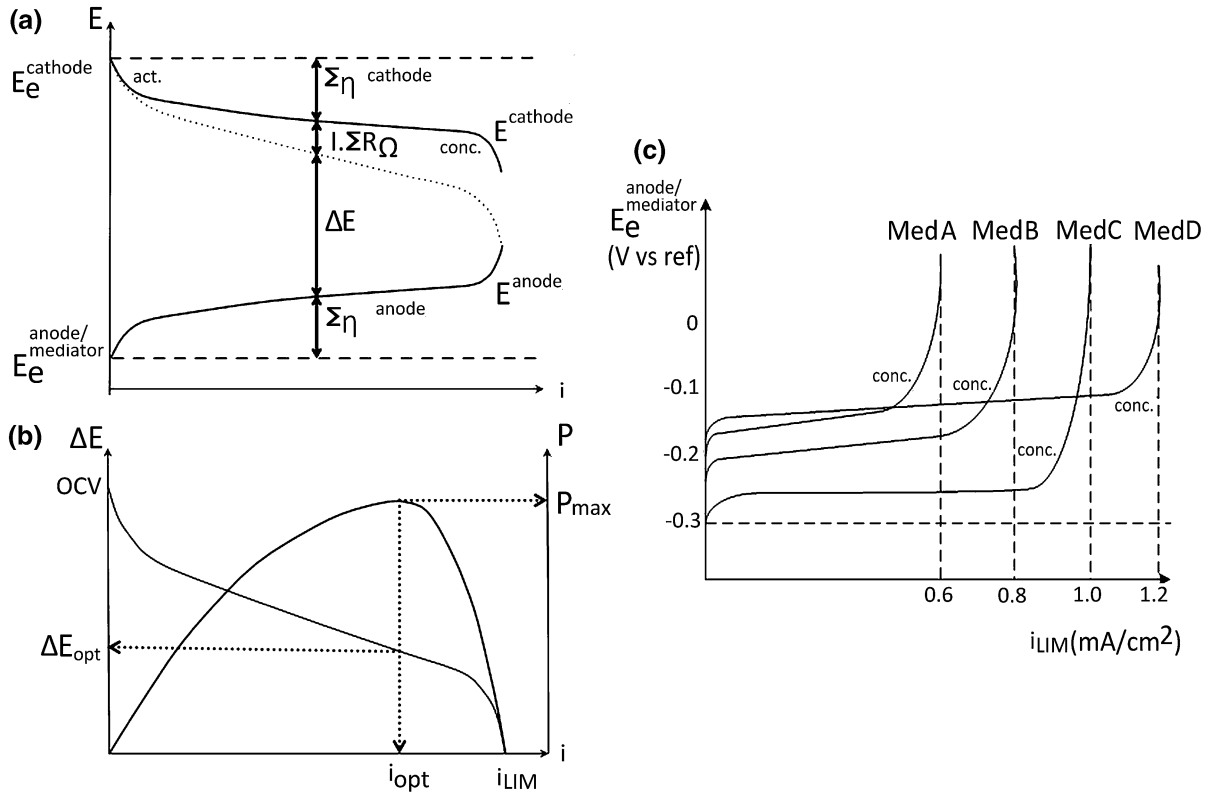

Fig. 4 A typical fuel cell performance of mediated MFCs (updated from Clauwaert et al. 2008)

in the electrolyte solution (i.e. has a low molecular weight).

3. Maximizing the exchange current (i_o) between the mediator and the anode, thus minimizing Tafel slope or charge resistance, generally is determined by $\eta \geq 0.118/n$ V (Bard and Faulkner 2001).

   - Mediator reoxidation at the anode surface should be fast (high i_o), and this can be achieved by increasing the concentration of mediator and by improving the roughness (active site) of the anode electrode.

In practice, not all of these requirements can be met. Hence, researchers will face an inevitable trade-off between these factors to obtain an enhanced performance of a mediated MFC. Due to the availability and sustainability of oxygen-based cathode, improving the oxygen reduction reaction is also a must to boost the overall performance of mediated MFCs.

3 Potential integration of an MFC into an anaerobic biofiltration system (BF-MFC)

3.1 Advantages and operation of BF-MFC

As previously discussed, chemical mediators are not applicable in liquid phase wastewater treatment using MFC technology due to the problems occured. These problems are not exist if the gaseous feeds and redox mediators are combined in the anodic chamber, since soluble mediator will not flow out of the anode chamber while supplying the gas continuously through the reactor (Evelyn et al. 2012). This type of MFC would have several advantages: the improvement of the electron transfer onto the anode electrode, the possibility of using redox mediator for multiple times (recyclable) thus reducing the cost; and more importantly the elimination of separation stage and environmental problems.

