Challenges in upscaling microbial electrochemical reactors for copper recovery from acidic leachates

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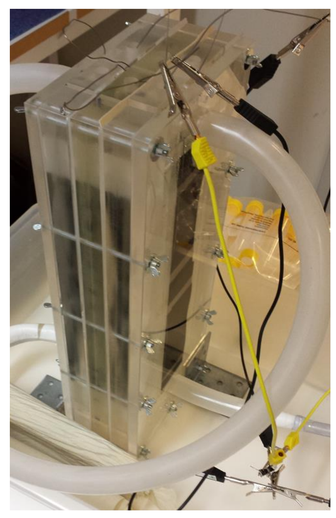
INTRODUCTION

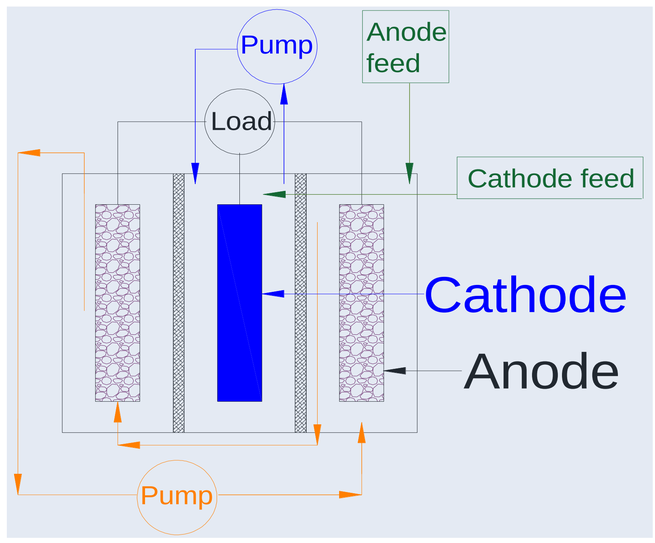
Metals in incineration ashes and contaminated soil pose great threats to the environment since they can leach and spread toxicity. On the other hand, metals in waste stream can also have high economic value and can be seen as unutilized resources. Microbial electrochemical reactors have previously been investigated for recovery of metals e.g. Cu from wastewater (Ter Heijne et al. 2010). We have previously investigated ml-scale reactors for recovery of Cu and other metals (Pb, Cd, and Zn) from acidic leachates (Modin et al. 2012; Fedje et al. 2015). The aim of this study was to design an up-scaled microbial fuel cell for Cu recovery from highly acidic soil leachate and to investigate the challenges encountered when operating such a reactor.



METHODOLOGY

- 3 chamber reactor – the two outer anode chambers were hydraulically connected, the inner chamber housed the cathode.
- 35x5x2 cm^3 chambers.
- A 30x5x0.318 cm^3 carbon felt anode placed in each anode chamber
- A 30x5x0.025 cm^3 titanium plate cathode
- Two 35x5 cm^2 anion exchange membranes (AMI-7001S) separated the chambers

➢ Reactor started up in batch mode
➢ Later, operation changed to continuous feed of both anolyte and catholyte



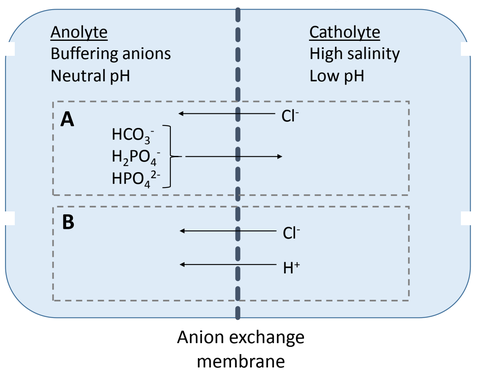
Schematic of the experimental setup

❑ Anode fed with real domestic wastewater amended with CH_3COONa and HCO_3Na
❑ Cathode fed with synthetic leachate containing NaCl, $CuSO_4$ and HCl

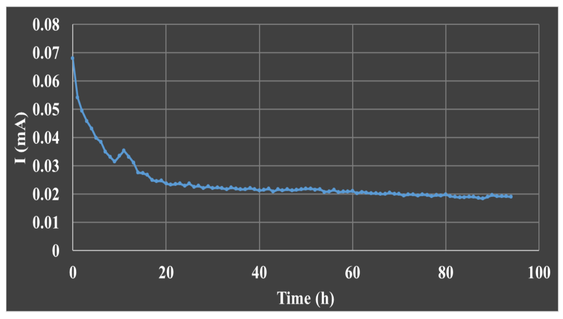
RESULTS AND DISCUSSION

Several challenges were encountered when operating the reactor:

1. Acidifictation of the anolyte. When the catholyte was highly acidic (pH<3), diffusion of H^+ from catholyte to anolyte and diffusion of bicarbonate in the opposite direction led to alkalinity loss and pH drop in the anode chamber, which killed bioelectrochemical activity.

