Short Communication

Microbial Fuel Cell-driven caustic potash production from wastewater for carbon sequestration

CrossMark

Iwona Gajda [a,*], John Greenman [a,b], Chris Melhuish [a], Carlo Santoro [c], Ioannis Ieropoulos [a,b]

[a] Bristol BioEnergy Centre, Bristol Robotics Laboratory, University of the West of England, BS16 1QY, UK
[b] Biological, Biomedical and Analytical Sciences, University of the West of England, BS16 1QY, UK
[c] Department of Chemical and Biological Engineering, Center for Micro-Engineered Materials (CMEM), The University of New Mexico, MSC01 1120, Albuquerque, NM 87131-0001, United States

HIGHLIGHTS

- MFC shows potassium recovery from wastewater in the form of caustic potash (KOH) and electricity.
- Caustic catholyte (pH > 13) has been formed on the surface of the cathode electrode.
- The catholyte mineralised to kalicinite locking carbon dioxide into potassium bicarbonate salt.
- MFCs cogenerate electricity and fix carbon dioxide as a way of carbon negative technology.

ARTICLE INFO

ABSTRACT

This work reports on the novel formation of caustic potash (KOH) directly on the MFC cathode locking carbon dioxide into potassium bicarbonate salt (kalicinite) while producing, instead of consuming electrical power. Using potassium-rich wastewater as a fuel for microorganisms to generate electricity in the anode chamber, has resulted in the formation of caustic catholyte directly on the surface of the cathode electrode. Analysis of this liquid has shown to be highly alkaline (pH > 13) and act as a CO_2 sorbent. It has been later mineralised to kalicinite thus locking carbon dioxide into potassium bicarbonate salt. This work demonstrates an electricity generation method as a simple, cost-effective and environmentally friendly route towards CO_2 sequestration that perhaps leads to a carbon negative economy. Moreover, it shows a potential application for both electricity production and nutrient recovery in the form of minerals from nutrient-rich wastewater streams such as urine for use as fertiliser in the future.
© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The growing consumption of fossil fuels is increasing the emissions of carbon dioxide, which is a major greenhouse gas (GHG), contributing to global warming. To limit the impact of CO_2 emissions, there is a need to develop efficient carbon capture and storage technologies (CCS). Direct CO_2 capture from ambient air ("air capture") is currently under consideration as an option for stabilising global CO_2 concentrations. The most developed air capture technologies are based on carbon dioxide absorption by aqueous solutions of NaOH or KOH used as sorbents (Stucki, 1995), which is a process known as wet scrubbing. However, the

major drawback is the energy intensive regeneration process requiring high temperatures of used sorbent (Goeppert et al., 2012). Using potassium hydroxide as a sorbent for example, the absorption process is accompanied by the precipitation of $KHCO_3$ (kalicinite), which is separated from the solution, transferred to a regeneration unit, and then heated to 100–200 °C in order to decompose back to K_2CO_3. A recent method of sorbent regeneration from wastewater includes the use of bioelectrochemical systems (BES) where electrical power can be used to produce acid and alkali solutions (Zhu et al., 2013). This incorporates wastewater treatment and the recycling of its elements into useful products and chemicals with the use of microbial activity and external power input (Kelly and He, 2014) for example, to produce caustic soda in Microbial Electrolysis Cells (MEC) (Rabaey et al., 2010). The Microbial Fuel Cell (MFC) however, generates electricity (with no external electrical input) as a result of microbial oxidation of organic pollutants in the anode (Habermann and Pommer, 1991).