Multiple-cycle method is one type in variable resistance method to obtain polarization curve in MFC and is considered accurate (Watson et al. 2011). This is

a single-cycle procedure left at a fixed external resistance for a long enough time (1–2 days) that steady state behaviour is found before the polarization curve is taken, and different external resistance is applied for each new feed (Watson et al. 2011; Zhang et al. 2010; Fan et al. 2007). According to Watson et al. (2011), there could be changes in the measured power production because of the changes in microbial populations particularly when using liquid-phase substrates (i.e. wastewater). The longer time requirement and the introduction of a new feed are causes of the phenomenon observed. Such behaviour should not be found with gas-phase substrate and mediator system because there would be no changes in the substrate affecting the microbial population. This is another advantage of the MFC system utilising gaseous feeds.

Biofiltration is normally an aerobic process to drive complete oxidation of the gaseous contaminants (Nanda et al. 2012; Gostomski and Cudmore 2005). If the gas stream lacks oxygen, air is normally added thus not to limit oxygen diffusion through the inner active biomass (biofilm) layers. Degradation of gaseous pollutants in biofilter can also be carried out under anaerobic conditions, although the aerobic process is thought to be faster than the anaerobic one and the energy obtained by microbes is lower by several fold (Popat and Deshusses 2009). Anoxic biofilters treating several toxic gases such as hydrogen sulfide, and NOx biofiltration have been reported (Soreanu et al. 2008; Jun et al. 2008). Accessibility of electron acceptors (in this case redox mediators) determines the amount of biodegradation of gaseous pollutants, and energy derived from metabolism is utilized only for the cells maintenance (Angelidaki and Sanders 2004). Combining an anaerobic gas feed with a mediator in biofilter is possible, and waste gas biofiltration can be novelty integrated into an MFC (BF-MFC). Combining the two technologies would have two important benefits i.e. reducing carbon footprint and energy recovery. The system could operate in two stages: with the first stage removing the gaseous contaminants by anoxic biofiltration and producing a stream of reduced mediator; and the second stage generating electricity and producing a stream of oxidised mediator to be recycled to the biofilter (Fig. 5). This figure also outlines the internal mechanism of biofilter, in which gaseous contaminants diffuses through the filter bed medium and adsorbs into a microbial biofilm/liquid phase attached to the filter medium (Devinny and Ramesh 2005). Microorganisms in the biofilm biodegrade and convert the contaminants to produce carbon dioxide (CO_2), water, and biomass. In the first step of biofiltration process i.e. the transfer of contaminants from the air to the water phase, the gas and liquid are generally assumed at equilibrium, and is described by Henry's law:

$$C_g = HC_l \tag{6}$$

where H is Henry's constant, Cg and C_l are concentration of the pollutant species in the gas and in the liquid phase, respectively.

The reactions at the biofilter, the anode and the cathode of the BF-MFC are as follows: Biofilter:

$$S + RM_{ox} + nH_20 \rightarrow CO_2 + RM_{red} + H^+ \tag{7}$$

Anode:

$$RM_{red} \rightarrow RM_{ox} + e^- \tag{8}$$

Cathode:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{9}$$

3.2 Process parameters of BF-MFC

Each technology (i.e. biofiltration and MFC) has its own critical process factors which can affect the performance. Combining the two technologies means that there are many more factors which should be considered. Based on the operation of biofilters, apart from oxygen requirement, process factors that need to be optimized to improve the efficacy of biofiltration include inlet pollutant concentration, microorganisms/biofilm, pH, temperature, moisture content, nutrients, and bed porosity (Ralebitso-Senior et al. 2012). For BF-MFC, this also should include redox mediator concentration. Subsequently, the most significant factors affecting MFC performance should also be included. Each of these important factors is described below.

