Industrial wastewater treatment with a bioelectrochemical process: assessment of depuration efficiency and energy production
Daniele Molognoni, Stefania Chiarolla, Daniele Cecconet, Arianna Callegari and Andrea G. Capodaglio

ABSTRACT
Development of renewable energy sources, efficient industrial processes, energy/chemicals recovery from wastes are research issues that are quite contemporary. Bioelectrochemical processes represent an eco-innovative technology for energy and resources recovery from both domestic and industrial wastewaters. The current study was conducted to: (i) assess bioelectrochemical treatability of industrial (dairy) wastewater by microbial fuel cells (MFCs); (ii) determine the effects of the applied organic loading rate (OLR) on MFC performance; (iii) identify factors responsible for reactor energy recovery losses (i.e. overpotentials). For this purpose, an MFC was built and continuously operated for 72 days, during which the anodic chamber was fed with dairy wastewater and the cathodic chamber with an aerated mineral solution. The study demonstrated that industrial effluents from agrifood facilities can be treated by bioelectrochemical systems (BESs) with >85% (average) organic matter removal, recovering power at an observed maximum density of 27 W m⁻³. Outcomes were better than in previous (shorter) analogous experiences, and demonstrate that this type of process could be successfully used for dairy wastewater with several advantages.

Key words | bioelectrochemical systems, bioenergy, dairy industry wastewater, eco-innovative technologies, electro-active bacteria, wastewater treatment

INTRODUCTION
The pursuit of renewable energy sources, efficient industrial processes, and energy and chemicals recovery from wastes is regarded, at present, as a high research priority. Technological applications in decentralized treatment facilities and renewable energy sources are being proposed and investigated in different sectors, including wastewater management (Capodaglio & Callegari 2016; Capodaglio et al. 2016a, 2017; Capodaglio 2017). Wastewater treatment, necessary for the preservation of water and environmental quality, often requires considerable energy inputs to obtain desired targets. On average, the energetic consumption of conventional-type (aerobic) wastewater treatment processes is about 0.2 to 0.8 kWh m⁻³, depending on various factors (wastewater characteristics, location and, not least, specific process type). In the case of aerobic processes, the energy used for mixed liquor aeration alone can be more than 50% of the total energy used by the facility (Spellman 2013). Notwithstanding possible energy recovery from traditional-type biological processes (Capodaglio et al. 2016b; Capodaglio & Callegari 2017), they are still considered energy-intensive technologies.

Microbial fuel cells (MFCs) provide a potentially attractive alternative to traditional wastewater treatment processes (Capodaglio et al. 2016c). These are bioelectrochemical systems (BESs) based on electro-active bacteria (EABs) catalysis, allowing direct conversion of chemical energy contained in organic biodegradable substrates into electrical energy (Rabaey & Verstraete 2005). In MFCs, EABs catalyse one or both oxidation and reduction reactions, making up a complete redox system, with each reaction occurring in a separate chamber (i.e. anode and cathode). These chambers, containing the respectively
Bioelectrochemical processes are characterized by several potential advantage, compared to other state-of-the-art wastewater treatment technologies. Above all, they happen to be extremely versatile in terms of treatable substrates. Their use in treating simple substrates, such as: glucose (Chaudhuri & Lovley 2003), volatile fatty acids (Daghio et al. 2015) and alcohols (Kim et al. 2007) have been reported. Examples of syngas and biochemical product production (bioalcohol, acetate, butyric acid) with BESs have also been recently described (Kumar et al. 2017). MFCs have also been employed with complex mixtures, such as: domestic wastewater (Capodaglio et al. 2015; Koók et al. 2016), brewery wastes (Wang et al. 2008), dairy wastes (Kelly & He 2014; Faria et al. 2017) and agrifood industry effluents (Abourached et al. 2016). Even in the case of landfill leachates (usually considered somewhat refractory to biological treatment), organic removal rates up to 7.0 kg chemical oxygen demand (COD) m⁻³ d⁻¹ have been reported (Puig et al. 2011). These rates were greater than those of common aerobic processes (0.5–2 kg COD m⁻³ d⁻¹) and close to those of anaerobic digestion (8–20 kg COD m⁻³ d⁻¹).

