Effect of increasing anodic NaCl concentration on microbial fuel cell performance

Olivier Lefebvre, Zi Tan, Shailesh Kharkwal, How Y. Ng *

Centre for Water Research, Department of Civil and Environmental Engineering, National University of Singapore, 1 Engineering Dr. 2, Singapore 117576, Singapore

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ABSTRACT

High salinity effluents represent an estimated 5% of the wastewater generated worldwide. In microbial fuel cells, high salinity is usually considered beneficial to power production because increased conductivity facilitates proton transfer and therefore decreases the internal resistance of the system. However, high salt concentrations are known to adversely affect the physiology of anaerobic microbial consortia. In this study, the effect of increasing NaCl concentration in the anode chamber of a microbial fuel cell fed with sodium acetate was tested. Adding up to 20 g L⁻¹ of NaCl enhanced the overall performance of the system, reducing the internal resistance by 33% and increasing the maximum power production by 30%. Higher NaCl concentration proved detrimental to the system. However, the Coulombic efficiency started to be affected at a much lower NaCl concentration of 10 g L⁻¹, showing that the anodophilic bacteria are sensitive to NaCl at relatively low concentrations.

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1. Introduction

Many industrial sectors (petroleum, leather, food processing, etc.) generate saline pollution and up to 5% of the effluents worldwide can be considered saline (Lefebvre et al., 2007). In a few cities, such as Hong Kong, toilets are flushed with seawater, generating saline sewage. With increasing water scarcity expected in the course of the century, such practice is expected to become more common resulting in the release of even more saline wastewater. The biological treatment of saline wastewater has become an emerging topic in the last decade even though elevated salt concentrations can be a major obstacle (Lefebvre and Moletta, 2006). In a recent study, Lefebvre et al. (2007) specified that the extent of inhibition also depends on the complexity of the substrate with simple compounds such as ethanol being biodegradable at higher NaCl concentrations than complex industrial wastewater such as distillery vinasses.

Microbial fuel cell (MFC) is an emerging technology that can generate bioelectricity from a variety of substrates including wastewater. In an MFC, the substrate is degraded anaerobically by a biofilm of bacteria covering the anode of the system, releasing protons and electrons in the process. These combine at the – generally abiotic – cathode of the system to produce electricity and water. An important limitation of MFC systems is related to the slow rate of proton transfer (Lefebvre et al., 2011). This could be improved by increasing the salinity – and therefore, the conductivity – of the system. And indeed, in a two-chamber MFC, in which the biological reaction (anode) is physically separated from the abiotic reaction (cathode) by a membrane, increasing the ionic strength of the catholyte resulted in improved power generation (Fan et al., 2008; Gil et al., 2003). However, there is a lack of systematic studies regarding the effect of the ionic strength of the anolyte on the system.

In the anode chamber of an MFC, increased salinity might induce antagonistic effects – on the one hand increasing the conductivity of the system, but on the other hand affecting the physiology of the biofilm. The main study on this topic was conducted by Liu et al. (2005) who observed improved overall performance of their single-chamber MFC fed with sodium acetate following an increase of ionic strength from 100 to 400 mM by adding NaCl. However, the highest ionic strength tested in that study only corresponded to a NaCl concentration of 23 g L⁻¹, a level of salinity that can be well tolerated by an anaerobic ecosystem evolving on a simple substrate as shown by Lefebvre et al.
(2007). Noteworthy, the MFCs of Liu et al. (2005) were inoculated with domestic wastewater. The nature of the inoculum is an important parameter because it can affect the MFC performance; MFCs operated with pure cultures typically allow higher Coulombic efficiencies but this does not necessarily translate into higher power densities (Rabaey et al., 2004). Furthermore, it may not be practical to maintain the pure culture and MFCs inoculated with a mixed culture may prove more stable in the long run. Finally, considering that salt tolerance is known to vary widely from organism to organism (McCarty and McKinney, 1961), using a mixed culture can provide an insight into the salt tolerance of anodophilic bacteria as a functional group, which is arguably of broader interest. With the emergence of microbial desalination cells (MDCs) in which desalination is driven by microbial processes at the anode of the system (Cao et al., 2009), there is even more need for understanding the behavior of the anode at high salinities because MDCs typically result in increased salinity in the anode chamber of the system.