3.2.1 Inlet gaseous pollutant concentration

The best performance of aerobic biofilters achieved when treating a pollutant with concentration less than 1,000 ppm. It has been mentioned that a higher inlet

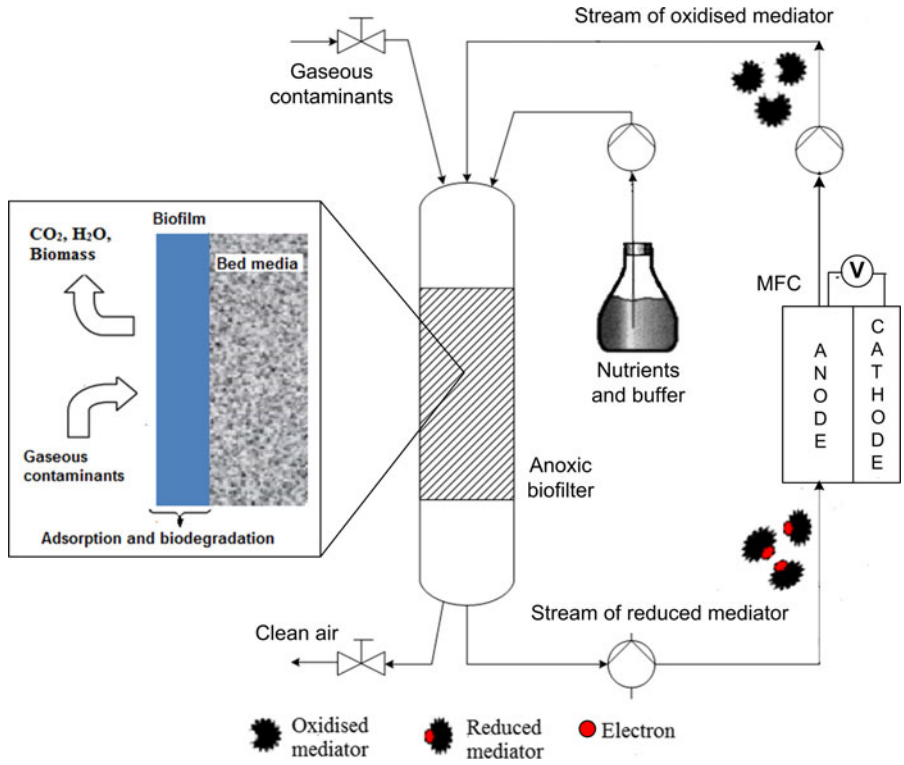

Fig. 5 A schematic flow diagram of the BF-MFC

pollutant concentration will lead to oxygen transfer limitation, hence anaerobic zones, decreasing the elimination capacity (EC) (Detchanamurthy and Gostomski 2012). It is well known that oxygen mass transfer is the biggest concern in air biofiltration. In anoxic biofiltration, insufficient oxygen availability is not a problem since oxygen is not needed for the biodegradation. A higher gas concentration may be able to use and to create the anoxic condition, however target gas is mostly determined by the discharge concentration, composition, flow rate, pH, temperature, and the cost required for temperature adjustment to improve gas solubility (Ralebitso-Senior et al. 2012). In addition, degradation rate of a substrate is also crucial factor affecting electricity production of MFC. Many anoxic biofilter applications have been reported in the range of tens to hundreds of parts per million of pollutant concentration (Lee et al. 1999). Attention must also be made to account for the concentration of electron acceptor (i.e. redox mediator), and the redox potential of the donor electron as well as the electron acceptor due to their cometabolism.

3.2.2 Degrading microbes and biofilm

Monoculture of bacteria, fungi or consortium of microorganisms (e.g. soil) has been used in biofilters (Ralebitso-Senior et al. 2012), and the selection fully depends on the target gas and bed materials (Mudliar et al. 2010). The time required by microorganisms to develop biofilm may take few days to few weeks, but it can be shortened by introducing an acclimatized culture for example from an existing biofilter (Legrand et al. 2011). Usually, biofilm thickness of 1 mm or less in average is observed (Shareefdeen and Singh 2005). There is diffusion limitation of nutrients above this active thickness level (Devinny et al. 1999). Excess accumulation of biomass (thick biofilm) in aerobic biofilters leads to mass transfer problems, this can be seen from clogging, pressure drop, and gas channeling (Yang et al. 2010). In BF-MFC system, thick biofilm is not desired. Development of an effective thin and evenly distributed biofilms to enable transport of gaseous substrates into the biofilm surface could be maintained due to operation under anoxic condition. The mass transfer from gaseous substrate into biofilm

is expected not to become a limiting factor. However, research can be carried out to predict penetration profile of (gaseous) substrate and nutrients into the biofilm (Ralebitso-Senior et al. 2012).