A cathode pH increase occurs whether a cation or anion exchange membrane is used (Fornero et al., 2008) and this is thought to be due to the oxygen reduction reaction (ORR): $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ that occurs in the cathode chamber (Kinoshita, 1988). The cations transported from the anode combine with OH^- to produce alkali in the cathode half-cell. The transfer of alkali ions through the proton exchange membrane plays a major role in the charge balance of the ion flux from the anodic into the cathodic chamber. This leads to the formation of pH gradients between the anode and the cathode and adds to the pH splitting effect within dual-chamber MFCs (Harnisch et al., 2008). Attempts at producing alkaline solutions have been demonstrated in BES systems with the use of electrodialysis coupled with a Microbial Fuel Cell system (Chen et al., 2013), although these modifications still required consumption of electricity to drive the processes. However, for the efficient production of alkaline sorbents, the electrical energy source needs to be carbon-neutral in order to accomplish green and sustainable CO_2 sequestration. Therefore, using reversed electrodialysis incorporated into a BES system may be one option to produce acid and base solutions, by creating a multi-chamber device containing a bipolar membrane and an external source of salt solution (Zhu et al., 2013).

Recent advancements have demonstrated that an MFC (without any external electrical or chemical input) may drive the production of chemical sorbents and produce electricity (Gajda et al., 2014). MFC recovers energy from various organic substrates, such as wastewater, urine and even pre-treated cellulose. MFC is a discipline with an exponentially growing research field, with rapid advances in materials and engineering that drive its development towards multifaceted applications. It has been suggested previously that the use of MFCs may replace MECs and eliminate the major energy requirement for the external power supply (Qin and He, 2014). This work is following such a path presenting the potential for wastewater recycling and electricity production with the formation of a caustic potash sorbent. It has been previously shown that sodium salts may be recovered on the cathode as a mechanism for driving carbon sequestration (Gajda et al., 2014), and the current work focuses on potassium remediation based on a similar concept. This work is aiming to explore potassium hydroxide formation in a simple MFC reactor with a microbial anode and an open to air Pt-free cathode. It is therefore proposed that the MFC can now utilise potassium-rich wastewater, and result in the formation of potassium carbonates/bicarbonates (kalicinite) in the cathode. This is particularly important in terms of future use of MFC systems in practical applications utilising potassium rich wastewaters such as urine. Utilising urine for electricity and recovery of elements is very important for improving sanitation in developing countries and may also give the opportunity for caustic catholyte reuse as a cleaning, flush agent in smart toilets. Recovering potassium and its use as a carbon sink, followed by the mineralisation into bicarbonate, has a potential use as fertiliser as well as stabilising the carbon cycle.

2. Materials and methods

Twelve dual-chamber MFC reactors (forming four experimental groups, with 3 replicates each) were made from acrylic material for both the anode and cathode chambers, which were of equal 25 mL volume. The anode electrode was 3-dimensional carbon fibre veil material (PRF Composite Materials, UK) of 270 cm² total macro-surface area, with a carbon loading of $20\,g\,m^{-2}$ that had been folded down and pierced with the Ni–Cr wire. A cation exchange membrane (CEM) was used as the separator (CMI7000, Membranes International, USA). Three types of 2-dimensional gas diffusion cathode electrodes included: (i) microporous layer on carbon cloth (MPL); (ii) MPL on carbon fibre veil (Veil MPL); and (iii) activated carbon (AC) on carbon cloth. MPL (carbon black mixed with PTFE) and AC (activated carbon mixed with PTFE) were prepared as previously described (Santoro et al., 2012, 2014). All 2-D cathodes measured 10 cm² and the three dimensional carbon veil (Veil) used as the control for the 270 cm² area, had been folded down such that its projected contact area with the membrane was 10 cm². All cathodes had been mechanically pressed to maintain good physical contact between the cathode electrode and the CEM membrane. The anode chambers were inoculated with activated sewage sludge (Wessex Water, UK), and the cathode chambers were kept empty, keeping the electrodes enclosed within the 25 mL cathode chamber. This was to maintain air exposure for the cathode and at the same time prevent it from drying out. Diluted activated sludge was mixed with 20 mM potassium acetate and used as the carbon-energy feedstock for the anodic microbial community. The anodes were fed by circulating the feedstock from a 1 L tank, at a flow rate of $48\,mL\,h^{-1}$, using a Watson Marlow multichannel peristaltic pump. The experimental set-up was operated in laboratory conditions with temperature controlled at 22 °C. A schematic representation of the experimental setup, is shown in Fig. 1.

