



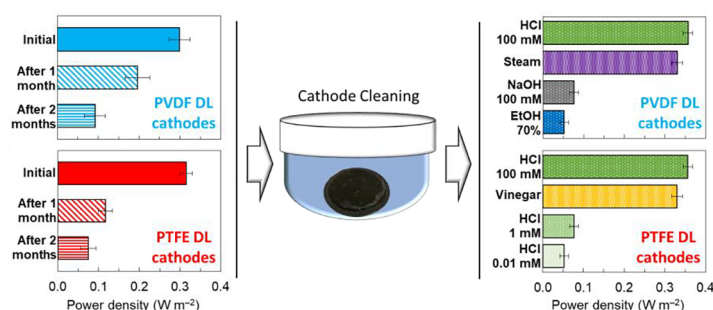
# Impact of cleaning procedures on restoring cathode performance for microbial fuel cells treating domestic wastewater

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Degradation of cathode performance over time is one of the major drawbacks in applications of microbial fuel cells (MFCs) for wastewater treatment. Over a two month period the resistance of air cathodes ( $R_{Ct}$ ) with a polyvinylidene fluoride (PVDF) diffusion layer increased of 111% from  $70 \pm 10 \text{ m}\Omega \text{ m}^2$  to  $148 \pm 32 \text{ m}\Omega \text{ m}^2$ . Soaking the cathodes in hydrochloric acid (100 mM HCl) restored cathode performance to  $R_{Ct} = 74 \pm 17 \text{ m}\Omega \text{ m}^2$ . Steam, ethanol, or sodium hydroxide treatment produced only a small change in performance, and slightly increased  $R_{Ct}$ . With a polytetrafluoroethylene (PTFE) diffusion layer on the cathodes,  $R_{Ct}$  increased from  $54 \pm 14 \text{ m}\Omega \text{ m}^2$  to  $342 \pm 142 \text{ m}\Omega \text{ m}^2$  after two months of operation. The acid concentration was critical for effectiveness in cleaning, as HCl (100 mM) decreased  $R_{Ct}$  to  $28 \pm 8 \text{ m}\Omega \text{ m}^2$ . A lower concentration of HCl ( $< 1 \text{ mM}$ ) showed no improvement, and vinegar (5% acetic acid) produced  $48 \pm 4 \text{ m}\Omega \text{ m}^2$ .

## 1. Introduction

Domestic wastewater treatment has a large cost in term of energy consumed per cubic meter of wastewater of  $0.6 \text{ kWh m}^{-3}$  (McCarty et al., 2011) or about  $100 \text{ W m}^{-3}$  (assuming a 6 h hydraulic retention time, HRT). Microbial fuel cells (MFCs) have been proposed as an innovative technology to achieve energy neutral wastewater treatment by

extracting the chemical energy contained in the wastewater as electrical energy (Park et al., 2018; Xin et al., 2018). Exoelectrogenic bacteria on the anode transfer the electrons from the degradation of the organic matter in solution to the cathode where the oxygen reduction reaction on the cathode exposed to air completes the circuit (Supporting Information) (Logan et al., 2019; Ye et al., 2019). Power densities produced by MFCs fed domestic wastewater are typically low

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(< 0.8 W m<sup>-2</sup>) (Yang and Logan, 2016), or ~20 W m<sup>-3</sup>, and show a decrease in power production over a relatively short period of time of few weeks (Goglio et al., 2019; Rossi et al., 2018; Zhang et al., 2017). This degradation in MFC power output is due to a decrease of the cathode performance, mainly because of the precipitation of salts in the porous structure of the activated carbon cathodes (An et al., 2017; Santini et al., 2017). The formation of a biofilm on the solution side of the cathode has a small impact on performance, as it primarily slows the diffusion of H<sup>+</sup> to the cathode and diffusion of OH<sup>-</sup> from the cathode, which can result in a local alkalisation of the solution in contact with the electrode (Erable et al., 2018; Yuan et al., 2013).

Maintaining operation of an MFC may likely require cathode removal and cleaning in order to maintain long-term performance in terms of power generation. As a result, several innovative MFC reactors designs have been developed to allow easy removal of the electrodes for maintenance. For example, one MFC configuration was modified to allow replacement of the air-cathode without draining the electrolyte by placing the cathode at the top of the reactor (Oliot et al., 2016), and a multilayer cathode was regenerated by replacing the external layer of the conductive carbon paint with a new layer of identical carbon loading (Pasternak et al., 2016). However, in both cases, this required cathode or catalyst replacement rather than cathode regeneration. Different materials can be used or added to reduce cathode performance deterioration. For example, after 27 weeks, MFCs with copper current collector cathodes maintained power densities 19% larger than MFCs using stainless steel as current collector in the cathodes due to the antimicrobial activity of copper (Myung et al., 2018). Frequent removal of the biofilm on the cathode increased the performance of cubic MFC by 39% after one month of operation, compared to a non-cleaned cathode. However, even though daily cleaning of the cathodes improved the performance of the cells, the power output after one month was still half of that obtained with new cathodes (Rossi et al., 2018).

