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Review

Impact of reactor configuration on pilot-scale microbial fuel cell performance

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ABSTRACT

Different microbial fuel cell (MFC) configurations have been successfully operated at pilot-scale levels (>100 L) to demonstrate electricity generation while accomplishing domestic or industrial wastewater treatment. Two cathode configurations have been primarily used based on either oxygen transfer by aeration of a liquid catholyte or direct oxygen transfer using air-cathodes. Analysis of several pilot-scale MFCs showed that air-cathode MFCs outperformed liquid catholyte reactors based on power density, producing 233% larger area-normalized power densities and 181% higher volumetric power densities. Reactors with higher electrode packing densities improved performance by enabling larger power production while minimizing the reactor footprint. Despite producing more power than the liquid catholyte MFCs, and reducing energy consumption for catholyte aeration, pilot MFCs based on air-cathode configuration failed to produce effluents with chemical oxygen demand (COD) levels low enough to meet typical threshold for discharge. Therefore, additional treatment would be required to further reduce the organic matter in the effluent to levels suitable for discharge. Scaling up MFCs must incorporate designs that can minimize electrode and solution resistances to maximize power and enable efficient wastewater treatment.

1. Introduction

Microbial fuel cells (MFCs) use microorganisms on electrodes to produce electricity from the degradation of organic matter (Logan et al., 2019). In an MFC a biofilm containing exoelectrogenic bacteria colonizes the anode, oxidizing the organic matter in solution, and producing electrons for the oxygen reduction reaction (ORR) at the cathode. Advances in MFC engineering have allowed development of reactors avoiding the use of expensive ion exchange membranes to separate the electrodes, and precious catalysts on the cathode, and have used relatively inexpensive carbon anode materials with high surface areas, making this technology appealing for wastewater treatment (Logan et al., 2015). Activated sludge is the most common biological wastewater treatment in the developed world, but due to the high energy required for aeration, it consumes approximately 1% of the global retail electricity sales (Scholz, 2016). Employing MFCs for wastewater treatment could reduce the high operating costs of activated sludge treatment technologies by coupling the oxidation of the organic matter in wastewater with the production of electrical energy and avoid aeration. Due to the urgency of reducing energy consumption in wastewater treatment as an aim to diminish climate change, novel technologies for efficient wastewater treatments such as MFCs need to be demonstrated at the relevant scales.

MFCs using wastewater have been demonstrated at laboratory-scales (up to several liters) more than a decade ago, and continuous improvements on the design and engineering have led to the recent (2014 to 2022) development of several large-scale, pilot MFCs having a liquid volumes larger than 100 L based on different configurations (Babanova et al., 2020; Blatter et al., 2021; Das et al., 2020; Dong et al., 2019; Feng et al., 2014; He et al., 2019; Hiegemann et al., 2019; Leininger et al., 2021; Liu et al., 2017; Mohamed et al., 2021; Rossi et al., 2022b; Sugioka et al., 2022; Walter et al., 2020) Therefore, for the first time, there is now a sufficient number of studies to make it possible to directly compare results for these large reactors (versus laboratory-scale systems) and investigate the impact of the different reactor configurations on performance. There have been many reviews on the performance of smaller MFCs (Lovley, 2006; Pant et al., 2010; Santoro et al., 2017), but smaller reactors can have design features that may not translate to larger-scale systems. For example, H-cell reactors, while optimal to investigate the performance of pure culture bioelectrochemical systems,

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would not be useful at larger scales due to the high internal resistance (Rossi and Logan, 2020). Electrical connections to the circuit for a smaller electrode, such as a single pressure connection to a wire in a 28 mL cube type reactor, may not be practical for larger electrodes (Wang et al., 2015); water pressure can, for larger systems, cause leakage across air cathodes (Feng et al., 2014; Rossi et al., 2019); dissolved oxygen might be more difficult to maintain in larger, aqueous-phase cathodes than smaller systems (Dong et al., 2019; He et al., 2019); the cost of materials such as Pt might not be affordable in larger systems that would require less expensive materials (Feng et al., 2014); and the methods used to producing smaller laboratory MFCs might not be possible for making larger reactors, such as hand-made cathodes compared to more industrialized cathode preparation processes. An earlier analysis in 2015 suggested that performance tended to decline with increased scale of the system, and that electrode packing densities decreased with size resulting in lower volumetric power densities than smaller systems (Logan et al., 2015). However, at that time there was insufficient data to more critically examine the performance of larger MFCs. Therefore, a review of these larger systems can now be accomplished and looking only at these more recent, larger-scale systems will provide greater insight into the actual performance of more practical-sized, pilot-scale MFCs.

In this study, we reviewed the performance of these larger MFCs based on electrical power produced normalized by the electrode area and reactor volume, and wastewater treatment capacity based on chemical oxygen demand removal (COD) for 13 different pilot scale MFC studies having a collective volume larger than 100 L, independently by the size of the individual modules composing the MFC, differentiating the performance based on the MFC configuration (aerated liquid catholyte or air-cathodes), anode material, electrode packing density and wastewater type and strength (Babanova et al., 2020; Blatter et al., 2021; Das et al., 2020; Dong et al., 2019; Feng et al., 2014; He et al., 2019; Hiegemann et al., 2019; Leininger et al., 2021; Liu et al., 2017; Mohamed et al., 2021; Rossi et al., 2022b; Sugioka et al., 2022; Walter et al., 2020). A few studies (Ge and He, 2016; Jadhav et al., 2020; Liang et al., 2019, 2018), despite having a volume >100 L, have been excluded from the analysis due concerns relating to calculations or results reported in the paper, or a lack of sufficient information to enable comparisons to other studies, as explained in the Supporting Information. The 100 L MFC volume cut-off was selected based on the number of studies available in the literature and the relevant wastewater flow-rate per capita. Assuming a wastewater production per capita of approximately ~200 L/d (Cheng et al., 2021; Koutsou et al., 2018; Mesdaghinia et al., 2015) and HRTs of ~6 h, typical for wastewater treatment (Hao et al., 2013; Huang et al., 2011; Rossi et al., 2019b), a 100 L MFCs allow processing of a relevant wastewater flux (~400 L/d) while a 10 L MFC is not sufficient even for one person. Studies on MFCs with 1000 L volumes were too scarce for a thorough review of the literature.