The purpose of this study was to assess the effect of increasing anodic salt (NaCl) concentration (up to 40 g L⁻¹) on both the biological (biofilm) and physical (conductivity) components of the MFC that are likely to be affected by salinity. The performance of the system was evaluated in terms of its electrical properties (i.e., electromotive force, internal resistance, maximum power generation), substrate (sodium acetate) removal efficiency and Coulombic efficiency (CE).

2. Methods

2.1. Microbial fuel cell

This study was conducted using a two-chamber MFC design comprising an anode chamber and a cathode chamber separated by a proton exchange membrane. The anode chamber had an effective dimensions of 11 × 6.55 × 2 cm and was crafted with multiple vertical channels (width of 0.6 cm) (Fig. S1a). The anode consisted of a sheet of carbon cloth glued on top of the anode chamber. The anodic working volume was of 32 mL. The proton exchange membrane (Selemon, Asahi, Japan) was glued on top of the anode and the anode compartment was inserted into the cathode compartment (see Fig. S1). The cathode compartment (effective dimension of 15 × 8 × 4 cm, working volume of 480 mL) was left open to the atmosphere and filled with Inconel 718, obtained from a local recycling factory, to be used as the cathode material (Fig. S1b). The composition of Inconel 718 was as follows: Ni (52.5%), Cr (19%), Fe (18.5%), others (10%).

2.2. Operating strategy

An illustration of the two-chamber MFC and its operating mode is provided in Fig. 1. The MFC was first inoculated with domestic wastewater for 3 months. As explained above, inoculation with sewage is a common practice in the MFC research and results in the development of a mixed culture, which allows studying a complex anodophilic ecosystem, representative of practical MFC systems. After successful inoculation, the feed was replaced with a synthetic solution (pH = 7) containing nutrients, minerals and vitamins following Oh et al. (2004). Sodium acetate was used as the carbon source at a concentration of 1.8 ± 0.1 g L⁻¹ and was fed upward into the anode chamber at a rate of 0.2 mL min⁻¹, ensuring a hydraulic retention time of 2.7 h and a loading rate of 15.8 ± 0.8 g L⁻¹ d⁻¹ of sodium acetate, based on the anodic working volume. The anodic effluent was then allowed to enter the cathode chamber at the bottom where it flowed upward (cf. Fig. 1). This configuration was proven beneficial by numerous works, facilitating proton transfer – hence resulting in increased power generation – while eliminating the need for the phosphate buffer solution typically used as catholyte in two-chamber MFCs (Freguia et al., 2008). Simultaneously, it provides aerobic polishing of the anode-treated effluent, making it possible to reach very high COD removal efficiencies. Active aeration was provided at the bottom of the cathode compartment using an aquarium pump and air diffuser.

The medium of Oh et al. (2004) contains a variety of salts including potassium chloride, ammonium chloride, sodium bicarbonate and sodium phosphate salts, resulting in an initial total dissolved solids (TDS) concentration of 5 g L⁻¹. This initial TDS concentration will not be mentioned any further in this paper, as the study focused on the effect of added NaCl. After reaching steady-state, the salinity was increased in stages by supplementing NaCl to the medium. Thus, it should be kept in mind that the addition of 5, 10, 20 and 40 g L⁻¹ of NaCl resulted in an overall TDS concentration of 10, 15, 25 and 45 g L⁻¹, respectively.