One method of effective cathode cleaning procedure was based on a combination of scraping the biofilm from the cathode surface to remove external fouling, followed by soaking the electrode for several hours in a cleaning solution (Zhang et al., 2017). However, specific protocols for this method were not examined, and different cleaning solutions have been used to clean cathodes. For example, cleaning was accomplished by soaking air cathodes in sodium hydroxide (NaOH) for up to 24 h (Zhang et al., 2017), while others have washed the cathode surface with a lysis solution of 200 mM NaOH and 0.1% Triton X-100 heated to 60 °C (Pasternak et al., 2016). Soaking the electrodes in 100 mM hydrochloric acid (HCl) for only 2 h also completely restored MFC performance (Rossi et al., 2017). Recent interest in the development of large scale reactors and their integration in the existing wastewater treatment infrastructure (Hiegemann et al., 2016) suggests these and other methods for effective cleaning of cathodes should be examined and compared, so that wastewater treatment plant operators could use the most optimal approaches. In this study, we evaluated the use of several different methods in order to determine the best approach to clean the cathode and restore performance. These methods were soaking in NaOH (100 mM), ethanol (EtOH, 70% v/v), HCl (100 mM, 1 mM, 0.01 mM), and vinegar (5% acetic acid) solutions, or steam cleaning. These approaches were tested using activated carbon (AC) cathodes in small (28 mL) MFCs that had different diffusion layers (DLs) made of polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE).

## 2. Materials and methods

### 2.1. Construction and operation of the MFCs

The MFCs were cubic-shaped reactors constructed from polycarbonate blocks with an inside cylindrical chamber 3 cm in diameter and 4 cm in length. The anodes were graphite fiber brushes (2.5 cm in both diameter and length) wound using two titanium wires, that were heat treated at 450 °C in air for 30 min prior to use, and placed

horizontally in the middle of the MFC chamber (Feng et al., 2010). Brush anodes were placed near the cathode (anode to cathode spacing of  $d_{An-Ct} = 1.3$  cm) with the brush end perpendicular to the cathode. A photograph of the reactor and its components can be found in the [Supporting Information](#). Anodes were acclimated in MFCs and used in other studies for over two years at a fixed external resistance of 1000 Ω, at a constant temperature (30 °C), prior to their use here with new cathodes.

Cathodes with polyvinylidene fluoride (PVDF) DL were fabricated as previously described (Yang et al., 2014). Briefly, 10% (w/v) PVDF solutions were prepared by dissolving PVDF powder (~534 000 Da; SigmaAldrich) in N,N-dimethylacetamide (DMAc), with vigorous stirring using a vortex mixer at room temperature (25 °C) to completely dissolve the polymer. One mL of the solution was then mixed with 0.3 g of activated carbon (AC) powder (Norit SX plus, Norit Americas Inc., TX) and 0.03 g of carbon black (CB) (Vulcan XC-72, Cabot Corporation, USA). The mixture was homogenised and then spread directly onto an 11.3 cm<sup>2</sup> circular section of stainless steel mesh (50 × 50, type 304, McMaster-Carr, USA) with a spatula. The cathodes were then immersed into deionized (DI) water for 15 min at room temperature to induce phase inversion. Cathodes were air-dried in a fume hood for 24 h and immediately used in MFCs. Commercially available cathodes (VITO CORE®, VITO, Mol, Belgium) contained an activated carbon catalyst, a 70% porous DL made of a thin layer of polytetrafluoroethylene (PTFE), and a stainless steel current collector.

Domestic wastewater was collected once a week from the primary clarifier of the Pennsylvania State University Waste Water Treatment Plant, and stored at 4 °C prior to use. The chemical oxygen demand (COD) and the soluble COD (sCOD) of the wastewater used during polarization tests are reported in the [Supporting information](#). The average conductivity of the wastewater at 25 °C was  $1.3 \pm 0.1$  mS cm<sup>-1</sup>. All results are presented as the average and standard error of tests using duplicate reactors.