A 300 Ω resistor was connected between the anode and cathode of each MFC, to measure the voltage output using a Picolog ADC24 (Pico Technology, UK) and power has been calculated as previously
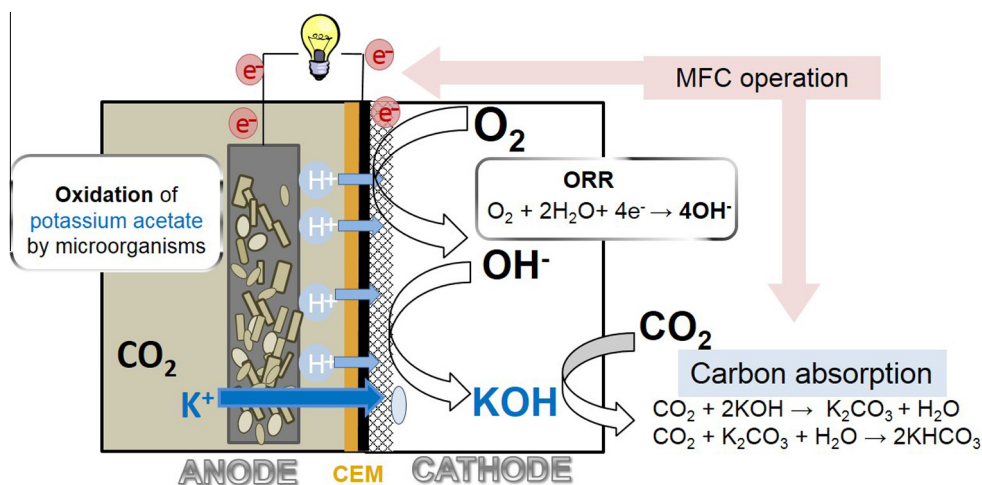

Fig. 1. Schematic description of the MFC reactor and the forming catholyte.

reported (Ieropoulos et al., 2008). The catholyte pH was measured using a handheld Hanna 8424 pH meter (Hanna Instruments, UK) and solution conductivities were measured using 470 Jenway conductivity metre (Camlab, UK). To determine the elements present as crystallised cathodic salts, the elemental analyses and elemental mapping were performed using energy dispersive X-ray fluorescence spectroscopic (EDX) (Philips XL30 SEM) with detection limits of 0.1–100% wt. X-ray diffraction (XRD) analysis on salts crystallised from the catholyte was determined using powder measurements, performed on a Bruker D8 Advance Diffractometer with the results further analysed using a search/match software package in the identification of XRD spectra. Microscopic images of the mineralised catholyte samples were taken by a digital microscope (KH-7700, Hirox, Japan). Anolyte samples were collected at the feedstock reservoir (1 L) connected to the MFCs and compared with the control tank that is not connected to the MFCs in the same environment conditions. Chemical oxygen demand (COD) measurement was performed on filtered anolyte samples (0.45 μm filters, Millex, USA) using the potassium dichromate oxidation method (COD HR, Jenway, UK) and a MD 200 photometer (Lovibond, UK).

3. Results and discussion

The power performance and the synthesis of clear catholyte are shown in Fig. 2 and the process of catholyte formation is shown in Fig. 1. Fig. 2A shows the performance data when each MFC was connected to the 300 Ω external resistive load. The average power data show that the best performing AC generated 270 μW ± 19 μW, the second best MPL produced 144 μW ± 20 μW, Veil MPL gave 152 μW ± 32 μW and Veil generated 105 μW ± 34 μW, during an 18-day operation. All MFCs generated catholyte that was collected in the syringe attached to the cathode half-cell, and it was shown to be directly related with the power output performance; AC generated 20.8 mL ± 2.8 mL, MPL 16.7 mL ± 3.9 mL, Veil MPL 15.5 mL ± 0.2 mL and Veil 14.6 ± 1.8 mL (Fig. 2B). Plotting the catholyte against the power generation shows the linear relationship between the two parameters, as illustrated in Fig. 2B. Activated carbon cathode has shown to be the best performing both in power generation as well as formation of catholyte, which is in agreement with earlier reports (Gajda et al., 2014). As previously suggested, the catholyte formed is due to the electro-osmosis where cations are dragging water molecules across the CEM membrane (Gajda et al., 2014; Kim et al., 2009).