2. MFC configuration: liquid catholyte and air-cathodes

Two different types of cathode configurations have been primarily used in pilot-scale MFCs for providing oxygen to the cathode for the oxygen reduction reaction: liquid catholytes and air-cathodes (Fig. 1). In liquid catholyte MFCs, the cathode is submerged in a liquid and the oxygen reduction reaction occurs on the electrode surface in contact with the solution (Fig. 1A). Due to the low solubility of oxygen in water (~ 0.2 mM), the liquid catholyte is typically sparged with air either directly in the cathode chamber or prior to flowing into it. A separator can be placed between anode and cathode to minimize oxygen transfer to the exoelectrogenic biofilm on the anode (Cheng et al., 2006; Lin et al., 2004).

In air-cathode MFCs, the cathode separates the liquid chamber from the air, and this configuration is often referred to as a "single chamber" air-cathode MFC. In pilot-sized reactors, multiple pairs of electrodes are typically used and therefore an air chamber in addition to the liquid anode chamber is required between two cathodes facing each other allowing for passive air flow (Fig. 1B). The air chamber allows a passive flow of oxygen to the cathode for the reduction reaction. The oxygen in air diffuses through a hydrophobic layer and reaches the catalyst immobilized on the cathode where it is reduced, consuming the electrons generated at the anode and producing electrical energy. Water leakage through the cathode in the air chamber is typically prevented by using a thick hydrophobic layer on the air side of the electrode. The porosity of the hydrophobic surface can be tuned to minimize water leakage and control oxygen diffusion (Zhang et al., 2011). Air cathodes, due to the large area exposed to the air, do not require aeration, allowing passive diffusion of oxygen through the hydrophobic layer.

2.1. Impact of cathode configuration on power density of pilot MFCs

A total of 13 pilot MFC studies were identified in the refereed literature based on having a total volume larger than 100 L and containing sufficient information for analysis (Babanova et al., 2020; Blatter et al., 2021; Das et al., 2020; Dong et al., 2019; Feng et al., 2014; He et al., 2019; Hiegemann et al., 2019; Leininger et al., 2021; Liu et al., 2017; Mohamed et al., 2021; Rossi et al., 2022b; Sugioka et al., 2022; Walter et al., 2020). The power densities used to characterize reactor performance in 8 of these studies (Babanova et al., 2020; Blatter et al., 2021; Feng et al., 2014; Liu et al., 2017; Mohamed et al., 2021; Rossi et al., 2022b; Sugioka et al., 2022; Walter et al., 2020) were those obtained after the startup phase and during stable operation of the reactor under a specified load or resistance. In 5 of the studies reviewed here data were not immediately available for electrical power production during

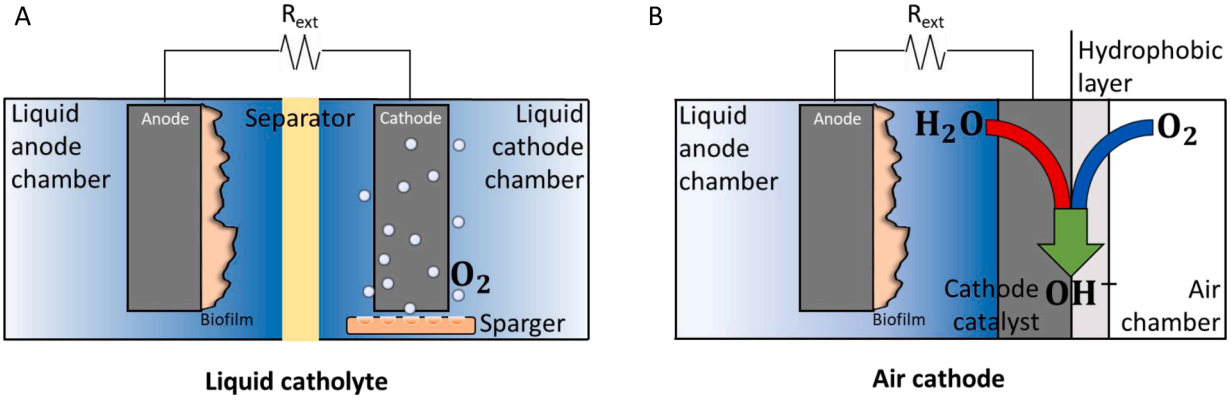

Fig. 1. Comparison of two general types of MFC configurations with wastewater added only in the anode chamber. (A) Liquid catholyte configuration where the catholyte is aerated and kept separate from the anolyte using a separator to minimize oxygen crossover to the anode. (B) Air-cathode configuration where the cathode requires a separate air chamber.

operation, and thus power density from polarization tests was used (Das et al., 2020; Dong et al., 2019; He et al., 2019; Hiegemann et al., 2019; Leininger et al., 2021). Typically, data from stable operation are more reliable compared to results from polarization curves. Based on these 13 studies the pilot MFCs employing air cathodes (6 studies) produced an average of 2 × more power based on the electrode area than the liquid catholyte MFCs (Fig. 2). The average power density of the air cathode MFCs was 49 ± 27 mW m^{-2} (6–95 mW m^{-2}) compared to 21 ± 14 mW m^{-2} (8–44 mW m^{-2}) for the liquid catholyte MFCs.

Comparison of power densities requires consideration of factors other than cathode configuration such as operational conditions, wastewater strength, and electrode sizes. Using polarization data rather than stable operational results can overestimate power than can be produced under steady state conditions if the scan is conducted too quickly (Velasquez-Orta et al., 2009). The power produced using a rapid scan rate can be overestimated due to the capacitance of the bacterial biofilm (Heijne et al., 2018) and electrode materials (for example activated carbon) (Liang et al., 2019). The magnitude of the capacitance increases with the electrode size, and therefore the time to reach steady state conditions where this discharge of capacitance does not affect the current at a specific resistance or scanned voltage, will require longer periods of time (Liang et al., 2019). Wastewater strength, conductivity, and alkalinity (buffer capacity) can also influence performance. For example, the area power density reported in the air cathode study by Babanova et al., was larger (75% greater) than the average power density of the other air cathode MFCs using brush anodes (Babanova et al., 2020). One reason for the increased power could be due to the swine wastewater used in that study had a much higher chemical oxygen demand (COD; >1 g/L) than the other studies (COD of ~0.3 g/L) that used domestic wastewater, providing more substrate for the bioanode. Another possible reason could be due to the smaller MFC module size, which limited hydraulic pressure on the cathode and reduced ohmic losses by minimizing electrode size.

