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

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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 mineralized 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 carbon negative economy. Moreover, it shows a potential application for both electricity production and nutrient recovery in a mineral form from nutrient-rich wastewater stream such as urine for use as fertilizer in the future.

Key words: Microbial Fuel Cell, caustic potash, kalicinite, carbon capture, wet scrubbing,
1. Introduction

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\(_2\)CO\(_3\). 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 Cell (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\(_2\)O + 4e\(^-\) → 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.
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 and Microbial Fuel Cell coupled 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 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, wastewater, urine and including 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 formation of 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 microbial anode and open to air Pt-free cathode. It is therefore proposed that the MFC can now utilise potassium–rich wastewater, and result in
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 carbon sink followed mineralisation into bicarbonate has a potential use as fertiliser and stabilising carbon cycle.

2. Materials and Methods

Twelve dual–chamber MFC reactors (forming four experimental groups, with 3 replicates each) were made from polycarbonate 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. Cation exchange membrane (CEM) was used as 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., 2014, 2012). 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 carbon-energy feedstock for the anodic microbial community. A recirculation flow rate of 48 mL h\(^{-1}\) set using a peristaltic pump (Watson Marlow, UK) was applied between the anode chambers and the 1L anodic tank to supply the feedstock. The experimental set-up was operated in laboratory conditions with temperature controlled at 22 °C.

A 300 Ω resistor was connected between the anode and cathode to measure the voltage output using a Picolog ADC24 (Pico Technology, UK) and power has been calculated as previously 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 meter (Camlab, UK). To determine elements present in crystallised cathodic salts, the elemental analyses and elemental mapping were performed using the energy dispersive X-ray fluorescence spectroscopic unit (EDX) (Philips XL30 SEM) with detection limits of 0.1–100% wt. X-ray diffraction (XRD) analysis on salts crystallized from the catholyte was determined using powder measurements, performed on a Bruker D8 Advance Diffractometer with the results being 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 (1L) 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 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 Figure 1. Figure 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, MPL 144 µW ±20 µW, Veil MPL 152 µW ±32 µW and Veil 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 (Figure 1B), 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 Figure 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 to earlier report (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).
Figure 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).

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 electrode 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.

![Figure 3. EDX shows atomic content (%) in crystalized salt obtained from all samples (A) and the pH and conductivity analysis of the catholyte samples (B).](image)

Results showed that all Pt-free cathodes used in this study including plain carbon veil, activated carbon, and MPL (applied to 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 to 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 added 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 Figure 3. 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 Supplementary Information. Potassium bicarbonate
(kalicinite) is the product of potassium carbonate binding further with CO2, 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).
Figure 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.

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 (Figure 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. This is due to natural 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 ground 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.

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