3.2.3 pH and temperature

For a good operation of biofilters, pH and temperature control are required. Neutrophilic pH (6–8) has been reported optimal for gas biofiltration, although there were cases in which the degradation occurred in alkaline or acidic condition (González-Sánchez et al. 2008; Yang and Allen 1994). Insertion of buffer agents or irrigation of filter bed with nutrient solutions that contain pH buffers are the methods suggested to maintain the pH (González-Sánchez et al. 2008; Zilli et al. 2000). The performance of redox mediators may also be affected by pH, therefore a careful pH control should be made to account for their presence. Biofilters and MFCs are mostly operated at ambient temperature due to microbial activity at this condition. Adjustment of the inlet gas temperature can be done to control the temperature between 20 and 40 °C (Ralebitso-Senior et al. 2012).

3.2.4 Moisture content

Drying of bed material may lead to significant reduction in the biodegradation rate, but excess water may inhibit the mass transfer. Depending on filtering materials, generally moisture contents between 40 and 60 % by weight are required for optimal biofilter operation (Ralebitso-Senior et al. 2012), but in some cases it may reach the range between 65 and 75 % (Giri et al. 2010). Biofilters are often limited in the number of microbes present due the drying of bed material (Lee et al. 1999). However, control of moisture levels in a biofilter can be maintained through inlet gas humidification and/or direct application of water to the bed through sprinkler (Mudliar et al. 2010).

3.2.5 Nutrients

Gaseous pollutants are the carbon and energy source for microbial activity. Depending on the needs, other macro (N, P, K, and S) and micronutrients (trace elements) are supplied periodically to the filter bed in order to sustain the reaction rate. Usually, filter beds such as composts fulfil some of the nutrients required as they contain various nutrients. The growth-limiting substrate in the system may be determined from periodic chemical analysis of biofilm (Ralebitso-Senior et al. 2012).

3.2.6 Bed porosity

Preventing/delaying clogging and channeling (thus large pressure drop) of the biofilter is necessary to maintain an even gaseous pollutants flow rate and to extend the bed lifespan, therefore information on bed porosity is important. For this purpose, regular monitoring of biofilter performance is essential. Today, tools such as 16S/18S rRNA/rDNA DGGE analysis, carbon and nitrogen mass balance calculations for determining EPS production have been used (Girard et al. 2011). The bed porosity treating VOC in the range of 35–40 % was suggested by Leson and Winer (1991).

3.2.7 Redox mediator concentration

As already discussed, a high (and an optimal) concentration of redox mediator is required to obtain a high mass transport limiting current (I_{LIM}). The current production increases with the increases of the mediator concentration (Rahimnejad et al. 2011; Evelyn et al. 2012), although there is an optimum value which is influenced by the amount of organisms (Sugiura et al. 2011). By varying concentration of selected mediator in cooperation with microbes and substrates used (as well as paying attention to the redox potentials selected), the optimal concentration can be determined.

3.2.8 Electrodes

Choice of electrodes is fully determined by the performance and cost. A variety of carbon and metal materials have been explored to develop anode and cathode electrodes, which vary in configuration (planar to a three-dimensional structure) and surface area (Wei et al. 2011). For example, packed and brush structure electrodes are more appropriate for large scale MFCs due to its high surface area, although the cost and the power generation are still not feasible for large scale applications (Wei et al. 2011). Advances

have been made to reduce the cost of materials and to improve the current generation, such as the use of a novel non-platinized activated carbon (AC) based gas porous air cathode (Pant et al. 2011b).

3.3 Ion exchange membrane

Cation-exchange, anion-exchange, and ultrafiltration membranes have been studied to determine their effects on MFCs performance (Kim et al. 2007a). Many MFCs have used Nafion® as the cation exchange membrane, but this membrane is very expensive, and using a membrane can increase the internal resistance (Liu and Logan 2004). Nowadays, many MFCs are designed with separators or coatings on the cathode instead of the ion-conductive membranes (Zhang et al. 2011b).

3.3.1 Oxidant in the cathode

As discussed, oxygen based cathode is mainly used due its practical applicability, with typical maximum potential of +0.3 V (Bruce and Rabaey 2012). Metal (i.e. platinum, ferric ion, manganese oxides, cobalt) and non-metal catalysts (i.e. biocathodes and activated carbon) have been reported to facilitate and improve oxygen reduction reaction at the cathode (Zhang et al. 2011a; Roche et al. 2010; Sanchez et al. 2010; Chen et al. 2008; Zhao et al. 2005). Nitrate has also been suggested as an alternative oxidant due to its its high solubility relative to oxygen (Clauwaert et al. 2007).