The size of the electrodes can impact internal resistance, and therefore power, and the main source of the internal resistance can shift as electrodes become larger. The cathode area (0.037 m^2) of the MFC by Babanova et al. (2020) was approximately one order of magnitude lower than those used in the other air-cathode studies [1 m^2, (Feng et al., 2014); 0.72 m^2, (Hiegemann et al., 2019); 0.62 m^2, (Rossi et al., 2022b)]. The ohmic resistance of a material increases with distance according to:

$$R_A = \rho\, l \quad (1)$$

where R_A (Ω m^2) is the area-based resistance, ρ is the material resistivity and l is the distance. As the electrode area is increased, R_A changes due to the larger distance the electrons have to travel (for example over the length of carbon cloth) from where they are generated to the point of extraction (connection to the wire collecting the current). Therefore, the electrode resistance will likely increase for large electrodes, resulting in a loss of power as the electrode size increases even though cathodes are made using relatively conductive materials. This increase in electrode resistance for the larger electrodes used in pilot-scale MFCs reduces the impact of electrode spacing or solution conductivity for these larger systems compared to laboratory-scale systems. For example, it was previously reported that 34% of the internal resistance (223 ± 16 mΩ m^2) of a laboratory-scale (28 mL) MFC fed domestic wastewater was due to the anode resistance (75 ± 9 mΩ m^2), 24% to the cathode resistance (54 ± 7 mΩ m^2) and 39% to the solution resistance (87 mΩ m^2). However, when a similar design was used in a much larger, 85 L MFC, where the electrode dimensions were increased from 7 cm^2 to 0.62 m^2, the cathode resistance increased to 555 ± 24 mΩ m^2 (62% of the internal resistance), and anode resistance to 238 ± 18 mΩ m^2 (27% of the

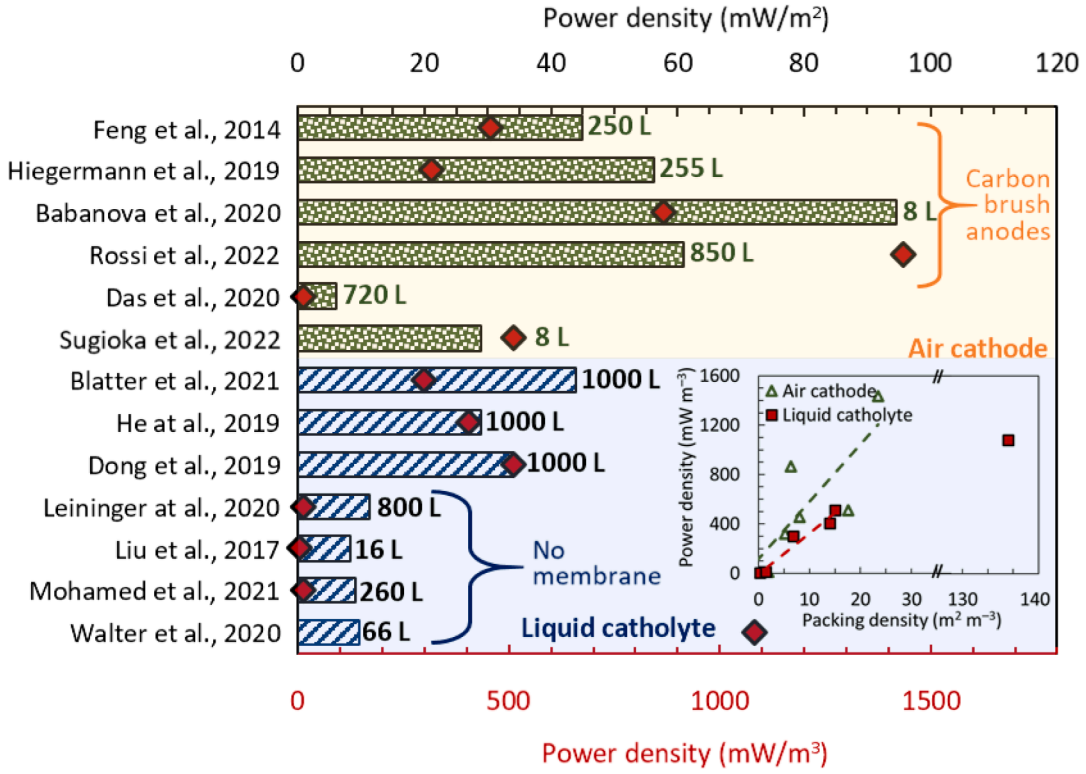

Fig. 2. Electrode area-normalized (bars) and volumetric power density (diamonds) of air-cathode or liquid catholyte pilot-scale MFCs (total volume > 100 L). The number next to the column indicates the volume of a singular module of the reactor. The studies were grouped based on the cell configuration, using carbon brush anodes or membranes, for example. In the insert is showed the impact of the electrode packing density on the volumetric power density. All the studies used domestic wastewater except Babanova et al. (2020) (swine wastewater); Leininger et al. (2021) (digestate and domestic wastewater mix); Mohamed et al. (2021) (wastewater and river sediment mix) and Walter et al. (2020) (urine).

internal resistance) while the solution resistance was 93 mΩ m^2, corresponding to only 10% of the overall internal resistance (Rossi et al., 2019). Therefore, while solution resistance and electrode spacing can be important in smaller, laboratory-scale reactors, in pilot scale systems have a much smaller relative impact due to the larger resistances of the electrodes.