2.3. Analytical methods and calculations

The cell voltage was measured with a multimeter connected to a computer by a data acquisition system (M3500A, Array Electronic, Taiwan). Under normal operating conditions, the cell voltage was monitored on an hourly basis across an external resistance of 5 Ω and the current was determined using the Ohm’s law. Polarization curves were obtained by decreasing the applied external resistance and recording the pseudo steady-state voltage and power curves were calculated from the polarization curves using the Joule’s law. The cell electromotive force (Eemf, V) and internal resistance (Rint, Ω) were determined using a linear regression (least squares method) on the linear part of the polarization curve that corresponds to the Ohmic zone. The electromotive force was estimated as the intercept of the regression with the Y-axis whereas the internal resistance was the opposite of its slope. The maximum power (Pmax, W) supplied by the MFC was calculated as:

\[ P_{\text{max}} = \frac{E_{\text{emf}}^2}{4R_{\text{int}}} \]  

(1)

In this study, both Pmax and Rint were normalized to the anodic working volume. Acetate concentration was determined by gas chromatography (GC-2010 Shimadzu, Japan) after filtration with 0.45-μm filter. The Coulombic efficiency (CE) was determined as:
where $M$ (g/mol) is the molecular weight of sodium acetate, $I$ (A) is the current, $F$ is the Faraday's constant (96,485 C mol$^{-1}$ of electrons), $b$ is the number of moles of electrons produced per mole of sodium acetate, $q$ (L s$^{-1}$) is the flow rate and $\Delta$NaAc (g L$^{-1}$) is the difference in the influent and effluent sodium acetate concentrations. All experiments were performed in triplicate.

3. Results and discussion

3.1. Effect of increasing NaCl concentration on electricity generation

The polarization curves obtained with increasing NaCl concentration are displayed in Fig. 2a. $E_{\text{emf}}$ and $R_{\text{int}}$ initially averaged $0.44 \pm 0.01$ V and $1.8 \pm 0.1$ mΩ m$^2$, respectively, resulting in $P_{\text{max}}$ of $27 \pm 1$ W m$^{-3}$ (Fig. 2b) in the absence of NaCl apart from that initially contained in the medium of Oh et al. (2004). With addition of NaCl, $E_{\text{emf}}$ was unaffected whereas $R_{\text{int}}$ initially decreased, reaching a minimum of $1.2$ mΩm$^2$ at a NaCl concentration of $20$ g L$^{-1}$, a reduction by 33% as compared to the initial conditions. This corresponded to the optimal $P_{\text{max}}$ of $35 \pm 2$ W m$^{-3}$ achieved in this study. Therefore, the addition of $20$ g L$^{-1}$ of NaCl benefited electricity generation with an increase of $P_{\text{max}}$, by 30% as compared to the initial conditions. This confirms the trend observed by Liu et al. (2005) in reaction to a comparable increment of salinity, even though in their study $P_{\text{max}}$ increased more, by 83%. The difference can be explained by the different design (double- versus single-chamber MFC), operating conditions (continuous- versus batch-mode) and difference in biofilm maturity (months versus days).

When the NaCl concentration was further increased to $40$ g L$^{-1}$, the impact on power generation became detrimental, reducing $P_{\text{max}}$ to $18 \pm 1$ W m$^{-3}$, a 50% decrease from the optimal conditions at $20$ g L$^{-1}$ of added NaCl. It can be clearly seen from Fig. 2a that the reason for the power drop was not a reduction of $E_{\text{emf}}$ which remained stable at $0.42 \pm 0.02$ V – but instead could be attributed to an increase of $R_{\text{int}}$, reaching $2.4 \pm 0.3$ mΩm$^2$, which is an increase of 100% from the previous condition. $E_{\text{emf}}$ Stability under high NaCl concentrations indicates that the mechanisms for electron transfer remained unchanged; however, anodophilic cells dehydration in these conditions might have resulted in slower electron transfer rates, causing a drastic increase of $R_{\text{int}}$.