### 2.2. Electrochemical measurements

Single cycle polarization tests were conducted by varying the external resistance (1000, 500, 200, 100, 75, 50 Ω at 20 min intervals) after filling the reactor with fresh solution and keeping it in open circuit conditions for 2 h, for a total test duration of 4 h. The voltage drop ( $U$ ) across an external resistor was recorded by a computer-based data acquisition system (2700, Keithley Instrument, OH). Current density ( $j$ ) and power density ( $P$ ) were calculated from the current ( $i$ ) and the total exposed cathode projected area ( $A = 7$  cm<sup>2</sup>), as  $j = U/RA$  and  $P = iU/A$ , where  $R$  is the external resistance. During each polarization test a reference electrode (RE) was placed close to the anode brush with the tip touching the titanium wire, to measure the anode potentials ( $E_{An,m}$ ). The RE used to measure the electrode potentials (Ag/AgCl; model RE-5B, BASi, IN; +0.209 V versus a standard hydrogen electrode, SHE) was placed in the current path between the electrodes. The RE was 0.5 cm in diameter, with a tip diameter of 0.4 cm. All potentials are reported here versus SHE. The measured cathode potential ( $E_{Ct,m}$ ) was calculated using the whole cell voltage as  $E_{Ct,m} = U + E_{An,m}$  as previously described (Yang et al., 2018). The anode and the cathode potentials were then corrected based on the conductivity of the solution and their distance from the reference electrode (Logan et al., 2018) as:

$$R_{\Omega} = \frac{100 d_{An-Ct}}{\sigma} \quad (1)$$

$$E_{An} = E_{An,m} - \left( \frac{10^{-3} R_{\Omega} d_{An-RE}}{A d_{An-Ct}} \right) i \quad (2)$$

$$E_{Ct} = E_{Ct,m} + \left( \frac{10^{-3} R_{\Omega} d_{Ct-RE}}{A d_{An-Ct}} \right) i \quad (3)$$

where  $d_{An-Ct}$  is the distance between anode and cathode (1.3 cm),  $\sigma$  is

the average conductivity measured for the wastewater ( $\text{mS cm}^{-1}$ ), and  $d_{\text{An-RE}}$  and  $d_{\text{Ct-RE}}$  are the distances between the anode or the cathode and the RE (cm). The measured electrode potentials (not corrected for conductivity) are reported in the [Supporting information](#).

The performance of the electrodes was examined using the recently developed electrode potential slope (EPS) method ([Rossi et al., 2019](#)). The method assumes that, following a rapid decrease in potential due to activation losses over the initial small increase in current, the electrode potential become function of the current density. Under these circumstances, the system is operating under steady state conditions, and the linearized portion of the electrode potential can be used to assess anodic ( $E_{\text{An},eo}$ ) and cathodic ( $E_{\text{Ct},eo}$ ) potentials that better describe the electrode performance in terms of experimental electrode potentials. The slopes of the linearized portion of the electrode potentials can be used to express the performance of the anode and cathode as two resistances, with the solution resistance and the membrane (if present), as the final component of the total internal resistance of the cell ([Cario et al., 2019](#)). The linearized portion of the electrode potentials in polarization plots of potential as a function of current density was fit to  $E = m j + b$ , where  $j$  is the current density, the slope  $m$  is defined as the specific resistance of the anode ( $R_{\text{An}}$ ) or cathode ( $R_{\text{Ct}}$ ) in units of  $\text{m}\Omega \text{ m}^2$ , and the y-intercepts are used to calculate the experimental open circuit potentials of the anode ( $E_{\text{An},eo}$ ) or cathode ( $E_{\text{Ct},eo}$ ) ([Rossi et al., 2019](#)).