Not all the air cathode MFCs had higher power than the liquid catholyte reactors. In the study by Das et al. (2020), it was reported a power density of only 6.0 mW m^{-2} in polarization tests, approximately one order of magnitude lower than that reported in the other air cathode MFCs, likely due to a suboptimal electrode configuration (Das et al., 2020). In that study, even though air cathodes were used, a clayware ceramic membrane was sandwiched between the carbon felt anode and the cathode. It has been previously reported that flat anodes placed in direct contact with the membrane and the solution not forced through the anode, typically results in mass-transfer limitations due to a poor substrate and ion transport between the electrodes (Cario et al., 2019). All the other pilot scale reactors with air cathodes MFCs (Babanova et al., 2020; Das et al., 2020; Feng et al., 2014; Hiegemann et al., 2019), except in Das et al. (2020) and Sugioka et al. (2022), used carbon brush anodes, producing approximately 4 times larger power density (64 ± 18 mW m^{-2}) than the studies not using carbon brush anodes (18 ± 11 mW m^{-2}), indicating that carbon brush anodes should be the preferred choice for pilot scale MFC reactors.

The MFC developed by Feng et al. used a precious metal catalyst (Pt/C) at the cathode, which produced performance (45 mW m^{-2}) similar to the other air-cathode MFCs using a comparable configuration and no precious metal cathode catalyst (59 ± 2 mW m^{-2}; air cathode and brush anode, domestic wastewater (Hiegemann et al., 2019; Rossi et al., 2022b)), but increased the overall cost of the MFC by approximately 32% compared to activated carbon cathodes (Feng et al., 2014). Precious metal catalysts are not needed for MFCs due to the relatively low current densities compared to abiotic hydrogen fuel cells, and these metal catalysts can rapidly become deactivated due to chemicals contained in the wastewater (Santoro et al., 2016; Zhang et al., 2009).

The use of a membrane or separator between anode and cathode, coupled with catholyte aeration, increased the performance of the liquid catholyte MFCs (Fig. 2). The average power density (36 ± 6 mW m^{-2}) in the three studies with an aerated liquid catholyte and separator between anode and cathode (Blatter et al., 2021; Dong et al., 2019; He et al., 2019) was approximately 4 × larger than that produced by MFCs without a separator and aerated catholyte (10 ± 1 mW m^{-2}) (Leininger et al., 2021; Liu et al., 2017; Mohamed et al., 2021; Walter et al., 2020). This suggests that sparging the catholyte with air to maintain a high oxygen concentration in the chamber was needed to sustain the current generation while a separator avoids the sparged oxygen to interact with the anodic biofilm and decrease performance. Unfortunately, air sparging of the catholyte substantially increase the operational cost of the MFC. For example, He et al. reported that sparging air in the catholyte required an additional 3.63 × 10^{-2} kWh m^{-3} for their MFC, representing the largest energy consumption process with pumping (2.51 × 10^{-4} kWh m^{-3}) (He et al., 2019). The energy consumed for aeration was slightly reduced in a following study to 2.34 × 10^{-2} kWh m^{-3} by optimizing the energy consumption using intermittent aeration and an optimized cathode material (Dong et al., 2019). Despite the energy input required for aeration and the low electrical energy produced by the MFC in that study, wastewater treatment was accomplished consuming only 12% (0.034 kWh m^{-3}) of the energy typically required for an activated sludge process (0.3 kWh m^{-3}) (He et al., 2019; McCarty et al., 2011), indicating that MFCs, despite the low electrical energy production, can accomplish wastewater treatment at a fraction of the energy cost of current wastewater treatment technologies.

The volume of the MFC module was not as critical to performance as reactor design and materials as smaller modules did not always produce more power. For example, the pilot MFC producing the largest power density (95 mW m^{-2}) used many small individual modules with a volume of 8 L (Babanova et al., 2020). However, this power density was only 56% larger (61 mW m^{-2}) than that of an MFC with a single module 100 × larger (850 L) (Rossi et al., 2022b). Another MFC using modules of only 8 L produced only 29 mW m^{-2} (Sugioka et al., 2022), or about half of the power density produced by the 850 L MFC. The low power density produced in the study by Sugioka et al. was likely due to the different tubular reactor configuration using a separator and a flat carbon felt anode with the wastewater flowing behind it compared with the plate and frame designs using brush anodes in the other two systems. Previous work indicated that tubular MFCs can be a viable alternative to conventional plate and frame configuration (Janicek et al., 2014), but most of the larger MFCs have used the plate and frame configuration, likely due to the easier scalability, operability and maintenance.

2.2. Additional challenges for using air cathodes in MFCs

The main challenge for large scale air cathode MFCs is manufacturing cathodes with high electrical conductivity and large surface area, and ensuring the cathode is leak-proof. Water leakage is not a concern in liquid catholyte MFCs but for air cathode MFC, water leaking in the air chamber would disrupt MFC operation by reducing the amount of oxygen in contact with the cathode catalyst. In a pilot air-cathode MFC where the cathodes were subjected to 0.7 m water height pressure, after only 6 months of operation, 10 out 32 cathodes were leaking, greatly reducing the performance of the reactor (Rossi et al., 2022b). In another study (Feng et al., 2014), high water pressure was avoided to minimize water leakage by orienting the 1 m^2 cathodes horizontally so that the water height was only 0.25 m. Although large and leak-proof cathodes can be manufactured, increasing the size of the cathodes also increases the electrode resistance, which is detrimental for the MFC performance. It has been previously estimated that the electrical power loss could be as much as 47% by increasing the size of a carbon mesh electrode from 0.001 to 1 m^2 at current density of 3 A m^{-2} (Cheng et al., 2014b). Thus, large air cathodes with resistance to leakage under high water pressures, along with high electrical conductivity, need to be developed to increase the performance of pilot-scale MFCs (Rossi et al., 2019).

3. Volumetric power densities of pilot MFCs

The impact of the MFC configuration on the volumetric power density was consistent with that of the area-normalized power density, with larger volumetric power density produced by air cathode MFCs compared to liquid catholyte MFC. The volumetric power density was 600 ± 452 mW m^{-3} (12–1435 mW m^{-3}) for the air cathode MFCs, approximately 2 times larger than that of the liquid catholyte reactors (332 ± 361 mW m^{-3}; range: 3–1081 mW m^{-3}). Liquid catholyte MFCs with separator and catholyte aeration produced slightly more power (405 ± 86 mW m^{-3}) than liquid catholyte MFCs without separator if a study using urine and small electrode spacing was included (277 ± 464 mW m^{-3}) (Walter et al., 2020). However, the volumetric power density of liquid catholyte MFCs without aeration and separators largely decreased when considering only MFCs treating domestic wastewater (8 ± 4 mW m^{-3}) indicating that the low oxygen concentration in the wastewater resulted in lower power generation unless there was catholyte aeration. Energy recovery was also larger for the air-cathode MFCs than liquid catholytes. Three air-cathode MFCs (Hiegemann et al., 2019; Rossi et al., 2022b; Sugioka et al., 2022) had an average energy recovery of 11 ± 6 Wh m^{-3}, which was more than twice that (5 ± 6 Wh m^{-3}) produced using a liquid catholyte in four studies (Blatter et al., 2021; Dong et al., 2019; He et al., 2019; Leininger et al., 2021).