The gravity drop design allows the cathode to avoid flooding and collect the catholyte so that the diffusion of hydroxide ions from the cathode back to the anode, may be prevented. Moreover, it allows washing out any possible salt precipitation on the cathode electrode surface, as the empty chamber limits evaporation and prevents the electrode from drying out. High strength salt solutions (externally supplied) have been used in Forward Osmosis (FO) systems where FO may be incorporated in Osmotic MFCs (OsMFCs) to draw and recover water from the anode (Zhang et al., 2011). In contrast, the MFCs in our system were not supplied externally with high strength solutions and water has been successfully recovered as the catholyte. It has been demonstrated that the carbonates may be successfully used as draw solutions in OsMFC (Qin and He, 2014) therefore an MFC that is able to synthesise its own draw solution is particularly attractive.

Results showed that all Pt-free cathodes used in this study including plain carbon veil, activated carbon, and MPL (applied to
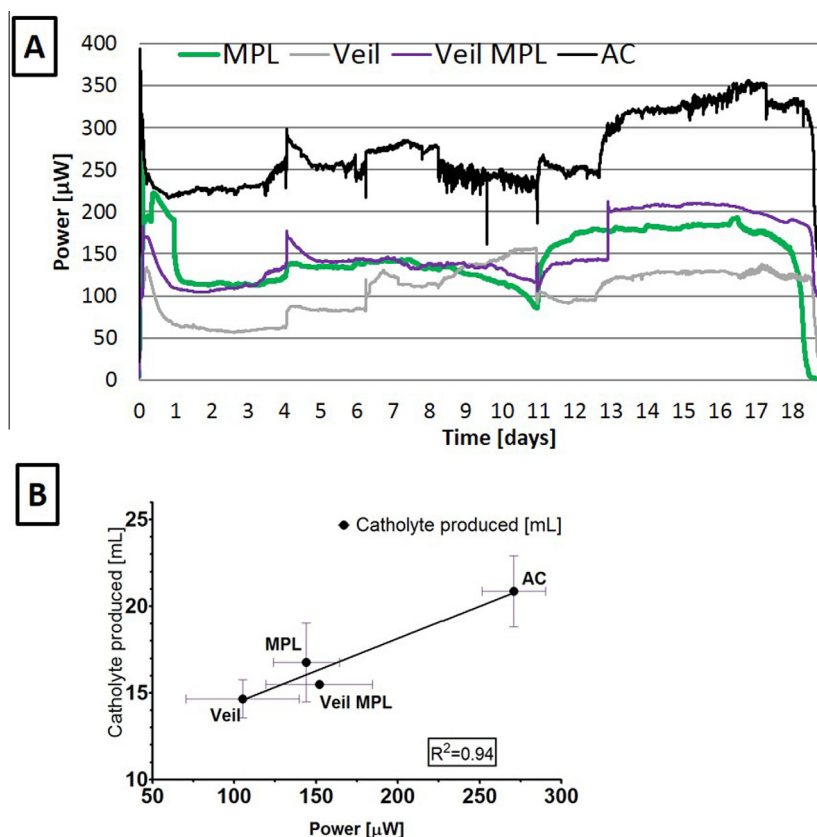