### 2.3. Cathode cleaning

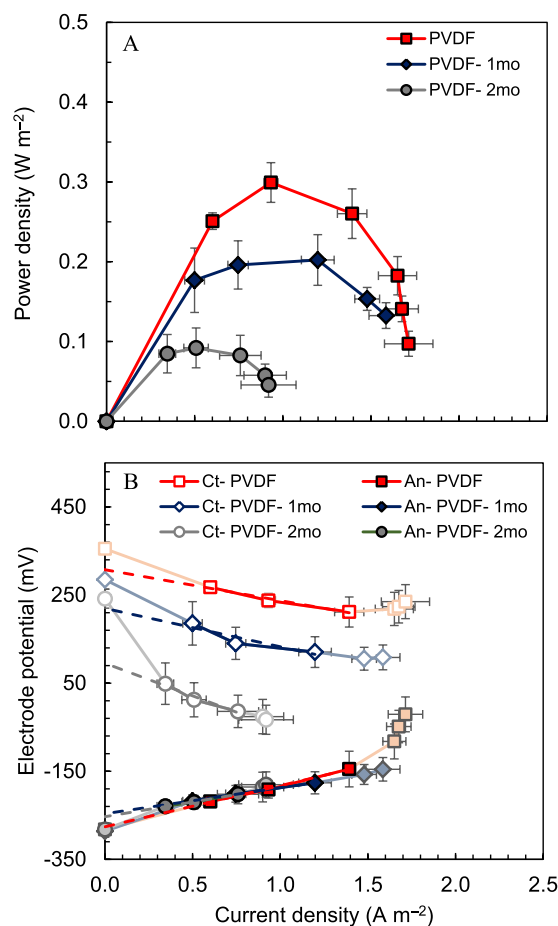
PVDF DL or PTFE DL cathodes were cleaned after two months of operation, and the performance recovery after cleaning was assessed by polarization tests based on changes in cathode resistances and experimental open circuit potentials. PVDF DL cathodes were soaked in 100 mM HCl, 100 mM NaOH or 70% ethanol, or steam cleaned. The solution side of the electrodes was first scraped with a spatula to gently remove the biofilm, then each electrode was soaked for 2 h with no agitation in 25 mL of the cleaning solution. After this treatment, the cathodes were immersed in distilled water for 3 h, rinsed by distilled water 3 times, and placed back in the MFCs for performance evaluation through polarization tests. Cathodes were steam cleaned using a commercially available hand steamer (Bissell steam shot hard-surface cleaner, 39N7A/39N71) by continuously steaming the solution side and the air side of the cathode at a distance of 10 cm for 1 h. After steam cleaning, the cathodes were soaked in distilled water for 3 h, rinsed with distilled water 3 times, and placed back in the MFCs for performance evaluation through polarization tests.

PTFE DL cathodes were cleaned with HCl at three different concentrations (100 mM, 1 mM, or 0.01 mM) or with a commercially available distilled white vinegar solution (5% acetic acid; Weis Markets, Inc.) in the same manner described above for the cathodes cleaned by soaking in the different solutions.

## 3. Results and discussion

### 3.1. MFC performance over time for cathodes with PVDF DLs

The initial maximum power density from polarization tests obtained with PVDF DL cathodes was  $0.30 \pm 0.02 \text{ W m}^{-2}$ , decreasing by 33% to  $0.20 \pm 0.03 \text{ W m}^{-2}$  after one month, and by 70% to  $0.09 \pm 0.02 \text{ W m}^{-2}$  after two months of operation ([Fig. 1](#)). The measured cathode potential at open circuit conditions was  $E_{\text{Ct},mo} = 355 \pm 4 \text{ mV}$ , while the experimental cathode potential from the slope of the polarization curve produced a lower experimental potential of  $E_{\text{Ct},eo} = 307 \pm 10 \text{ mV}$ . Both measured and experimental cathode potentials decreased over a two months period to  $E_{\text{Ct},mo} = 285 \pm 21 \text{ mV}$  and  $E_{\text{Ct},eo} = 220 \pm 31 \text{ mV}$  (1 month), and to  $E_{\text{Ct},mo} = 242 \pm 22 \text{ mV}$  and  $E_{\text{Ct},eo} = 95 \pm 18 \text{ mV}$  (2 months). The decreases in the cathode measured and experimental potentials were



**Fig. 1.** (A) Power density curves and (B) anode and cathode potentials following correction for ohmic resistance of the MFCs with PVDF DL cathodes after one (1 mo) or two (2 mo) months of operation with domestic wastewater. Anode and cathode potentials not corrected for ohmic losses are reported in the [Supporting information](#). The dashed lines represent the linearization of the data that would be obtained from polarization tests, while the thick solid lines show the linearized portion of the slopes that are used to calculate the anode ( $R_{\text{An}}$ ) and cathode ( $R_{\text{Ct}}$ ) resistances.

likely related to a shift in the local cathode pH in the activated carbon catalyst, and therefore a thermodynamic change in the oxygen reduction reaction. It was shown that the presence of a biofilm shifted the catholyte pH in the close proximity of the cathode up to 11 units of pH in wastewater ([Yuan et al., 2013](#)). Each unit of pH increase will result in a decrease of the cathode theoretical potential of 59 mV. Thus, the decrease in the experimental cathode potential was likely to be altered in proportion to the growth of the biofilm on the cathode.

The cathode specific resistance increased from the initial  $70 \pm 10 \text{ m}\Omega \text{ m}^2$  to  $87 \pm 36 \text{ m}\Omega \text{ m}^2$  after one month, and doubled to  $148 \pm 32 \text{ m}\Omega \text{ m}^2$  after two months of operation. The cathode resistance was likely also negatively affected by a slower diffusion of ions from the catalyst surface due to the presence of the biofilm, as well as precipitated salts in the pores of the activated carbon ([Santini et al., 2017](#)).