Another goal in wastewater treatment is to minimize the areal footprint of the treatment plant. The MFC footprint can be reduced by increasing the electrode packing density. The electrode packing density has been previously reported to be one of the key parameters for scaling up MFCs and is defined as the total projected area of the electrodes

normalized by the reactor volume (Logan et al., 2015). Higher electrode packing densities enable larger volumetric power densities by using smaller reactor sizes, accomplishing wastewater treatment in a more compact unit. Volumetric power densities produced by pilot MFCs increased with electrode packing density (Fig. 2, insert). For example, increasing the electrode packing density from 5.2 to 24 m^{-2} m^{-3} in air cathode MFCs increased the volumetric power density by 450% (from 318 to 1435 mW m^{-3}) (Hiegemann et al., 2019; Rossi et al., 2022b). In liquid catholyte MFCs with separator and aerated catholyte, the power density was 300 mW m^{-3} with a packing density of 6.7 m^{-2}, and increased to 510 mW m^{-3} with a packing density of 15 m^{-2} m^{-3} (Blatter et al., 2021; Dong et al., 2019). The largest volumetric power density in the liquid catholyte MFCs was obtained by Walker et al. (2020) by using a large electrode packing density of 134 m^2 m^{-3}, approximately 20 times larger than that of the other liquid catholyte MFCs (7 m^2 m^{-3}). Likely, using urine in that study, characterized by a low solid content allowed to use a reduced spacing between the electrodes and minimize clogging of the reactor which could have been a concern in the other liquid catholyte MFCs using domestic wastewater. Air cathode MFCs and liquid catholyte MFCs showed different but proportional increases in volumetric power density with increased packing densities (air cathode, R^2 = 0.61; liquid catholyte R^2 = 0.96 – excluding the urine study) (Fig. 2, insert).

4. Wastewater treatment based on COD removal

Liquid catholyte MFC configuration produced effluents with lower COD than air cathode MFCs when treating domestic wastewater, suggesting a tradeoff in higher power densities and COD reduction for the two configurations (Fig. 3). The reported effluent COD was 247 ± 206 mg L^{-1} (70 – 640 mg L^{-1}) in six air cathode MFC studies (Babanova et al., 2020; Das et al., 2020; Feng et al., 2014; Hiegemann et al., 2019; Sugioka et al., 2022) and 151 ± 223 mg L^{-1} (25–596 mg L^{-1}) for the liquid catholyte MFCs (Blatter et al., 2021; Dong et al., 2019; He et al., 2019; Leininger et al., 2021; Liu et al., 2017; Mohamed et al., 2021). However, in two studies using the liquid catholyte configuration, the effluent COD was very high, likely due to the type of wastewater used in those studies. For example, Leininger et al. (2021) used a mix of digestate and sewage which resulted in a large effluent COD content (596 mg L^{-1}), also coupled with a low COD removal rate (Leininger et al., 2021). The study by Walter et al. was focused on treating urine while producing sufficient power to sustain illumination of the toilets. The COD removal was approximately 69%, however, due to the large COD content of the urine (6000 ± 1000 mg L^{-1}), the effluent had the largest COD (2000 ± 500 mg L^{-1}) among the other liquid catholyte studies (151 mg L^{-1}) (Walter et al., 2020). In the other five studies the average effluent COD was 40 ± 13 mg L^{-1} (Blatter et al., 2021; Dong et al., 2019; He et al., 2019; Liu et al., 2017; Mohamed et al., 2021). On a percentage basis the liquid catholyte MFCs removed an average of 73 ± 25% of the influent COD, approximately 21% more than the air-cathode MFCs (52 ± 19%). The average HRT was lower for the liquid catholyte MFCs (15 h) compared to the air cathode configuration (38 h), indicating that the higher treatment efficiencies of the liquid catholyte MFCs was not due to longer treatment times. Lower effluent COD concentrations for the liquid catholyte MFCs could be due to the COD removed by biofilm or suspended microorganisms using oxygen from air sparged in the cathode chamber. Increasing the oxygen availability can improve organic matter removal, resulting in a combined MFC/aerated treatment (Cha et al., 2010).

As a result of the high COD concentrations in the effluent of the air cathode MFCs effluent, and for some of the liquid catholyte MFCS, additional treatment would be required to further reduce the COD to a level suitable for discharge. Typically, the BOD is about half the COD. Thus, the nominal regulation of effluent BOD to <30 mg/L would translate to an effluent COD of ~60 mg/L. MFCs have been previously integrated with an additional anaerobic treatment process to further