Although showing high treatment capacity and additional advantages over other biological processes (e.g. low biomass yields, possibility of operating at low temperatures, lack of substantial aeration needs, direct electricity conversion), MFCs are still characterized by drawbacks, including low electricity production (reported range is 10–100 W m⁻³ of total reactor volume), limiting the industrial appeal of this technology (Rozendal et al. 2008).

Attempts at MFC optimization include development of cheaper (non-platinum) cathodic catalysts (Santoro et al. 2015), electrode modification and combination of different constituent materials (Fiset & Puig 2015), development of biocathodes (Xia et al. 2015), hydraulic and electrical combination of multiple units (Ieropoulos et al. 2008) and methods for handling external resistance (Molognoni et al. 2014).

Agrifood substrates (pig manure, brewery, dairy or winery effluents) are particularly suited for MFC application, due to the high organic content (COD up to 10 g L⁻¹) and biodegradability (biochemical oxygen demand (BOD)/COD ratio usually higher than 60%) (Cercado-Quezada et al. 2010). BES application to dairy wastewaters has been investigated in recent years, as summarized in Table 1, where it can however be seen that observed COD removal efficiency and extracted power density are not necessarily directly related. This depends on cell construction (materials and shape) and on the microbial population balance dynamically established in the system. Factors affecting biofilm formation and maturation on electrodes, linked to system design (materials and configuration, e.g. electrode materials, type of cathode), operating parameters (e.g. concentration and type of substrate, pH, temperature) and biological parameters (e.g. diversity and abundance of microbial resource, type of microbial culture) are investigated so as to overcome current drawbacks (Saratale et al. 2017a). The use of complex substrates increases BES bacterial community complexity, and can lead to interrelated connections between single microbes (Vilajeliu-Pons et al. 2016). Anode chamber anaerobic conditions may lead

<table>
<thead>
<tr>
<th>MFC configuration</th>
<th>Feed mode</th>
<th>Test duration</th>
<th>Inoculum source</th>
<th>dP (W m⁻³)</th>
<th>η COD (%)</th>
<th>CE (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC-MFC</td>
<td>Batch</td>
<td>n.a.</td>
<td>Sludge from anaerobic digester</td>
<td>0.08</td>
<td>≈100</td>
<td>2</td>
<td>Antonopoulou et al. (2010)</td>
</tr>
<tr>
<td>DC-MFC</td>
<td>Batch</td>
<td>n.a.</td>
<td>Industrial wastewater</td>
<td>1.1</td>
<td>95</td>
<td>14</td>
<td>Venkata Mohan et al. (2010)</td>
</tr>
<tr>
<td>SC-MFC</td>
<td>Batch</td>
<td>n.a.</td>
<td>Sludge from anaerobic digester</td>
<td>0.44</td>
<td>82</td>
<td>2</td>
<td>Velasquez-Orta et al. (2011)</td>
</tr>
<tr>
<td>Tubular</td>
<td>Batch</td>
<td>n.a.</td>
<td>Sludge from activated sludge reactor</td>
<td>20.2</td>
<td>91</td>
<td>27</td>
<td>Mardanpour et al. (2012)</td>
</tr>
<tr>
<td>SC-MFC</td>
<td>Batch</td>
<td>n.a.</td>
<td>Dairy wastewater + Shewanella oneidensis</td>
<td>0.41</td>
<td>86</td>
<td>3</td>
<td>Nimje et al. (2012)</td>
</tr>
<tr>
<td>DC-MFC</td>
<td>Batch</td>
<td>n.a.</td>
<td>Dairy wastewater</td>
<td>2.7</td>
<td>91</td>
<td>17</td>
<td>Elakkiya &amp; Matheswaran (2015)</td>
</tr>
<tr>
<td>DC-MFC</td>
<td>Continuous</td>
<td>30 days</td>
<td>Dairy wastewater + Lactobacillus pentosus</td>
<td>0.02</td>
<td>62</td>
<td>n.d.</td>
<td>Vilas Boas et al. (2015)</td>
</tr>
<tr>
<td>DC-MFC</td>
<td>Continuous</td>
<td>20 days</td>
<td>Pre-screened municipal wastewater</td>
<td>1.9</td>
<td>63</td>
<td>24</td>
<td>Faria et al. (2017)</td>
</tr>
</tbody>
</table>

n.a., not applicable; n.d., not determined/not specified; SC-MFC, single-chamber MFC; DC-MFC, dual-chamber MFC; dP, power density; η COD, COD removal efficiency; CE, Coulombic efficiency.
to the appearance of unwanted side-reactions such as methanogenesis or heterotrophic denitrification (Capodaglio et al. 2015). It has also been demonstrated that in MFC processes, high fermented substrate concentrations favor methanogenic activity compared with exoelectrogenesis, reducing process’ Coulombic efficiency (hereafter CE) (Pinto et al. 2010).