The anode performance in terms of measured potentials and resistances were stable over the whole duration of experiment. The anode measured potentials at open circuit condition were quite consistent, with  $E_{\text{An},mo} = -282 \pm 8 \text{ mV}$  (initial),  $-286 \pm 14 \text{ mV}$  (after one month);  $-282 \pm 15 \text{ mV}$  (after two months). The experimental anode potentials decreased slightly after one and two months of operation, with the initial potential of  $E_{\text{An},eo} = -276 \pm 5 \text{ mV}$  (initial) decreasing to  $-246 \pm 3 \text{ mV}$  (after one month) and then  $-253 \pm 2 \text{ mV}$  (after two

months). The anode resistances showed no increases, or only slightly changed over time, with an initial resistance of  $R_{An} = 93 \pm 5 \text{ m}\Omega \text{ m}^2$ , compared to  $59 \pm 3 \text{ m}\Omega \text{ m}^2$  (after one month) and  $67 \pm 4 \text{ m}\Omega \text{ m}^2$  (after two months). These small variations after one and two months of operation could be due to changes in the composition of the wastewater (Kokko et al., 2018).

Considering a stable solution resistance of  $100 \text{ m}\Omega \text{ m}^2$  ( $1.3 \pm 0.1 \text{ mS cm}^{-1}$ ), and these anode resistances, it is clear that the cathode resistance was the limiting element in the whole cell performance after one and two months of operation (Rossi et al., 2019). For example, after two months the cathode resistance ( $R_{Ct} = 148 \pm 32 \text{ m}\Omega \text{ m}^2$ ) was 120% higher than the anode resistance ( $R_{An} = 67 \pm 4 \text{ m}\Omega \text{ m}^2$ ) and 48% higher than the solution resistance. However, in the initial polarization test the contribution of the anode resistance ( $R_{An} = 93 \pm 5 \text{ m}\Omega \text{ m}^2$ ), solution, and cathodes ( $R_{Ct} = 70 \pm 10 \text{ m}\Omega \text{ m}^2$ ) were all similar. Thus, degradation of the cathode was the main reason for the change in MFC performance over time.

### 3.2. Impact of the cleaning method on the performance of the PVDF DL cathodes

After cleaning using the stronger acid wash (100 mM HCl), the maximum power density from polarization tests of the MFC was completely restored to  $0.32 \pm 0.01 \text{ W m}^{-2}$ , as it was similar to that produced at the start of the test ( $0.30 \pm 0.02 \text{ W m}^{-2}$ ). Cathode cleaning with sodium hydroxide and ethanol solution resulted in similar maximum power densities of  $0.16 \pm 0.01 \text{ W m}^{-2}$  (EtOH 70%) and  $0.16 \pm 0.01 \text{ W m}^{-2}$  (100 mM NaOH) compared to the maximum power density of  $0.09 \pm 0.02 \text{ W m}^{-2}$  after two months. Steam cleaning produced a slightly higher maximum power density ( $0.19 \pm 0.02 \text{ W m}^{-2}$ ) (Fig. 2). The acid wash with 100 mM HCl was the most effective method for recovering the initial MFC performance, followed by the steam cleaning, probably due to their effectiveness in removing salt deposits in the activated carbon catalyst compared to that obtained with the ethanol and sodium hydroxide solutions. Overall, the non-acid treatments restored the performance to < 63% of the initial power density ( $0.30 \pm 0.02 \text{ W m}^{-2}$ ), but they were still 110% higher than that obtained after two months of operation ( $0.09 \pm 0.02 \text{ W m}^{-2}$ ).

The measured and experimental electrode potentials of the cathodes cleaned with 100 mM HCl were similar to the initial values ( $E_{Ct,m0} = 339 \pm 4 \text{ mV}$  and  $E_{Ct,e0} = 320 \pm 18 \text{ mV}$ ), and slightly higher than those obtained using other cleaning methods ( $E_{Ct,m0} = 301 \pm 9 \text{ mV}$  and  $E_{Ct,e0} = 305 \pm 1 \text{ mV}$ , Steam;  $E_{Ct,m0} = 290 \pm 14 \text{ mV}$  and  $E_{Ct,e0} = 282 \pm 5 \text{ mV}$ , 70% EtOH;  $E_{Ct,m0} = 304 \pm 11 \text{ mV}$  and  $E_{Ct,e0} = 251 \pm 13 \text{ mV}$ , 100 mM NaOH). This lack of a change in the cathode potentials strengthened our hypothesis that the biofilm was decreasing the thermodynamic potential of the cathode by favouring an increase in pH in the close proximity of the electrode.