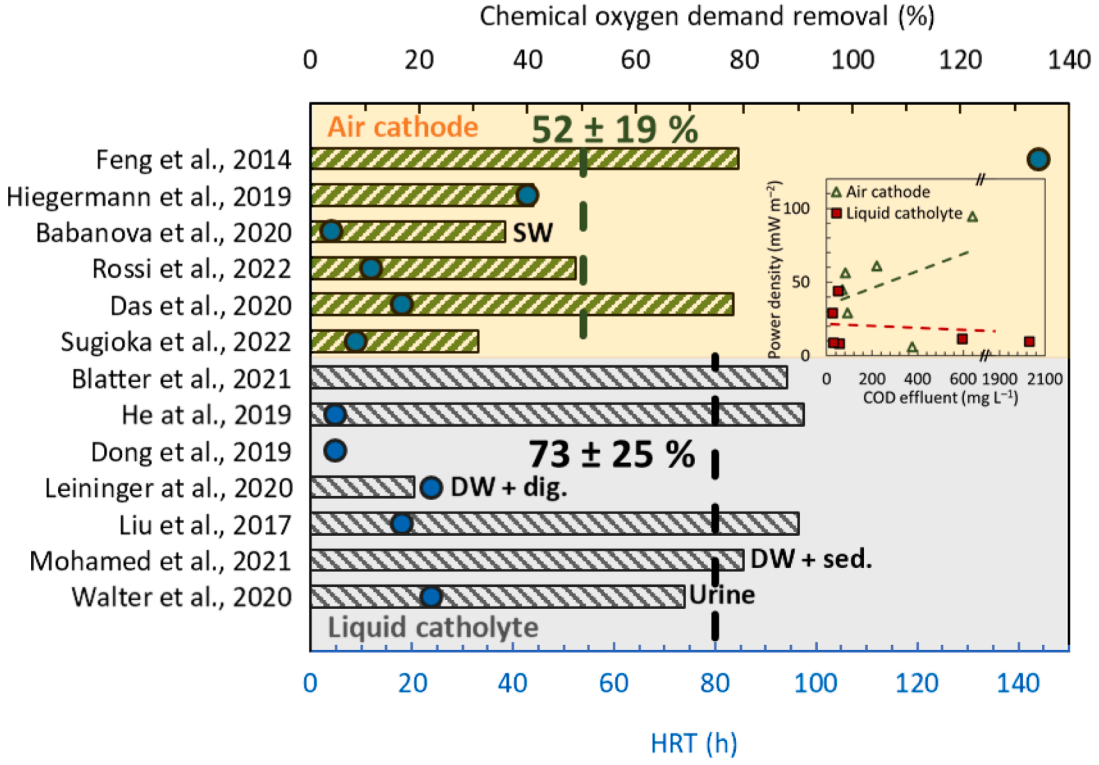

Fig. 3. COD removal in pilot scale MFCs (bars) at the correspondent HRT (circles). The acronym next to the column indicates the MFCs fed an influent different from domestic wastewater (swine wastewater, SW; domestic wastewater and digestate, DW+dig.; domestic wastewater and river sediment DW+sed.). The dashed lines represent the average COD removal for the liquid catholyte or air cathode configuration. In the insert is showed the impact of the effluent COD on the MFC power density.

reduce the COD. For example, effluent from MFC was treated in fluidized bed membrane bioelectrochemical reactor (MBER), reducing the COD to 28 ± 11 mg L^{-1} (MFC COD removal = 59%; MFC/MBER COD removal = 95%) (Li et al., 2014). In a different study, the MFC effluent (COD = 330 mg L^{-1}) was fed to an ultrafiltration/nanofiltration unit, producing a final COD of only 4 mg L^{-1} (Zinadini et al., 2017). Osmotic membrane bioreactors were used to reduce the COD concentration of an MFC effluent from 70 to 20 mg L^{-1} (Hou et al., 2016) while minimizing sludge production and therefore reducing membrane fouling. MFCs can also be combined with an anaerobic fluidized bed membrane bioreactor (AFMBR) to produce a final effluent COD of 16 ± 3 mg L^{-1}, requiring minimal energy input, comparable to the energy produced by the MFC (Ren et al., 2014). Innovative treatment technologies for reducing the MFC effluent COD content were also tested al larger scales. The MFC effluent of a pilot scale MFC was treated in a 600 L biofilter (BF), combining aerobic treatment and ultrafiltration, and reducing the COD content from 220 ± 105 mg L^{-1} in the MFC effluent to 36 ± 23 mg L^{-1} in the BF effluent (Rossi et al., 2022b). Thus, there are several different technologies available to reduce the COD content in MFC effluent before discharge, however, future studies should elucidate the overall energy consumption of these treatment processes at a pilot scale.

There was no significant relationship between effluent COD and area power density, due in part to the different electrode configurations (Fig. 3 insert). For example, in air cathode MFCs, the highest COD content in the effluent (640 mg L^{-1}) produced the highest power density (95 mW m^{-2}) in Babanova et al. (2020) when brush anode and gas diffusion cathodes were used, but the second highest COD content (375 mg L^{-1}) produced a maximum power density of only 6 mW m^{-2} in Das et al., using different electrodes (Das et al., 2020). The MFC reactor used by Das et al. (2020) used anode felt pressed against a ceramic membrane, which could have produced a higher mass transfer resistance than brushes and separators, thus lowering the performance even though the COD content in the effluent was large. If the study by Das et al. (2020), is excluded from the air cathode analysis, and only reactors using brush anodes and gas diffusion cathodes are considered, then there is a good correlation between the effluent COD and the MFC performance, with reactors producing larger power with higher COD content in the effluent (Figure S1). The MFCs with liquid catholytes showed limited impact of the COD effluent on the power density, with MFCs producing between 8 and 44 mW m^{-2} with a COD effluent < 100 mg L^{-1} and 11 mW m^{-2} with a COD effluent of 596 mg L^{-1}. The study using urine produced a low power density (10 mW m^{-2}) compared to the other studies, even though the COD content was the largest (6000 ± 1000 mg L^{-1}). It is not possible to compare nitrogen and phosphorus removals for these systems as these two nutrients were only reported in two of these 13 pilot-scale studies. In the future, N and P removals should be measured and reported to better identify the downstream processes needed to produce a treated effluent that can meet discharge limits.

5. Improving pilot MFC performance

The above analysis of pilot-scale performance suggests there are many factors that can limit MFC performance in terms of power production and COD removal. The following suggestions are made for improving reactor design and MFC performance as well as for obtaining data that can help in understanding the factors that are limiting performance such as electrode and solution resistances, and COD concentrations.