The dairy industry is particularly relevant in Italy, as the country is one of the leading producers in the world in this sector, with just 2.2% share of world’s milk production, but over 6% of cheese production. In industrial cheese-making, 2–4 liters of wastewater are produced per liter of processed milk (APAT 2007), generating 19,106 m³ yr⁻¹ of process water, rich in organic matter (easily biodegradable organic substrates, lactose, but also slowly biodegradable lipids and proteins) and other nutrients (Table 2). Nitrogen is mainly present in organic form, bonded in milk proteins, while phosphorus is mainly in orthophosphate form (Fang & Yu 2000), while additives used for process and facilities disinfection can significantly affect the pH and alkalinity of wastewater produced.

Literature concerning dairy (industrial) wastewater treatment has shown nonhomogeneous results from mainly batch or short-term continuous studies. The highest reported power density so far (20.2 W m⁻³) was achieved by Mardanpour et al. (2012), using a tubular MFC loaded with 0.5 mg Pt cm⁻² catalyst at the cathode. Other studies have demonstrated that cathode catalysts may be avoided without negative effects on organic matter removal efficiency, but with considerable reduction of power density (90% lower) and CE (44% lower) (Venkata Mohan et al. 2010; Elakkiya & Matheswaran 2015). Applications of continuously fed MFCs treating dairy wastewaters achieved worse results than batch systems, in terms of both power density and COD removal, but achieved higher CEs (Faria et al. 2017). MFC electrical performance usually increases with increasing organic loading rates (OLRs) at the anode (Venkata Mohan et al. 2010); on the other hand, Elakkiya & Matheswaran (2015) noticed that high anolyte’s COD concentration (up to 2,800 mg L⁻¹) can cause membrane fouling and a gradual decrease of electric production. Also, high loads of proteins and lipids can lead to the development of unsustainably thick anodic biofilm, which suffer from high concentration overpotentials (Cercado-Quezada et al. 2010).

The aim of this study is to evaluate the extended performance of an MFC, continuously operated for over 3 months with undiluted, real dairy wastewater collected at the treatment plant (WWTP) of a large-scale cheese factory in the vicinity of the authors’ institution, that requested to be kept un-named. To the authors’ knowledge, this study is to date the longest-running MFC study on dairy wastewater. High pollutant removal efficiency and improved sustainability of the wastewater treatment process may tempt many such facilities to switch their wastewater treatment technology from the usual activated sludge technology to MFC-based processes. For this to happen, greater knowledge of the process and the demonstration of consistent, achievable results are however needed.