The changes in the specific resistances of the cathodes best explains the different performance after the cleaning procedures.  $R_{Ct}$  of the electrodes cleaned with 100 mM HCl was  $74 \pm 17 \text{ m}\Omega \text{ m}^2$ , significantly lower than the cathode resistance obtained after steam cleaning ( $250 \pm 1 \text{ m}\Omega \text{ m}^2$ ) and after ethanol ( $264 \pm 6 \text{ m}\Omega \text{ m}^2$ ) and sodium hydroxide washing ( $206 \pm 18 \text{ m}\Omega \text{ m}^2$ ). Comparing the experimental cathode potentials and the specific resistances obtained after cleaning and those obtained after two months of operation it is clear that the performance recovery was mainly due to the increase in the electrode potentials, experimental and measured, as the cathode resistance significantly increased after the cleaning processes. All the cleaning methods showed that the removal of the biofilm positively impacted the cathode potential as the biofilm induced a pH increase in the close proximity of the electrode catalyst. However, the impact of the non-acid washes was limited if not negative on the cathode specific resistance.

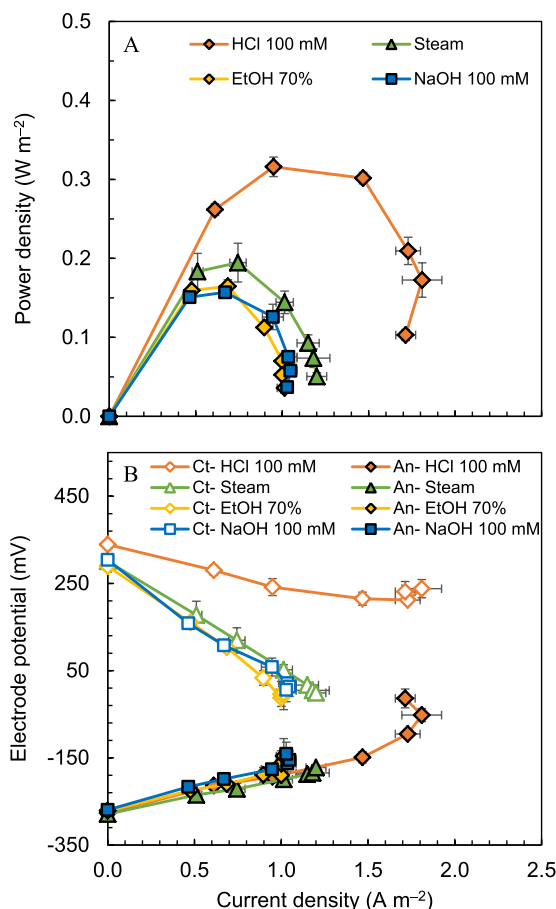


Fig. 2. (A) Power density curves and (B) anode and cathode potentials of the MFCs with PVDF DL cathodes treated with ethanol (70%), steam, sodium hydroxide (100 mM NaOH) and hydrochloric acid (100 mM HCl) following correction for ohmic resistance after two months of operation. Anode and cathode potentials not corrected for ohmic losses are reported in the [Supporting information](#).

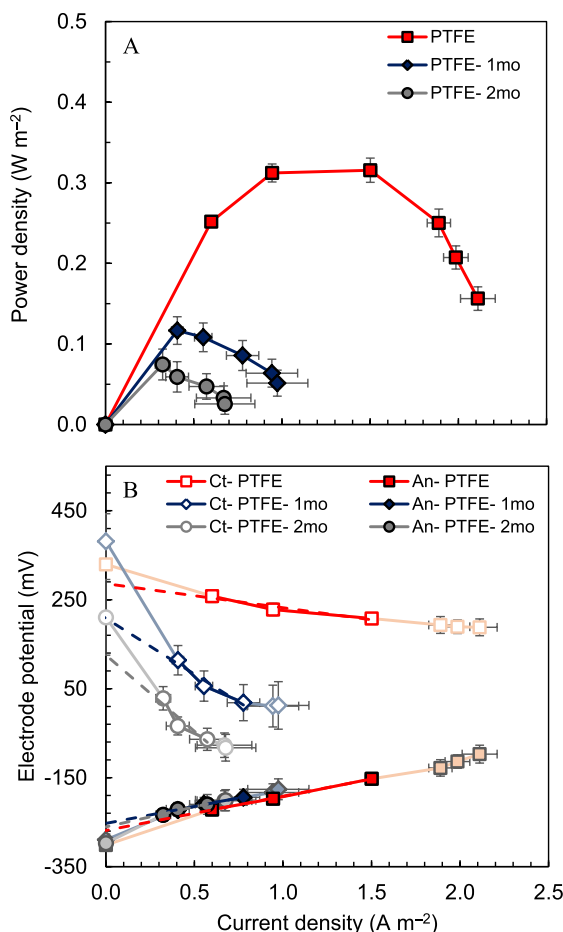
The anode measured potentials did not change during the tests and ranged from  $-270 \text{ mV}$  to  $-279 \text{ mV}$  with an average  $E_{An,e0} = -262 \pm 6 \text{ mV}$  and a stable anode resistance of  $R_{An} = 76 \pm 5 \text{ m}\Omega \text{ m}^2$ . The anode was not a factor in changing the performance before and after the cleaning processes.