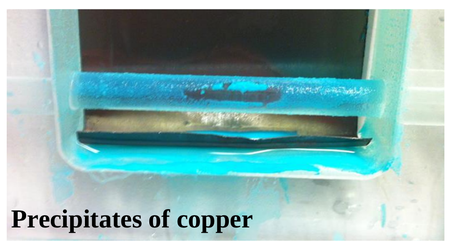


Mechanisms for acidification of the anolyte

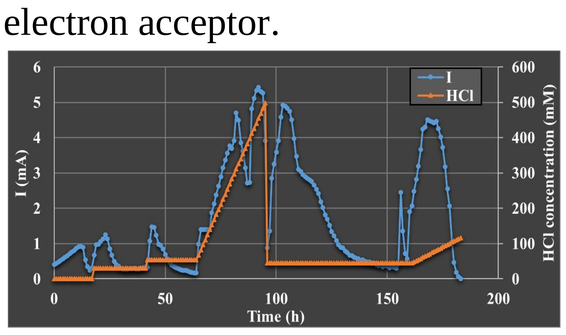


Current logged when anolyte was acidified (pH 1)

2. Precipitation of copper. The pH of the catholyte was adjusted to prevent acidification of the anolyte. This led to precipitation of copper hydroxides. When Cu^{2+} precipitated, the current generated in the reactor dropped because of lack of electron acceptor.

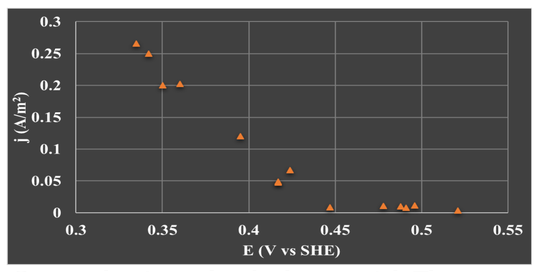


Precipitates of copper

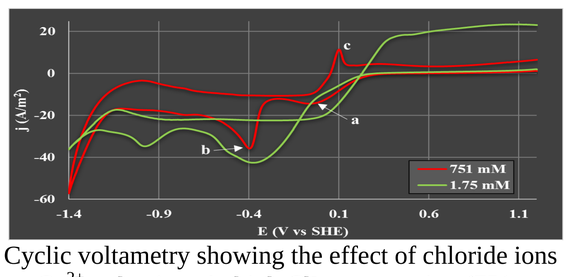


Current generation was related to HCl additions to the catholyte. Current dropped because of too little HCl, which led to Cu^{2+} precipitation (e.g. ~30 h) or because of too much HCl, which led to anolyte acidification (~90 h).

3. Low current density. Both O_2 and Cu^{2+} reduction can occur on the cathode. At low current densities, the cathode potential is high and all electrons are used to reduce O_2.

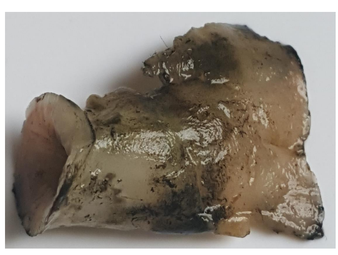


Current density and cathode potential. The cathode potentials were too high for Cu^{2+} reduction.

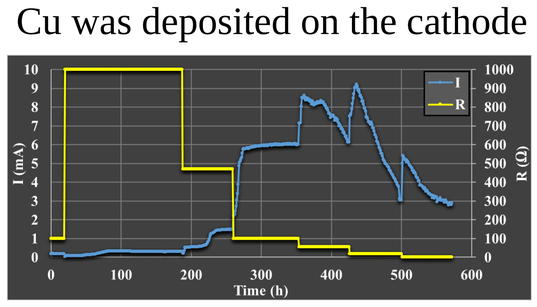


Cyclic voltametry showing the effect of chloride ions on Cu^{2+} reduction. At high Cl^-concentration (751 mM), there is a two step reduction Cu^{2+} to $CuCl_2^-$ (peak a) and $CuCl_2^-$ to Cu(s) (peak b). The oxidation peak (c) is also shifted in the negative direction.

4. *Clogging*. Operation with real domestic wastewater led to some problems with clogging of tubes. The photo to the right shows a sludge plug from the tubing in the reactor.



With the pH of the catholyte controlled at 3.5-3.7, stable current generation could be obtained in the reactor. By downsizing the cathode, a current density of about 1.5 A/m^2 was obtained and some Cu was deposited on the cathode surface.



Improved current generation with pH-controlled catholyte.

Copper accumulation on undersized cathode

CONCLUSIONS AND RECOMMENDATIONS

❑ This study highlighted the importance of up-scaled reactor designs to identify challenges in the operation and control of microbial electrochemical cells. For example, our previous studies with ml-scale reactors masked problems with acid diffusion from catholyte to anolyte because of small membrane and over-dimensioned anode compartments (e.g. Modin et al. 2012). This became evident for the litre-scale reactor used in this study.
❑ Careful control of catholyte pH is needed to prevent precipitation of Cu^{2+} and acidification of the anolyte.
❑ A sufficient current density is needed to bring the cathode potential to a value that is low enough to allow Cu^{2+} reduction. 1.5 A/m^2 was needed in this study. In a previous study with Cu cathode, 1 A/m^2 was required (Rodenas Motos el. 2015).
❑ A completely anaerobic catholyte may reduce the competition from O_2 and thereby lead to lower cathode potential even at low current density. However, completely excluding O_2 may be practically difficult.
❑ The high Cl^- concentration present in leachate shifts the required cathode potential for Cu(s) formation to a lower value.
❑ Measures to reduce clogging of the reactor and discharge system are recommended.

REFERENCES AND ACKNOWLEDGEMENTS

Fedje et al., 2015. Metals, 5(3): 1328-1348.
Modin et al., 2012. Journal of Hazardous Materials, 235-236: 291-297.
Rodenas Motos et al., 2015. Frontiers in Microbiology, 6: 527.
Ter Heijne et al., 2010. Environmental Science & Technology, 44: 4376-4381.

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