Develop cost analysis. Future studies on pilot-scale systems should include some analysis of the cost for installation and operation compared to existing technologies. Most of the studies reviewed here used custom made cathodes and reactor configuration. A recent technoeconomic analysis indicated that MFCs can potentially be economically beneficial for conventional wastewater treatment, with estimated yearly costs (€1700–2300/yr) approaching those for conventional wastewater treatment (Savla et al., 2021). However, that analysis did not consider the cost for electrode or membrane replacements and when they might be needed. Thus, future pilot MFCs studies should clarify the stability of performance and the potential frequency for part replacements. In a previously developed life cycle cost assessment (LCCA) based on the results obtained from a pilot-scale MFC reviewed here it was estimated that electrode cost primarily contributed to initial capital costs while electrode replacement due to fouling and chemical consumption for cleaning cathodes was the main driver in operational costs for MFC (Cropek, 2021; Rossi et al., 2022b). The system was designed to treat approximately 19,000 L d^{-1} of domestic wastewater and compared with a state-of-the-art aerobic membrane bioreactor (MBR) treatment system for small-scale on-site wastewater systems. It was estimated that, despite initial capital costs that were larger for the MFC system compared to MBR, the estimated annual energy cost to operate the MFC-BF system was approximately 50 × lower than that of the conventional MBR system due to the absence of continuous aeration and the positive electrical energy generated by the MFCs. Future studies should elucidate the capital and operational costs associated with MFC operation and installation and develop economical methods to scale up electrochemically active and robust electrodes for pilot-scale MFCs. Additionally, the organic matter effectively converted in electricity during MFC operation should be measured and the coulombic efficiency reported to identify the optimal reactor architecture to maximize it.

Improve solution chemistry. The buffer capacity of the wastewater plays a critical role in determining MFC performance as both cathodic and anodic reactions are pH dependent (Rossi et al., 2020a; Torres et al., 2008). At the cathode, the oxygen reduction reaction produces hydroxide ions, increasing the local electrode pH while the anodic oxidation of organic matter at the anode generates protons, as described in the following equations assuming acetate oxidation at the anode (near neutral pH) and oxygen reduction at the cathode (neutral to alkaline pH):

$$CH_3COO^- - +4H_2O \rightarrow HCO_3^- + H_2CO_3 + 8e^- - +8H^+ \quad (3)$$

$$O_2 + 2\ H_2O + 4e^- \rightleftarrows 4OH^- \quad (4)$$

Due to the negligible concentration of H^+ and OH^- (0.1 μM) compared to other ions present in wastewater at pH 7, protons and hydroxide ions are not effectively transported away from the electrode, and tend to accumulate near the electrode surface, producing large differences in the local pH environment (Popat and Torres, 2016; Rossi et al., 2020a; Torres et al., 2008). A high cathode pH decreases the performance by reducing the cell voltage by 59 mV/pH following the Nernst equation (Popat et al., 2012). The acidic pH at the anode limits the maximum current density that can be delivered by the bioanode, due to the lower performance of exoelectrogenic bacteria in solutions when the pH decreases below 7 (He et al., 2008; Popat and Torres, 2016). Pilot scale MFCs typically use domestic and industrial wastewaters with low alkalinity, compared to tests performed in the laboratory using media with high buffer capacity. It would be beneficial to clarify the impact of the buffer capacity of the wastewater on the performance of pilot-scale MFCs and investigate the use of wastewater with large alkalinity, enabling better control of the local electrode pH, improving current densities by maintaining an anode pH closer to neutrality and higher cell voltages by limiting cathode basification (Popat et al., 2012).

Reducing the electrode resistances. The MFC internal resistance is the sum of the solution, anode (R_{An}) and cathode (R_{Cat}) resistances, and thus the electrode resistances must be reduced to increase power production of larger-scale MFCs (Rossi et al., 2019). The electrode resistances can be obtained by measuring the electrode potentials as a function of current using the electrode potential slope (EPS) method (Rossi et al., 2019). It has been shown that the electrode resistances will increase with electrode sizes and thus reduce performance at larger scale. For example, scaling up an air cathode from 7 to 4800 cm^2, using the same electrode configuration (stainless-steel mesh current collector pressed against an activated carbon catalyst and a PTFE hydrophobic layer), increased the

cathode resistance by 10 times, from 54 ± 7 mΩ m^2 (7 cm^2) to 555 ± 24 mΩ m^2 (4800 cm^2) using domestic wastewater as a feed. The higher electrode resistance was calculated to be due to increased resistivity of the electrode with its size due to the longer distances needed for charge transfer from the reaction point to the collection wire location (Cheng et al., 2014b). Another factor that can impact an air-cathode performance is the water pressure, as flooding of the cathode with water will decrease electrode performance (Cheng et al., 2014a). It was previously showed that the resistance of brush anodes was less impacted by the increase in size than the cathode resistance (Rossi et al., 2019). Increasing the brush anode area facing the cathode by 1270 times, from 4.9 cm^2 (2.5 cm by 2.5 cm) to 6200 cm^2 (22 brushes, 5.1 cm in diameter by 61 cm long), increased the anode resistance by 3.2 times (75 ± 9 mΩ m^2 to 238 ± 18 mΩ m^2), compared to 10 times for the cathode. Thus, the final cathode resistance was about 2.3 times that of the anode in the pilot-scale reactor. It is important that the three components of the resistances be reported in MFC studies in order to better understand the specific reasons for the change in internal resistance with reactor size.

Minimize electrode spacing. Coupled with electrode resistance, solution resistance represents a contributor to the MFC internal resistance. To maximize power densities the distances between the electrodes needs to be reduced to lower solution resistance. The solution resistance, R_Ω (Ω m^2), is:

$$R_\Omega = \frac{l}{\sigma} \quad (5)$$

where l is the electrode spacing, and σ is the solution conductivity. Therefore, the solution resistance increases in direct proportion to the electrode spacing and with lower solution conductivities (Logan et al., 2019; Rossi et al., 2019). Highly saline solutions are more conductive, but they inhibit microbial activities and thus power generation by bacteria colonizing the anode (Rossi et al., 2020b). It is important for the electrodes not be too close as this can lead to short circuiting if one electrode contacts the counter electrode. Inexpensive and non-conductive cloth or ceramic separators can be placed between the electrodes to avoid short circuiting. Air-cathode MFCs do not require a separator or solution between the separator and the cathode, and therefore they can have smaller spacing compared to liquid catholyte MFCs which have electrolytes in both chambers.

Despite being a large contributor to the MFC internal resistance in small size reactors, the solution resistance in pilot-scale MFCs is minor compared to anode and cathode resistances. For example, it was previously reported that solution resistance increased from 87 to 93 mΩ m^2 by scaling up an MFC from a projected area of 7 cm^2 to 6200 cm^2 due to a small increase in electrode spacing to avoid short circuiting. However, in that same study it was reported that anode resistance increased by 3 × (from 75 ± 9 mΩ m^2 to 238 ± 18 mΩ m^2) while cathode resistance increased by 10 × (from 54 ± 7 to 555 ± 24 mΩ m^2) (Rossi et al., 2019a). Thus, solution resistance has a smaller impact on the performance in large-scale systems compared to anode and cathode resistance, but reducing electrode spacing can also improve the solution chemistry and minimize pH imbalances between the electrodes (Rossi et al., 2022a).