**MATERIALS AND METHODS**

**Experimental setup**

A dual-chamber MFC was built according to a previously described design (Molognoni et al. 2016). It consists of an anode and a cathode chamber in a methacrylate cell, separated by a cationic exchange membrane (CEM) (CMI-7000, Membranes International Inc., USA) (Figure 1). The two chambers are filled with 800 g each of granular graphite (diam. 1.5–5 mm), decreasing their free volumes to 435 mL net anodic compartment (NAC) and 420 mL net cathodic compartment (NCC), respectively. Thin graphite rod electrodes (250 × 4 mm, Sofacel, Spain), previously washed in 1 M HCl and 1 M NaOH solutions to remove any metal and organic contamination, are introduced in each chamber for the external electrical connection. Cell circuits are equipped with an external 33 Ω resistance. This was chosen to be as close as possible to their assumed static internal resistance, based on previous experiences with similar cells.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total suspended solids (TSS)</td>
<td>mg TSS L⁻¹</td>
<td>250–2,700</td>
</tr>
<tr>
<td>Chemical oxygen demand (COD)</td>
<td>mg O₂ L⁻¹</td>
<td>650–3,000</td>
</tr>
<tr>
<td>Biological oxygen demand (BOD₅)</td>
<td>mg O₂ L⁻¹</td>
<td>300–1,400</td>
</tr>
<tr>
<td>Organic nitrogen (N₉)</td>
<td>mg N L⁻¹</td>
<td>10–140</td>
</tr>
<tr>
<td>Ammonium nitrogen (N-NH₄)</td>
<td>mg N L⁻¹</td>
<td>10–20</td>
</tr>
<tr>
<td>Nitrates (N-NO₃)</td>
<td>mg N L⁻¹</td>
<td>10–20</td>
</tr>
<tr>
<td>Phosphates (P)</td>
<td>mg PO₄ L⁻¹</td>
<td>10–130</td>
</tr>
<tr>
<td>Chlorides (Cl)</td>
<td>mg Cl L⁻¹</td>
<td>50–500</td>
</tr>
<tr>
<td>pH (–)</td>
<td>pH units</td>
<td>4–12</td>
</tr>
<tr>
<td>Alkalinity (HCO₃)</td>
<td>mg HCO₃ L⁻¹</td>
<td>250–650</td>
</tr>
</tbody>
</table>

Strained dairy wastewater collected periodically from a large local cheese factory, owned by a multinational group, was used as anode fuel. The waste, stored at 4°C to limit organic matter degradation prior to use, was fed through collapsible cans, at ambient temperature (23 ± 3°C) and light-shielded, to the anode. Semi-continuous feeding, consisting of a cyclical hourly routine, pumping a flow of 3 L d⁻¹ for 20 min every hour, and no flow for 40 min, was adopted to limit the amount of wastewater stored onsite. This resulted in an average feed rate to the cell of 1 L d⁻¹, although it was clear from previous tests that the cell had a much higher capacity. The cathode was fed at the same flow-rate with oxygen-saturated phosphate buffer medium (10 mM, pH 7) containing 819 mg L⁻¹ Na₂HPO₄, 507 mg L⁻¹ NaH₂PO₄, 1,000 mg L⁻¹ NaHCO₃, 130 mg L⁻¹ KCl, 310 mg L⁻¹ NH₄Cl and other trace elements (modified from Xia et al. 2014). An internal recirculation loop (50 L d⁻¹) within each chamber was added to maintain well-mixed conditions so as to minimize internal concentration gradients and the chance of clogging the granular graphite bed. The recirculation line of the cathode was also saturated with oxygen in an external aerator device.

The MFC was operated at ambient temperature for the entire experiment. Anodic potential was monitored with an Ag/AgCl reference electrode (+197 mV vs standard hydrogen electrode; SHE). Anode and overall cell potentials were recorded at 1-min intervals by means of a multifunction acquisition board (NI USB-6008, National Instruments Italy, Milan) connected to a LabVIEW™ equipped PC.

**Inoculation and operation**

Both anode and cathode chambers were each inoculated with 2.5 L of a solution composed of 30% (aerobic) activated sludge from the plant treating the dairy waste, 10% dairy wastewater and 60% distilled water, in closed electric loop mode, with an external 33Ω resistance, according to the strategy illustrated by Molognoni et al. (2014). In the anode chamber inoculum, 2-bromoethane sulfonate (2-BES) was also added at 10 mM concentration to inhibit initial methanogen biomass growth (Chae et al. 2013). During inoculation, a low recirculation rate (20 L d⁻¹) was maintained to promote, at the same time, adequate internal mixing and bacteria fixation onto the electrode and graphite surfaces.

After 3 days, the voltage produced exceeded 100 mV, and operation was switched to semi-continuous mode with undiluted wastewater, as described earlier. Collapsible storage containers allowed feeding without exposing wastewater to the atmosphere for prolonged periods. A new load of influent solution was added to the containers approximately every 3–5 days, to maintain quasi-stable COD concentration, from the cold-stored sample collected at the dairy plant. Even with regular pumping rates, measured anodic OLRs varied considerably during the experiment (0.2–6.6 kg COD m⁻³ d⁻¹). Such unplanned perturbations...

![Figure 1](https://iwaponline.com/wst/article-pdf/77/1/134/211396/wst077010134.pdf)
allowed the study of the influence of this parameter on MFC performance, in relation to both wastewater treatment efficiency and power generation.