3.3.2 MFC reactor design

Recent advances in MFC configurations have been reviewed currently by Zhou et al. (2012). Examples of the innovative configurations are overflow-type wetted-wall MFC (WWMFC), rotatable bio-electrochemical contactor (RBEC), and self-stacked submersible MFC (SSMFC) (Li et al. 2009; Cheng et al. 2012; Zhang and Angelidaki 2012b). Most of the latest configurations are designed for efficient biofilm attachment at the anodes or the cathodes (for biocathodes). In BF-MFC, oxidation of gaseous pollutants takes place in biofilter rather than in the anodic chamber of MFC. The MFC could be from a simple design, and selection of current collector materials and oxidant will highly affect the current production.

3.3.3 Method to obtain the polarization curve

A potentiostat or a variable external resistor is a common tool to obtain a polarization curve (Logan et al. 2006). In BF-MFC system, setting the anode potential (more positive potential than the mediator used) using a potentiostat would be more suitable due to receiving the reduced mediator stream from the biofilter. No methods on defining the optimal potentials have been accepted (Wagner et al. 2010), but finding the optimal values are required through further bioelectrochemical investigation for improving current generation.

3.4 Challenges to face and industrial application

Few challenges have been mentioned previously, however better knowledge on the key challenges of the two technologies (i.e. biofiltration and MFCs) is necessary to enable the integration. Biofilters are low cost and have been applied in many industries, however reducing its size (as a result of the low EC) is still the main challenge in this technology (Detchanamurthy and Gostomski 2012). As already discussed, excess biomass accumulation is the major cause of the low EC. When an MFC is integrated into an anoxic biofilter, accumulation of the biomass could be maintained due a limited ATP production in non-growth systems. The same method had also been investigated by Detchanamurthy and Gostomski (2012), but instead of redox mediators, metabolic uncouplers were used to limit the growth. Thus biodegradation rates in anoxic biofiltration are expected to be maintained and would cause no problem during scale-up. Industries would appear to introduce a plenty amount of toxic gaseous discharge, and target should be made for the elimination of gaseous contaminants while reducing the size through optimization various process parameters.

Not only to increase the power production, reducing the cost of materials is one of the major challenges in MFC technology (Bruce and Rabaey 2012). Scaling up of an MFC will require a better understanding of all components and conditions to detect the bottlenecks. Development of cost-efficient electrode materials and the advancement in MFC reactor configurations could bring the commercialization of this technology in the near future. Several companies such as Trophos Energy (USA), Lebone (USA), IntAct Labs LLC

Table 1 Potential application of BF-MFC and redox mediators for industrial gaseous pollutant treatment (modified from Ralebitso-Senior et al. 2012)