Fig. 2. Power performance (mean values) over 18 days of MFCs operation (A), amount of catholyte formed in the cathode half-cell based on various cathode materials and correlation of power to volume of liquid collected (B).
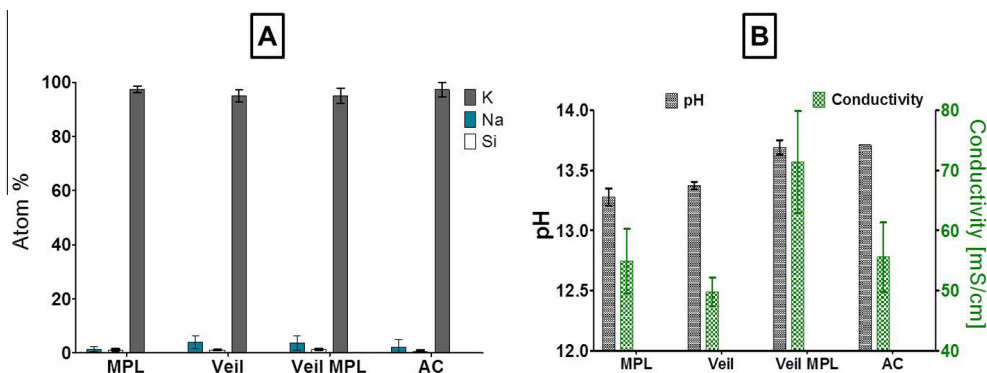
Fig. 3. EDX showing atomic content (%) in crystalised salts obtained from all samples (A) and the pH and conductivity analysis of the catholyte samples (B).
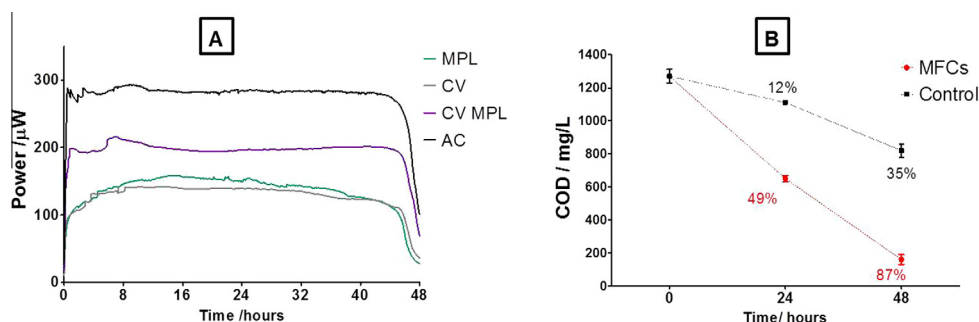

Fig. 4. MFC power performance (mean values) of the experimental groups during COD test (A), COD reduction for the 1 L of anolyte recirculated within the MFC system over 48 h vs 1 L of control anolyte (B) that was left to stand in a bottle, not treated by the MFCs.

both carbon cloth and carbon veil), generated electric current with simultaneous catholyte production in the cathode chamber. During the MFC operation, the production of catholyte on the surface of the cathode electrode was a direct result of electricity generation, and power output has been correlated with catholyte volume. Moreover, the elevated pH values of 13.20–13.78, as well as the increased conductivity levels, rendered the catholyte strongly basic and with a high salt content (Fig. 3B), which could be utilised as a draw solution for OsMFCs, which is a technique that has already been adopted in MECs (Qin and He, 2014). Previously, the same MFC system has been supplemented with real wastewater containing sodium acetate, and shown sodium recovery on the cathode in the form of sodium carbonate/bicarbonate salts (Gajda et al., 2014). Here, when the anode feedstock was potassium acetate, KOH was formed on the cathode half-cell with further crystallisation of potassium carbonate salts. To analyse the salt content of these samples, the collected liquid was left to evaporate, and the resulting crystals of solid salts were visibly shown to have hygroscopic properties. Moreover, the salts were shown to be soluble in water and insoluble in ethanol. Phase composition of the salt was studied by EDX and the dominant atomic content was potassium, with trace elements of sodium and silicon in all the tested samples, as illustrated in Fig. 3A. XRD analysis showed that the salt precipitants were of crystalline structure and further XRD powder diffraction pattern analysis, illustrated good comparison with the diffraction pattern of the mineral phase kalicinite (potassium bicarbonate) as shown in the Supplementary Information. Potassium bicarbonate (kalicinite) is the product of potassium carbonate binding further with CO_2, in a second stage reaction, which has been reported to be an excellent mechanism for carbon capture (Lee et al., 2006). In addition, OH^- can be used in electrocoagulation – a rapidly developing method for contaminant removal in waste streams, to control the cathodic pH gradient between the

anode and the cathode (Torres et al., 2008) and has also been shown to form minerals such as struvite and trona (Gajda et al., 2014; You et al., 2016).