### 3.3. MFC performance over time for cathodes with PTFE DLs

MFCs with PTFE DL cathodes produced an initial maximum power density of  $0.32 \pm 0.02 \text{ W m}^{-2}$  in polarization tests, similar to that obtained using PVDF DL cathodes ( $0.30 \pm 0.02 \text{ W m}^{-2}$ ) (Fig. 3). However, the decrease in maximum power density over time was more pronounced with this material than that observed with PVDF DL cathodes. After one month of operation the maximum power density decreased by 63% to  $0.12 \pm 0.02 \text{ W m}^{-2}$  and further by 78% to  $0.07 \pm 0.02 \text{ W m}^{-2}$  after two months of operation. The performance decrease was due to the degradation of the cathode over time as the experimental cathode potential decreased from  $E_{Ct,e0} = 286 \pm 15 \text{ mV}$  to  $E_{Ct,e0} = 208 \pm 37 \text{ mV}$  after one month, and to  $E_{Ct,e0} = 125 \pm 63 \text{ mV}$  after two months of operation. These experimental electrode potentials were similar to those obtained with PVDF DL cathodes.

The increase in the cathode resistance over time was much larger with PTFE DL cathodes than with the PVDF DL cathodes. The cathode resistance increased from the initial  $54 \pm 14 \text{ m}\Omega \text{ m}^2$  to





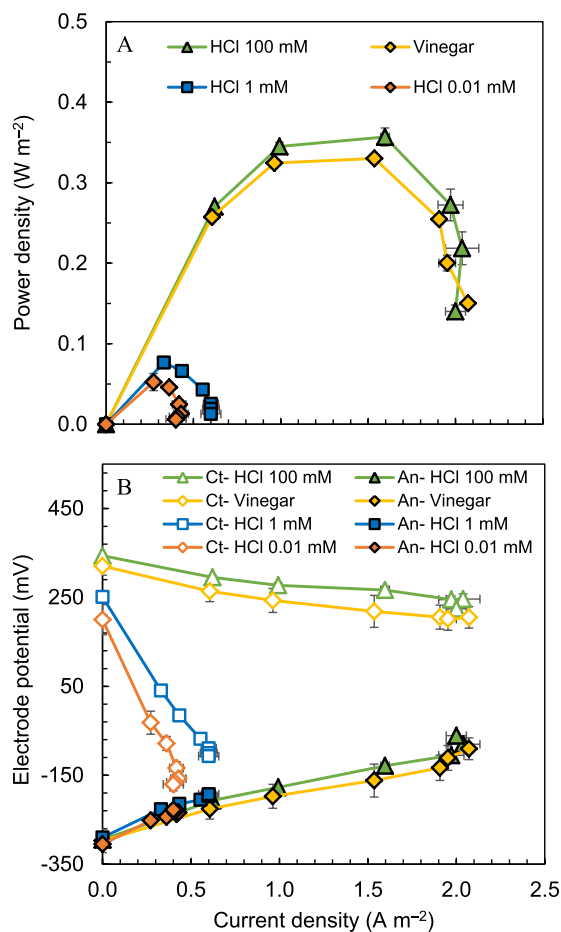
**Fig. 3.** (A) Power density curves and (B) anode and cathode potentials following correction for ohmic resistance of the MFCs with PTFE DL cathodes after one month (1 mo) and two months (2 mo) of operation with domestic wastewater. Anode and cathode potentials not corrected for ohmic losses are reported in the [Supporting information](#). The dashed lines represent the linearization of the data that would be obtained from polarization tests, while the thick solid lines show the linearized portion of the slopes that are used to calculate the anode ( $R_{An}$ ) and cathode ( $R_{Ct}$ ) resistances.

250  $\pm$  62  $m\Omega m^2$  after one month, and to 342  $\pm$  142  $m\Omega m^2$  after two months of operation. The cathode specific resistance with PTFE DLs was almost double of that obtained with PVDF DLs after one and two months of operation. Thus, the DL composition and porosity clearly affected the cathode specific resistance, and the performance decay, although it had a limited impact on the experimental electrode potentials.

The anode measured and experimental potential remained stable over the two months with an average  $E_{An,m0} = -296 \pm 5$  mV,  $E_{An,e0} = -261 \pm 7$  mV and a specific resistance  $R_{An} = 81 \pm 6$   $m\Omega m^2$ . These values were similar to those obtained with PVDF DL cathodes, and demonstrate that the anode potentials were not a factor in the decreased performance of these cathodes.