**Analyses and determinations**

Determination of COD was regularly performed at each new sample collection at the treatment facility (COD\textsubscript{in}), and every 2–5 days from the cell effluent (COD\textsubscript{out}), according to Standard Methods (APHA 2005). Anodic OLRs were calculated as the daily organic matter concentration (as COD) divided by the anode’s hydraulic retention time, adjusted every day, by dividing the known (fixed) NAC volume by the daily flow-rate value. Organic matter removal efficiency (η\textsubscript{COD} -%) was determined as described in Molognoni et al. (2014). Conductivity and pH were measured once a week for both anode and cathode influents and effluents (IntelliCAL\textsuperscript{™} probes + HQd\textsuperscript{™} Digital Meter, Hach Lange, Italy). Since their values were not substantially affected by the process (Table 3), no further mention of these will be made.

Current (I) and power (P) values were determined (Ohm’s Law) from MFC voltage measurement (V) at 1-min intervals. Power and current densities (dP and dl) were calculated dividing the respective values by the NAC volume of the cell. Polarization curves were determined using a potentiostat (NEV3, Nanoelectra, Spain) by imposing a linear potential decrease of 0.5 mV s\textsuperscript{−1} from the open circuit voltage (OCV) to a cell voltage of 0 mV. Internal resistance was calculated from polarization curves, by the power density peak method (Logan et al. 2006). Anodic CE was calculated from daily (average) data of current intensity and flow-rate. Organic matter removal was estimated based on COD measurements.

Energy loss factors were calculated, corresponding to each available polarization curve, using the energy balance equation with the methodology reported by Molognoni et al. (2014). In particular, anode and cathode overpotentials (η\textsubscript{An} and η\textsubscript{Cat}), ionic (E\textsubscript{ionic}), pH gradient (E\textsubscript{pH}) and membrane transport losses (E\textsubscript{t}) were evaluated. Ohmic losses other than ionic were not directly measured, but included in the terms η\textsubscript{An} and η\textsubscript{Cat} (Sleutels et al. 2009).

### RESULTS AND DISCUSSION

The MFC was operated for 75 days. On average, each sample collection (period) covered three treatment cycles, depending on the volume collected and on it being properly refrigerated. Overall, 11 periods (new sample collections) and 17 cycles (collapsible feed container replacement) covered the entire experiment duration. Collected samples were stored at T \leq 4 °C, and cell influent variables were measured at the start of each cycle as shown in Figure 2. COD removal efficiency varied throughout the experiment between 64% and 98%. Figure 3 shows the temporal evolution of influent COD concentration, anode feeding rates and resulting OLRs for the MFC. Feeding rates and mode were maintained at constant levels throughout the experimental period, but anodic OLR varied between a minimum of 0.2 and a maximum of 6.6 kg COD m\textsuperscript{−3} d\textsuperscript{−1}, due to the variability of the raw wastewater’s initial COD between samples and partial occasional clogging of feedlines, resulting in different losses in time.

Figure 4(a) shows recorded voltage generation, in terms of calculated daily averages and standard deviation. During inoculation, voltage increased gradually, up to 71 mV on day 3. Once semi-continuous feeding started, voltage increased exponentially, reaching 601 mV on day 6. From here onwards, it stabilized at 583 ± 47 mV. On day 21 an abrupt voltage drop was observed, due to problems in polarization curve measurement. The period from day 33, was characterized by less stable electrical behavior (525 ± 63 mV) due to some problems, including feeding pipe failure (day 34, fixed after a few hours). From day 48, performance of the cell decreased slightly (477 ± 84 mV), irrespective of the high OLR during this time (5.3 ± 1.2 kg COD m\textsuperscript{−3} d\textsuperscript{−1}). From day 60, performance was lower (395 ± 81 mV), most likely due to low OLR.

Current and power density (Figure 4(b)) followed the same trends as voltage (Figure 4). The maximum power density value recorded was 27.3 W m\textsuperscript{−3} NAC, favorably comparable with the highest values obtained in batch mode by Mardanpour et al. (2012). This indicates a very high efficiency of the MFC tested herein, as values obtained

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Anodic and cathodic pH and conductivity values (influent and effluent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anode</td>
</tr>
<tr>
<td>pH</td>
<td>In</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1.59 ± 1.28</td>
</tr>
</tbody>
</table>
in batch mode are usually higher than those observed in continuous running mode; results obtained therefore confirm the technical suitability of dairy effluent treatment by MFC technology, with bioenergy recovery.