The COD measurement was performed during a 48 h period of operation, when feedstock was recirculated within the system. Power output was stable for the majority of time, until the carbon energy depleted, which resulted in a rapid decrease, suggesting COD depletion (Fig. 4A). The COD analysis showed up to 87% reduction within the MFC system after 48 h whereas only 35% COD reduction was observed for the control feedstock that was left to stand in a room, under ambient conditions, for the same length of time. This was due to the oxidation of acetate and wastewater mixture occurring naturally by the microbial activity.

This paper demonstrates an innovative and energy-efficient system that exploits microbially assisted electrosynthesis for the recovery of valuable elements from wastewater, in the form of chemicals (KOH) and electricity. Such simple electricity generating operation provides a sustainable source of potassium-based draw solute for carbon capture, which has already been shown to be a more effective sorbent than sodium carbonate (Lee et al., 2006).

This proof-of-concept system provides the grounds for further optimisation studies with other wastewater types, including urine. Wastewater has always been regarded as a source of pollution that requires disposal and energy intensive treatment. Recent advances in MFC research have shown that wastewater may be seen as a resource for nutrients, water and bioenergy. These results have successfully shown the feasibility of coupling an electricity producing MFC with potassium-recovery in the form of caustic potash as a sorbent for carbon capture. This provides a sustainable source of alkaline draw solute in the form of kalicinite that could be extracted from wastewater directly by MFC operation, without the need for extra electrical or salt input. The results of this work invite further investigation into *in situ* generation of caustic potash

(KOH) directly from potassium-rich wastewater such as raw urine, which avoids the need for transport, handling and storage of concentrated caustic solutions.

4. Conclusions

This approach leads to carbon capture through wet caustic scrubbing on the cathode, which locks the carbon dioxide into carbonate salts, whilst simultaneously generating electricity. The MFC driven electrochemical conversion gives the opportunity to valorise waste streams and fix carbon dioxide as carbonate salts, hence showing the beginning stages of perhaps a carbon-negative cycle.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2016.04.004.

References

Chen, M., Zhang, F., Zhang, Y., Zeng, R.J., 2013. Alkali production from bipolar membrane electrodialysis powered by microbial fuel cell and application for biogas upgrading. Appl. Energy 103, 428–434. http://dx.doi.org/10.1016/j.apenergy.2012.10.005.
Fornero, J.J., Rosenbaum, M., Cotta, M.A., Angenent, L.T., 2008. Microbial fuel cell performance with a pressurized cathode chamber. Environ. Sci. Technol. 42, 8578–8584. http://dx.doi.org/10.1021/es8015292.
Gajda, I., Greenman, J., Melhuish, C., Santoro, C., Li, B., Cristiani, P., Ieropoulos, I., 2014. Water formation at the cathode and sodium recovery using microbial fuel cells (MFCs). Sustainable Energy Technol. Assess. 7, 187–194. http://dx.doi.org/10.1016/j.seta.2014.05.001.