3.2. Effect of increasing NaCl concentration on the treatment performance and Coulombic efficiency

Initially, the anode-treated effluent displayed a sodium acetate concentration of $1.35 \pm 0.14$ g L$^{-1}$, corresponding to a removal efficiency of $27 \pm 5$%. In par with power generation, the sodium acetate removal efficiency increased with NaCl concentration, reaching 31 ± 1%, 37 ± 3% and 42 ± 1% at a NaCl concentration of 5, 10 and 20 g L$^{-1}$, respectively. Thus at the optimum level of salinity ($20$ g L$^{-1}$), the sodium acetate concentration in the anode-treated effluent attained $1.04 \pm 0.01$ g L$^{-1}$, 23% lower than the initial value. The improvement of performance can be directly correlated to the increased power generation, requiring additional substrate as a source of electrons and protons. At a NaCl concentration of $40$ g L$^{-1}$, however, the sodium acetate removal efficiency dropped and attained $26 \pm 2\%$ ($1.23 \pm 0.02$ g L$^{-1}$ of sodium acetate). This again can be correlated to power generation; however, the salinity level did not impact on the quality of the cathode-treated effluent as sodium acetate was never detected, demonstrating the efficacy of using the aerobic cathode compartment as a mean to polish wastewater, as shown by others (Freguia et al., 2008).

In the initial conditions, CE averaged $52 \pm 8\%$. Higher values of CE have been reported in the literature (Freguia et al., 2008; Oh et al., 2004) but CE lower than 10% are more commonly reported (Ghangrekar et al., 2010; Puig et al., 2011; You et al., 2010). Obviously, direct comparison of CE between different studies is difficult due to the variety of substrates and designs used; however, the relatively high CE observed in this study shows that the MFC design provided efficient electron transfer. With a small increment of salinity ($5$ g L$^{-1}$ of NaCl), CE increased to $58 \pm 3\%$, but further increase of salinity resulted in dropping CE that averaged $34 \pm 9\%$, $28 \pm 1\%$ and $22 \pm 3\%$ at 10, 20 and 40 g L$^{-1}$ of NaCl, respectively.

3.3. Implications on the microbiology of anodophilic bacteria

Due to the impossibility of sampling biofilm from our MFC system over the course of the experiment, this study did not include any molecular analysis of the anodic microbial consortium; however, the evolution of the anodophilic bacteria as compared to the non-anodophilic ones can be followed using CE, arguably the optimal criterion to assess the level of activity of bioelectricity production. In contrast, conventional molecular analysis of the biofilm would likely reveal a complex community – as both anodophilic bacteria (Lefebvre et al., 2010) and salt-tolerant bacteria (Lefebvre et al., 2006) have been shown to be widespread among the bacterial kingdom – but it would provide little information regarding their level of activity. Indeed, high salt concentrations have been shown to have little impact on the microbiology of activated sludge and the biodiversity of a poorly performing anaerobic digester was similar to that of a highly efficient aerobic reactor fed with the same saline tannery wastewater (Lefebvre et al., 2006). This finding was confirmed in another study, in which the inhibition of anaerobic digestion by high salt concentration was not reflected by a.
reduction of microbial diversity (Lefebvre et al., 2007). In these conditions, CE might be the best tool to get insight of the salt-tolerance of anodophilic bacteria.