Analysis of average anode and cathode potentials shows that anode potential was fairly stable (\(-180 \pm 55 \text{ mV vs SHE}\), an indication that EABs had adequately colonized the system, and therefore were efficiently transferring electrons released by substrate oxidation (Table 4). By contrast, cathode potential had a higher variability, a likely reason being the observed voltage fluctuations, as it can also be concluded observing open circuit electrode potentials.

Figure 5(a) summarizes MFC wastewater treatment efficiency, both in terms of COD removal and CE. It can be observed that COD removal efficiency reached an average value of 85 ± 12% in the period from days 14 to 65 (system assumed in a well-settled steady state). These results are in line with, or better than, previous ones (Table 1).

Observed CE, representing the ratio of recovered electrons and the total amount of electrons made available by substrate oxidation (in other words, electricity production vs organic removal ratio) oscillated between 4% and 56%.

Figure 5(b), instead, shows OLR effects on COD removal and CE, calculated by averaging collected data. A clear dependency between OLR and \(\eta_{\text{COD}}\) cannot be easily inferred, although previous studies confirmed that better carbon removal efficiencies can be achieved in substrate limiting conditions (OLR < 1 kg COD m\(^{-3}\) d\(^{-1}\)) (Molognoni et al. 2016). CE appears to decrease exponentially with OLR increase. In this experiment, CE varied from 54% at low OLR (0.4 kg COD m\(^{-3}\) d\(^{-1}\)), to less than 5% at high OLR (5.8 kg COD m\(^{-3}\) d\(^{-1}\)). This phenomenon is usually due to competition between EABs and other co-existing microbial populations (i.e. methanogens, heterotrophs) in the anodic chamber. The former usually outcompete other populations more easily at low COD concentrations (Pinto et al. 2010).
Table 5 summarizes the main electrical parameters gathered by polarization curves (see also Figure 6). The cell showed a mean internal resistance of $15 \pm 8 \ \Omega$ (excluding days 21 and 44), lower than expected, and lower than the external resistance fixed at the start of the experiment. For this reason, the cell was operating on the ‘left side’ of its power curves (Figure 6(b)), that is, not at its maximum efficiency, represented by the power curve absolute maximum. Values of OCV, maximum power and short circuit current are in agreement with previous observations: the cell could potentially recover a maximum power of 20 mW (as on day 29) with an average value of 13.8 mW. An average power density of $32 \ \text{W m}^{-3} \ \text{NAC}$ was determined. Based on rough estimates, power recovery could have been up to 30% higher if the external resistance had been periodically adjusted to match the instantaneous value of $R_{\text{int}}$. This could not be technically done in this study, however, it could be a possible strategy to implement in future ones.

Energy losses, summarized in Table 5 and Figure 6(a), represent the difference between MFC electromotive force (i.e. theoretical maximum voltage achievable) and the actual, measured voltage at the electrodes. Losses depend on a number of factors (Puig et al. 2012); in this case cathode and membrane overpotentials ($\eta_{\text{Cat}}$ and $E_{\text{mem}}$, Figure 5) were the main loss contributors, respectively up to 35% and 27% of the cell total. pH gradients (between anode and cathode chambers) around 2 pH-units, accounted for about 23%, and anode and electrolyte overpotentials only slightly affected electrical behavior. The latter could be considered negligible, due to the relatively high conductivity of both anode and cathode media ($1.6 \pm 1.3 \ \text{mS cm}^{-1}$ for the anolyte, $4.5 \pm 2.9 \ \text{mS cm}^{-1}$ for the catholyte).

Figure 6(b) shows an example of the polarization curve obtained during the experiment. The practical importance of polarization curves in MFC operation is that they are an important indicator through which performance can be

Table 4 | Polarization curves recorded during the experimental period.