Source industries	Example gaseous pollutants	Catabolic species	Various potential redox mediators and their standard potentials (V vs NHE)
Waste treatments, manure composting plants and storage, piggery slurry animal, foundry effluents, waste oil, petrochemicals, municipal solid waste treatment facilities	Ammonia, amines	*Nitrosomonas* sp., *Vibrio alginolyticus*, *Stenotrophomonas nitritireducens*, *Luteimonas mephitis*, *Pseudoxanthomonas broegbernensis*, *Nitrosospira* spp.	Ethyl viologen (−0.480) Methyl viologen (−0.440)
Petrochemical production, distillery dried grains, food industries, bakeries, abattoirs, meat rendering plants, petrochemical production, landfill gas, waste oil, petrochemicals, poultry batteries, waste treatment plants, leather industries	Alcohols, hydrogen sulfide, dimethyl sulfide	*Candida utilis*, *Hyphomicrobium* spp., *Thiobacillus* sp., *thiothrix* spp., *Pseudomonas* sp., *Moraxella* sp., *Acinetobacter* sp., *Exiguobacterium* sp., *Hyphomicrobium, Microbacterium* sp., *Pseudomonas putida*	Benzyl viologen (−0.374) Neutral red (−0.325) Safranin (−0.289)
Fattening plants, livestock air, chemical industries, foundry effluents, composting plants, waste water, treatment plants, plastic processing, agrochemical, adhesives production, miscellaneous storage tanks, plywood production, construction, petrochemical, production, plastic processing	VOC	*Rhodococcus erythropolis, Devosia* sp., *Mesorhizobium* sp., *Burkholderia* sp., *Afipia* sp., *Sphingomonas* sp., *Nitrobacter* sp., *Alcaligenes defragrans, Methylophilales* sp., *enterobacter* sp., *Caulobacter crescentus, Shigella* sp., *Escherichia* sp., *Scedosporium* sp., *Paecilomyces* sp.	Antraquinone-2-disulfonate or AQDS (−0.184) 2-hydroxy-1,4-naphtoquinone or HNQ (−0.137) Resorufin (−0.051)
Oil refining, landfill gas, waste treatments, petrochemicals	BTEX, VFA, BTX, MTBE	*Sphingomonas* sp., *Microbacteria* spp., *Gordonia* spp., *Dietzia* spp., *Janibacter* sp., *Rubrobacter xylanophilus*	New methylene blue (−0.021) Gallocyanine (0.021)
Tobacco processing effluents, chemical industries, waste water treatment plants, petrochemical production, plastic processing, adhesives production, miscellaneous storage tanks, agrochemical	Toluene, benzene, styrene	*Rhodococcus* sp., *Paecilomyces* sp., *Rhodococcus pyridinovorans*, *Sporothrix variecibatus*, *Scedosporium apiospermum*, *Burkholderia cepacea*	Toluidine blue-O (0.034) Thionine (0.064) Phenazine ethosulphate (0.065)
Piggery slurry animal, manure composting and storage, landfill gas, chemical industries, agrochemical, waste water treatment plants	Methane	*Methylobacter* sp., *Methylosinus* sp., *Methylomicrobium* sp., *Methylomonas* sp., *Methylococcus* sp.	Phenothiazinone (0.130)
Vegetable oil production, fish and fat processing, Gelatine production, flavour and fragrant, manufacture, film coating, distillery dried grains, chemical industries and storage	Aldehydes and ketones	*Lactobacillus plantarum*, *Pseudomonas* sp.	2-6 Dichlorophenol indophenol (0.217) 2,3,5,6-TMPD (0.220) *N*′,*N*′,*N*′,*N*′-TMPD (0.278)
Resin processing, engine combustion power plants, hatcheries	Carbon monoxide, mercury, nitrous/nitric oxide	*Clostridium* spp., *O. carboxidovorans*, *Nitrobacter* sp.	Potassium ferricyanide (0.360)
Plywood production, wood drying	Monoterpenes	*Phanerochaete chrysosporium*	

(USA), Hy-SyEnce (USA), Plant-e (Netherlands) and Emefcy (Israel), are now in the beginning of the commercialization process, for either MFCs treating wastewater or producing valuable chemicals (Pant et al. 2011a). Collaboration MFC technology with gaseous pollutant treatment would appear as an

alternative for the near future. Utilization of redox mediators is additional challenging factor for BF-MFC due to its limitation in the current production (Evelyn et al. 2012). Understanding mechanism of interaction between the gaseous feeds with the microbes, microbial cell pathways with the electron mediators, and the electron mediators with the anode electrodes, along with the parameters involved might eliminate the obstacles. In addition, kinetics of electron transfer utilising redox mediators must also be thoroughly studied for example using cyclic voltammetry or linear sweep voltammetry method. As evidence and confidence of using biofiltration and MFC technology grows, these are expected to addresses the challenges and enhance the collaboration potential between large scales biofilters and MFC systems. Table 1 lists potential industrial applications of BF-MFC and a range of frequently used redox mediators (including their standard redox potentials) which can be added to the system.

4 Conclusions

A collaboration potential between anoxic gaseous pollutant treatment and electricity generation utilising redox mediators (BF-MFC) has been described. It is apparent that carbon–neutral process could be produced with the generation of energy. The process will also allow recycling the redox mediators used. Better knowledge is required on how to design and optimize the various process parameters for the successful of BF-MFC to be carried out. Elimination of the bottlenecks is a major challenge for application BF-MFC in industrial gaseous pollutant treatment. Other factors such as the establishment of suitable waste gases-microbes-mediator combination and the proper selection of strategies employing redox mediators need more attention. Further research is also needed to evaluate rigorously regarding efficiency, scalability, and economic performance of BF-MFC. Only with such a concerted effort, BF-MFC technology will be able to integrate and develop sufficiently to fulfil its potential.

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