The impact of NaCl concentration on the biological (anodophilic bacteria) and physical (conductivity) components of the microbial fuel cell using \( P_{\text{max}} \) and CE as criteria is illustrated in Fig. 3. The main observation is that CE was affected by a relatively low concentration of NaCl of 10 g L\(^{-1}\), a level of salinity where the overall performance of the MFC was improved. This allows segregating the physico-chemical impact of salinity (increased conductivity) from its biological impact on the activity of anodophilic bacteria. Conductivity increased proportionally with salinity and this benefited the MFC system as it facilitated proton transfer. This is the reason why increasing the ionic strength of the (usually abiotic) catholyte always benefits the system as demonstrated by others (Fan et al., 2008; Gil et al., 2003). However, this study shows that increasing levels of salinity in the anode compartment generated antagonistic effects. Increasing conductivity enhanced the power generation up to 20 g L\(^{-1}\) of NaCl, but higher salt concentration proved detrimental to the system, indicating relatively low tolerance of anodophilic bacteria to NaCl, as their activity (reflected by CE) was affected at NaCl concentration of 10 g L\(^{-1}\). In comparison, methanogenesis was shown to be inhibited by NaCl concentrations of 5 g L\(^{-1}\) while acidogenesis was only inhibited by NaCl concentrations higher than 20 g L\(^{-1}\) (Lefebvre et al., 2007). Among anaerobic microbial processes, this places bioelectricity production by MFC at an intermediate level of tolerance to NaCl. Finally, it should be noted here that De Schamphelaire et al. (2010) studied the effect of salinity on biocathodes and reached similar conclusions as ours, i.e., an initial improvement of performance with salinity up to medium level (5–15 g L\(^{-1}\)) followed by a decrease at higher values. They attributed this phenomenon to the salt sensitivity of bacteria colonizing the cathode of their system. This seems to indicate similar level of salt tolerance of both types of microbes involved in electron transfer with an electrode, i.e., anodophilic and cathodophilic organisms.

3.4. Implications for bioelectricity production from saline wastewater

As shown in this paper, the antagonistic effect of NaCl on the physical medium (conductivity of the anolyte) and on the biological medium (the biofilm) made bioelectricity production advantageous up to 20 g L\(^{-1}\), even though anodophilic bacteria started being inhibited at 10 g L\(^{-1}\). This makes MFC a suitable candidate for biological treatment of wastewater at salinity around seawater but not beyond. An insight into the few studies available in the literature dealing with treatment of saline wastewater in MFC confirms our findings. You et al. (2010) treated seafood wastewater in an MFC and were able to obtain reasonably high CE of 15%, while generating 9 W m\(^{-3}\) and removing 80% of the COD. However, Wang et al. (2010) showed that the maximum power and CE obtained from an MFC making use of Shewanella sp. DS1 isolated from deep-sea sediment decreased at NaCl concentrations higher than 3%. Attempts at generating bioelectricity under even higher salt concentrations resulted in considerably reduced power production. For example, Puig et al. (2011) were only capable of generating 0.3 W m\(^{-3}\) of electricity (CE < 2%) from very highly conductive (73,588 \(\mu\)S cm\(^{-1}\)) landfill leachate. Similarly, Mohan et al. (2009) attempted to treat high TDS (57 g L\(^{-1}\)) chemical wastewater with limited success with only 1.5 W m\(^{-3}\) of electricity output. In their study, however, the nature of the TDS was not mentioned, which could be a criterion of importance as sulphates and bicarbonates, for instance, have been shown to inhibit electricity generation from MFCs even at low TDS concentration (Ghangrekar et al., 2010).

An implication of the findings of this study is that the level of salinity of an effluent should be considered carefully before feeding it to an MFC system. If the salinity is above that of seawater, it might be advantageous to pretreat the wastewater by other means – i.e., by physicochemical or aerobic means, which are less sensitive to salt – before using the pretreated wastewater as the catholyte of an MFC, which would then benefit from the high salinity. Alternatively, such pretreated wastewater can be desalinated efficiently by MDC, generating electricity in the process (Cao et al., 2009).

4. Conclusions

In this study we analyzed the effect of increasing NaCl concentration on the performance of a two-chamber MFC. Up to 20 g L\(^{-1}\), NaCl proved beneficial to the system; however, CE was affected at a much lower NaCl concentration of 10 g L\(^{-1}\). The fact that anodophilic bacteria are sensitive to relatively low NaCl concentrations resulted in a drastic reduction of power production at high NaCl concentration of 40 g L\(^{-1}\). A direct consequence is that wastewater at salinity level higher than seawater should be considered with care before being fed to an MFC.

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Appendix A. Supplementary data


References