<table>
<thead>
<tr>
<th>Day</th>
<th>$R_{\text{int}}$ (Ω)</th>
<th>OCV (mV)</th>
<th>$E_{\text{anoc}}$ (mV vs SHE)</th>
<th>$E_{\text{catoc}}$ (mV vs SHE)</th>
<th>$P_{\text{max}}$ (mW)</th>
<th>$I_{\text{sc}}$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>21.2</td>
<td>NA</td>
<td>n.a.</td>
<td>n.a.</td>
<td>13.0</td>
<td>41.8</td>
</tr>
<tr>
<td>21*</td>
<td>41.4</td>
<td>NA</td>
<td>n.a.</td>
<td>n.a.</td>
<td>7.1</td>
<td>26.4</td>
</tr>
<tr>
<td>29</td>
<td>9.3</td>
<td>762</td>
<td>–247</td>
<td>515</td>
<td>20.3</td>
<td>67.3</td>
</tr>
<tr>
<td>44*</td>
<td>29.8</td>
<td>790</td>
<td>–254</td>
<td>536</td>
<td>9.7</td>
<td>38.8</td>
</tr>
<tr>
<td>48</td>
<td>15.2</td>
<td>723</td>
<td>–213</td>
<td>510</td>
<td>11.8</td>
<td>48.4</td>
</tr>
<tr>
<td>51</td>
<td>12.4</td>
<td>743</td>
<td>–217</td>
<td>526</td>
<td>14.7</td>
<td>51.0</td>
</tr>
<tr>
<td>65</td>
<td>17.2</td>
<td>698</td>
<td>–206</td>
<td>492</td>
<td>9.2</td>
<td>33.8</td>
</tr>
<tr>
<td>Average</td>
<td>15.0</td>
<td>732</td>
<td>–221</td>
<td>511</td>
<td>13.8</td>
<td>48.4</td>
</tr>
</tbody>
</table>

$R_{\text{int}}$, internal resistance; OCV, open circuit voltage; $E_{\text{anoc}}$, open circuit anode potential; $E_{\text{catoc}}$, open circuit cathode potential; $P_{\text{max}}$, maximum power point; $I_{\text{sc}}$, short circuit current. Measurements on days 21 and 44 were affected by operational issues (marked with *).
assessed: by drawing polarization curves, in fact, the appropriate $R_{\text{ext}}$ which best fits a specific cell for maximum performance can be determined, among other cell properties.

A variety of strategies can be adopted to reduce MFC energy losses, thus improving their electric power recovery. In this specific case it was determined (Table 4) that cathode overpotentials account for 35% of the losses, membrane overpotentials for 27% and pH gradient for 23%. Anodic and electrolyte could be considered to be negligible. Cathode overpotentials may be reduced by: (i) introducing new, more efficient electrode and catalyster materials (possibly, avoiding the economically unsustainable use of Pt); (ii) improving oxygen transfer kinetics at the cathode; (iii) relying on a biocathode (i.e. bacterial oxygen reduction, rather than chemical catalysis). Membrane overpotentials could be reduced by introducing different membranes with lower internal resistance, or less subject to biofouling, while pH gradient losses may be reduced by increasing pH buffer strength, or by reducing the hydraulic residence time of electrolytes by modifying the design of the system. Such corrective measures must be considered in relation with

![Figure 5](image_url)  
(a) Treatment efficiency of the MFC in terms of organic matter removal and Coulombic efficiency. (b) Organic loading rate (OLR) effect on COD removal ($\eta_{\text{COD}}$) and Coulombic efficiency (CE).

![Figure 6](image_url)  
(a) Energy-loss distribution, calculated for same-day polarization curves measurement. Curves obtained on days 21 and 44 were not considered, as they were affected by measurement issues. (b) Polarization curve recorded on day 48 of the experimental period.

<table>
<thead>
<tr>
<th>Energy loss</th>
<th>(mV)</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode ($\eta_{\text{Cat}}$)</td>
<td>181 ± 16</td>
<td>35%</td>
</tr>
<tr>
<td>Membrane ($E_t$)</td>
<td>139 ± 76</td>
<td>27%</td>
</tr>
<tr>
<td>pH gradient ($E_{\text{ApH}}$)</td>
<td>117 ± 29</td>
<td>23%</td>
</tr>
<tr>
<td>Anode ($\eta_{\text{An}}$)</td>
<td>60 ± 33</td>
<td>11%</td>
</tr>
<tr>
<td>Electrolytes ($E_{\text{ion}}$)</td>
<td>22 ± 7</td>
<td>4%</td>
</tr>
<tr>
<td>Total loss</td>
<td>518 ± 89</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 5 | Energy losses distribution of the cell (average values ± standard deviation, and percentage contribution)
their costs and efficiency, not only aiming for maximizing electricity recovery, but also in terms of wastewater treatment efficiency. In order to better understand the overall cell performance, the microbial community of the cell needs to be analyzed to properly characterize exoelectrogenic activity (Capodaglio et al. 2016c; Saratale et al. 2017b).