Goeppert, A., Czaun, M., Surya Prakash, G.K., Olah, G.A., 2012. Air as the renewable carbon source of the future: an overview of CO2 capture from the atmosphere. Energy Environ. Sci. 5, 7833. http://dx.doi.org/10.1039/c2ee21586a.
Habermann, W., Pommer, E., 1991. Biological fuel cells with sulphide storage capacity. Appl. Microbiol. Biotechnol. 35, 128–133.
Harnisch, F., Schröder, U., Scholz, F., 2008. The suitability of monopolar and bipolar ion exchange membranes as separators for biological fuel cells. Environ. Sci. Technol. 42, 1740–1746.
Ieropoulos, I., Greenman, J., Melhuish, C., 2008. Microbial fuel cells based on carbon veil electrodes: stack configuration and scalability. Int. J. Energy Res. 32, 1228–1240. http://dx.doi.org/10.1002/er.1419.
Kelly, P.T., He, Z., 2014. Nutrients removal and recovery in bioelectrochemical systems: a review. Bioresour. Technol. 153, 351–360. http://dx.doi.org/10.1016/j.biortech.2013.12.046.
Kim, J.R., Premier, G.C., Hawkes, F.R., Dinsdale, R.M., Guwy, A.J., 2009. Development of a tubular microbial fuel cell (MFC) employing a membrane electrode assembly cathode. J. Power Sources 187, 393–399. http://dx.doi.org/10.1016/j.jpowsour.2008.11.020.
Kinoshita, K., 1988. Carbon Electrochemical and Physicochemical Properties. John Wiley & Sons, Ltd.
Lee, S.C., Choi, B.Y., Ryu, C.K., Ahn, Y.S., Lee, T.J., Kim, J.C., 2006. The effect of water on the activation and the CO2 capture capacities of alkali metal-based sorbents. Korean J. Chem. Eng. 23, 374–379. http://dx.doi.org/10.1007/BF02706737.
Qin, M., He, Z., 2014. Self-supplied ammonium bicarbonate draw solute for achieving wastewater treatment and recovery in a microbial electrolysis cell-forward osmosis-coupled system. Environ. Sci. Technol. Lett. 1, 437–441. http://dx.doi.org/10.1021/ez500280c.
Rabaey, K., Bützer, S., Brown, S., Keller, J., Rozendal, R., 2010. High current generation coupled to caustic production using a lamellar bioelectrochemical system. Environ. Sci. Technol. 44, 4315–4321. http://dx.doi.org/10.1021/es9037963.
Santoro, C., Lei, Y., Li, B., Cristiani, P., 2012. Power generation from wastewater using single chamber microbial fuel cells (MFCs) with platinum-free cathodes and pre-colonized anodes. Biochem. Eng. J. 62, 8–16.
Santoro, C., Artyushkova, K., Babanova, S., Atanassov, P., Ieropoulos, I., Grattieri, M., Cristiani, P., Trasatti, S., Li, B., Schuler, A.J., 2014. Parameters characterization and optimization of activated carbon (AC) cathodes for microbial fuel cell application. Bioresour. Technol. 163, 54–63. http://dx.doi.org/10.1016/j.biortech.2014.03.091.
Stucki, S., 1995. Coupled CO2 recovery from the atmosphere and water electrolysis: feasibility of a new process for hydrogen storage. Int. J. Hydrogen Energy 20, 653–663. http://dx.doi.org/10.1016/0360-3199(95)00007-Z.
Torres, C.I., Lee, H.-S., Rittmann, B.E., 2008. Carbonate species as OH− carriers for decreasing the pH gradient between cathode and anode in biological fuel cells. Environ. Sci. Technol. 42, 8773–8777.
You, J., Greenman, J., Melhuish, C., Ieropoulos, I., 2016. Electricity generation and struvite recovery from human urine using microbial fuel cells. J. Chem. Technol. Biotechnol. 91, 647–654. http://dx.doi.org/10.1002/jctb.4617.
Zhang, F., Brastad, K.S., He, Z., 2011. Integrating forward osmosis into microbial fuel cells for wastewater treatment, water extraction and bioelectricity generation. Environ. Sci. Technol. 45, 6690–6696. http://dx.doi.org/10.1021/es201505t.
Zhu, X., Hatzell, M.C., Cusick, R.D., Logan, B.E., 2013. Microbial reverse-electrodialysis chemical-production cell for acid and alkali production. Electrochem. commun. 31, 52–55. http://dx.doi.org/10.1016/j.elecom.2013.03.010.