Maintain sufficiently high COD concentrations for maximizing power production. When the COD concentration gets too low power production can decrease due to insufficient mass transfer of substrate to the anodic biofilm (Zhang et al., 2015). In small MFCs (28 mL), the current density produced by bioanode (3.5 A/m^2) rapidly decreased when the COD concentration decreased to <200 mg/L, indicating that the performance of MFCs was limited by the substrate availability below this concentration (Stager et al., 2017; Zhang et al., 2015). Power production in pilot scale MFCs therefore can be greatly decreased if the reactor is operated to achieve COD levels suitable for effluent discharge. The impact of COD concentration on power generation using wastewater can be difficult to evaluate due to the highly variable nature of the wastewater composition over time. For this reason, it is important to obtain both operational data at typical COD concentrations as well as polarization data at different influent CODs.

Innovations in architecture and materials can improve performance. The design and engineering of pilot-scale systems requires developing reliable methods and equations to predict the performance at different scales. Over the last decade, innovations have improved the performance of lab-scale MFCs fed solutions with high buffer and substrate content, largely by optimizing the cell architecture to overcome solution chemistry limitations and reduce internal resistances. Using high substrate and buffer concentrations reduces anode and cathode resistances, while close electrode spacing enable smaller solution resistances (Rossi et al., 2020a). However, changes using well buffered media have not translated to comparable increases in power densities for wastewater-fed reactors (Fig. 4). Since 2013, the maximum power density of MFCs fed media with high buffer capacity and substrate content increased at an average rate of 0.83 W m^{-2} each year. Over the same timeframe, the maximum power of wastewater fed MFCs increased by only 0.05 W m^{-2} per year.

Novel architectures are being investigated in small scale MFCs to overcome limitations due to the wastewater composition. It was recently shown that a closely stacked configuration with the electrodes placed on either side of an anion exchange membrane to minimize the impact of local pH gradients and low solution conductivity improved power generation in MFCs fed media with low conductivity and buffer capacity (4 mM carbonate buffer), and produced a maximum power density of 1.34 ± 0.03 W m^{-2} (Rossi et al., 2021). The solution conditions were meant to reflect the composition of a typical domestic wastewater. However, even in an optimized configuration using closely stacked electrodes, the solution composition can have a large impact on the performance. For example, in a similar MFC configuration using well buffered media, the maximum power density was increased by 7 times, to 8.8 W m^{-2}. Thus, even if better configurations are developed to minimize the MFC internal resistance, the low wastewater conductivity, buffer capacity and substrate content can still largely impact the reactor performance. In addition, if wastewater is used in closely stacked configurations, pretreatment is likely needed to minimize total suspended solids that could lead to clogging of the cell. Moreover, membranes represent an additional capital cost during scale up. Laboratory experiments can therefore inform on changes that can improve reactor performance, but ultimately

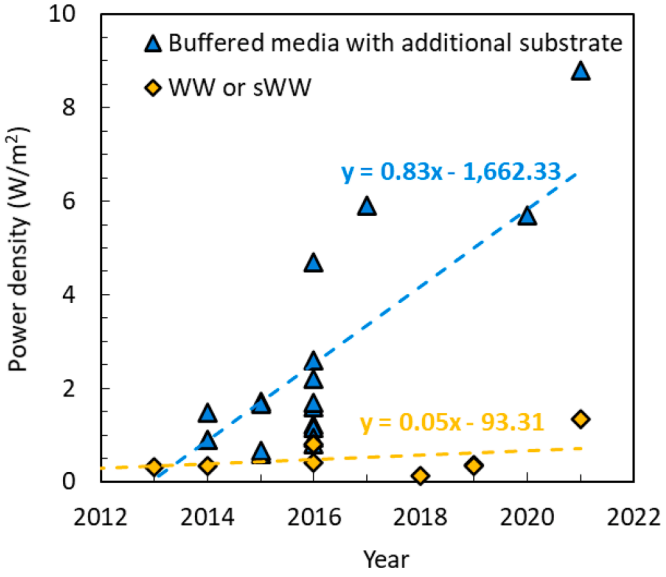

Fig. 4. Performance of lab-scale MFCs (volume < 50 mL) using similar configuration fed synthetic media with buffer capacity and substrate concentration or wastewater.

tests will need to be conducted at pilot scales to fully test the impact of new designs under actual operational conditions that can include highly variable pH, buffer capacities, conductivities, and substrate concentrations.

6. Conclusions

The analysis of the performance of 13 pilot scale MFCs with an overall volume larger than 100 L indicated that air-cathode MFCs produce more power than liquid catholyte, while requiring lower energy input by avoiding aeration of the cathode chamber. However, liquid catholyte MFCs produced effluents with lower COD content at similar HRTs than that of air cathode MFCs, suggesting that a tradeoff exists between air cathode MFCs, which generate more power but produce effluent with high COD content and liquid catholyte MFCs, generating low power and needing additional energy for aeration but producing an effluent with low COD content. Downstream processes should be identified to further decrease the COD concentration in the effluent of pilot scale air cathode MFCs and meet specification for discharge. Brush anodes and activated-carbon cathodes produced the highest power density in air cathode pilot MFCs, while using membranes and separator in a closed stacking configuration was detrimental for the performance. Pilot scale liquid catholyte MFCs needs to be developed using separators between anode and cathode, and aeration of the catholyte is required to increase maximum power density. The analysis presented here clearly indicates the most promising pilot scale MFC configurations for maximize power generation and wastewater treatment and suggested gaps in the current literature and understanding that need to be filled in future studies to move the MFC technology forward. Pilot scale MFCs have been effectively integrated into the existing wastewater treatment infrastructure in the studies presented here, enabling low cost wastewater treatment technologies.

CRediT authorship contribution statement

Ruggero Rossi: Formal analysis, Writing – original draft. **Bruce E. Logan:** Formal analysis, Writing – original draft.

Declaration of Competing Interest

The authors declare no competing interests.

Data Availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.119179.

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