**FUTURE DEVELOPMENTS**

The present study has demonstrated the long-term applicability of MFC processing of dairy industrial wastewater. In order to achieve real-scale applicability, further investigations are needed: starting with the definition of energy-loss distribution, implement design and operational process modifications that can minimize some or all of them. Some of them have been mentioned in the previous section and need detailed experimentation. Study of cell microbiome is also appropriate in order to suggest operational strategies for improving exoelectrogenic population activity.

Scale-up of the MFC systems from laboratory to pilot/demonstration scale has been shown to be a serious challenge in several applications. Although dairy wastewater has proven to be an ideal substrate for bioelectrochemical processes applications, design and materials issues interfere with the practical success and achieved efficiency of purely geometric scale-ups of small-scale systems (Escala et al. 2014). Scale-up by increasing the size/volume of individual MFCs has been shown to be sub-linear with decreasing power output per unit of mass, hence some design philosophy modifications might be necessary in this respect. A new approach using allometric scaling analysis has been recently suggested as perhaps the best way for extracting higher power (and achieving higher utilization efficiency of feedstock waste) from MFC systems (Greenman & Ieropoulos 2017).

Although MFC technology is not fully ready at this moment for full-scale applications, it might become a valid alternative to traditional wastewater treatment very soon. Also from the economic point of view, clearly establishing whether a technology can fully enter the market according to demonstrated profitability, analysis of MFC technology is rather optimistic. In a recent study encompassing different scenarios (one highly optimistic, one highly pessimistic, and the ‘most likely’) of two basic MFC application cases compared to conventional activated sludge process, results showed that under most of the considered scenarios (including the pessimistic one) MFC constitutes a more attractive option than conventional activated sludge, showing not only that the former is a promising alternative to the latter, but that it also offers potential economic benefits (Trapero et al. 2017).

**CONCLUSIONS**

This study aimed to demonstrate the feasibility of dairy wastewater treatment with bioenergy recovery through MFCs. A laboratory-scale cell was fed with dairy wastewater for three and a half months, longer than any other literature-reported application to this substrate. The process proved to be stable, with a high average COD removal efficiency of 85%, irrespective of OLR fluctuations over time, a value in the higher range of literature-observed efficiencies in continuous-mode MFC applications on dairy wastewater (Table 1). A maximum power density of just over 27 W m$^{-3}$ NAC was observed and recovered, the highest reported so far in similar applications. Coulombic efficiency decreased exponentially with increasing OLRs, with an optimal value of 54% recorded at a load of 0.4 kg COD m$^{-3}$ d$^{-1}$. This value also ranks highest among all those previously reported. Results, therefore, were for the most part better than in previously reported experiences (both batch and continuous), confirming that dairy wastewater treatment may represent an ideal application niche for MFC technology.

Most studies concerning MFCs focus on the interesting possibility of directly recovering electrical energy from the ongoing process. This study confirmed that a non-negligible amount of energy could in fact be recovered, and that perhaps this could have been further increased with more active process management or with the reduction of cell overpotentials. However, the energy recovery aspect is not the only valuable feature of bioelectrochemical processes. In addition to the generation and recovery of electrical energy, MFCs have additional advantages over traditional biological processes, whether aerobic or anaerobic. Compared to the former, MFCs offer a much lower energy demand, mainly in the form of lower aeration requirements (some cathode aeration is needed, but much less than, for example, in an activated sludge or MBR process), faster process kinetics, and much lower, almost negligible, sludge production. Compared to anaerobic technologies, MFCs still offer faster degradation rates, and also offer some, admittedly unwanted, biogas production that, although negatively affecting direct electricity generation through biomass population competition, may still be collected and usefully employed.
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