### 3.4. Impact of the cleaning method on the performance of the PTFE DL cathodes

Acid washing the PTFE DL cathodes with a concentrated acid restored the maximum power densities, with 0.36  $\pm$  0.01  $W m^{-2}$  using 100 mM HCl and 0.33  $\pm$  0.01  $W m^{-2}$  with vinegar (5% acetic acid) (Fig. 4). Acid cleaning with the lower concentration of hydrochloric acid solutions did not improve MFC performance as the maximum power densities (0.08  $\pm$  0.01  $W m^{-2}$ , 1 mM HCl; 0.05  $\pm$  0.01  $W m^{-2}$ ,



**Fig. 4.** (A) Power density curves and (B) anode and cathode potentials following correction for ohmic resistance of the MFCs with PTFE DL cathodes treated with hydrochloric acid (100 mM HCl, 1 mM HCl, 0.01 mM HCl) and a commercially available vinegar (5% acetic acid) after two months of operation. Anode and cathode potentials not corrected for ohmic losses are reported in the [Supporting information](#).

0.01 mM HCl) were similar to those obtained after two months of operation (0.07  $\pm$  0.02  $W m^{-2}$ ).

The cathode measured and experimental potentials after acid wash increased from  $E_{Ct,e0} = 125 \pm 63$  mV (after two months) to  $E_{Ct,m0} = 344 \pm 3$  mV and  $E_{Ct,e0} = 310 \pm 8$  mV for 100 mM HCl and  $E_{Ct,m0} = 321 \pm 21$  mV and  $E_{Ct,e0} = 292 \pm 5$  mV for the acid wash with the vinegar, these cathode potentials were similar to those obtained during initial operation ( $E_{Ct,m0} = 329 \pm 11$  mV,  $E_{Ct,e0} = 286 \pm 15$  mV). The higher experimental cathode potential, combined with a lower cathodic resistance ( $R_{Ct} = 28 \pm 8$   $m\Omega m^2$ ), were the reasons for the higher maximum power density of the MFC with the cathode washed with 100 mM HCl compared to that obtained after soaking in vinegar ( $R_{Ct} = 48 \pm 4$   $m\Omega m^2$ ). The performance of the cathodes washed with low concentrations of HCl were significantly lower than those obtained with the more concentrated acids. The increase in the experimental cathode potential was larger with the more concentrated acid (1 mM HCl) than with the 0.01 mM HCl.  $E_{Ct,e0}$  increased from 125  $\pm$  63 mV, obtained after two months of operations, to  $E_{Ct,e0} = 200 \pm 13$  mV with 1 mM HCl and to  $E_{Ct,e0} = 158 \pm 44$  mV with 0.01 mM HCl. However, the cathode performance after the cleaning process were lower due to a large increase of the cathode resistance from  $R_{Ct} = 342 \pm 142$   $m\Omega m^2$  (after two months of operation) to  $R_{Ct} = 487 \pm 29$   $m\Omega m^2$  (1 mM HCl) and to  $R_{Ct} = 683 \pm 124$   $m\Omega m^2$  (0.01 mM HCl).

The pH of all the cleaning solutions increased after soaking the cathodes. With 100 mM HCl the pH after treatment was 1.4 compared to the initial pH of 1.3. The pH of the vinegar solution increased from 2.4 to 3.3 but with 1 mM HCl it increased from 3.0 to 9.3 and from 4.8 to 9.5 with 0.01 mM HCl. Thus, with a low concentration of acid in solution, the salts deposited in the catalytic structure of the electrodes were not completely removed as demonstrated by a large change in pH, leading to similar or worse cathodic performance. The pH of the solutions used for cleaning the cathodes and of the same solutions after soaking are reported in the [Supporting information](#).

#### 4. Conclusions

The cathode specific resistance increased from  $70 \pm 10 \text{ m}\Omega \text{ m}^2$  to  $148 \pm 32 \text{ m}\Omega \text{ m}^2$  (PVDF DL) and from  $54 \pm 14 \text{ m}\Omega \text{ m}^2$  to  $342 \pm 142 \text{ m}\Omega \text{ m}^2$  (PTFE DL) after two months of operation in wastewater fed MFCs. Concentrated HCl or vinegar (acetic acid) completely restored the initial power densities. Other treatments were less effective, with recoveries of 63% (steam cleaning) and 53% recovery with NaOH (100 mM) or ethanol 70% (PVDF DL). Lower concentrations of HCl (1 mM, 10  $\mu\text{M}$ ) were ineffective for cathode regeneration. Thus, strong acid cleaning is needed to restore cathode performance.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biortech.2019.121759>.

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