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Microbial fuel cell – A novel self-powered wastewater electrolyser for electrocoagulation of heavy metals

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ABSTRACT

This paper describes the suitability of the Microbial Fuel Cell (MFC) for generation of electrical power with a simultaneous synthesis of active catholyte in the form of caustic solution. The active solution formed inside a terracotta based MFC reactor was a product of self-powered wastewater electrolysis utilizing i) wastewater with added sodium acetate as a carbon source and ii) neat urine. The catholyte solution that has been actively synthesized was harvested and used for precipitation of heavy metals such as: iron, copper and zinc showing its suitability for use in electro-coagulation (electro-flocculation). This proposed alternative approach to self-powered electrocoagulation is based on electrochemically formed caustic catholyte within the inner cathode chamber of the MFC and then used *ex situ* to form metal hydroxides that precipitate out from heavy metal solutions.

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Introduction

There is an increasing need for more cost-effective methods of treating metal polluted waste streams. The development of electrochemical processes for wastewater treatment, remediation and disinfection has become a viable option in the past two decades [1]. Many types of industrial wastewater have been found to be highly saline and can be treated by electrochemical methods. Industrial wastewater, which is polluted with heavy metal compounds, is usually treated with the use of adsorption [2], flotation [3] and physico-chemical techniques

such as electrocoagulation (EC) [4,5] and electro dialysis [6]. In general, electrocoagulation (also called electroflocculation) is a process that is used for water and wastewater treatment that destabilises finely dispersed particles. EC is one of the most effective techniques to remove colour dyes and organic pollutants from industrial wastewater [7]. In the process of electrocoagulation, chemical compounds, which adsorb the wastewater polluting agents, are obtained electrochemically. The EC technique uses a direct current source between metal electrodes immersed in polluted water, where sacrificial anode electrodes (aluminum or iron based) generate coagulants that destabilise contaminants [7,8]. In addition, the cathode,

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produces OH^- ions generated in the reduction reaction. EC is an alternative method to conventional (chemical) flocculation because it avoids using chemicals, such as chloride or sulphate. The coagulants (iron or aluminium) are being released from the sacrificial anode in an electrochemical cell. Metal ions produced at the anode and hydroxide ions produced at the cathode react in the aqueous medium to produce various hydroxide species. These coagulant ions lead to the aggregation and sedimentation (in the form of flocs) of the pollutant particles in the water. The water is treated in an electrolyser reactor where the two electrodes of opposite charge (anode and cathode) are placed. As a result of this electrolysis, the ion composition of the bulk water in the vicinity of the electrodes is changed as well as pH, conductivity etc. Electrochemically obtained hydroxides have high sorption ability due to their finely dispersed structure and developed specific surface. Chemical precipitation is widely used for heavy metal removal where the pH adjustment is used in basic conditions in order to achieve the conversion of dissolved metal ions into the insoluble solid phase according to the reaction (1):



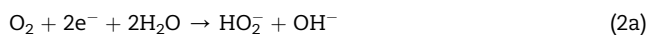
where:

M^{2+} represents the metal ions dissolved in the solution

OH^- represent the hydroxide ion as the precipitating agent (precipitant)

$\text{M}(\text{OH})_2$ is the insoluble metal hydroxide that is the product of the precipitation reaction

Microbial Fuel Cells (MFCs) are electrochemical devices that use the microbial metabolism to generate electric current while treating wastewater in the anode half-cell. Due to the MFC operation, protons and other cations migrate from the anode to the cathode to complete the reaction. Cathodic Oxygen Reduction Reaction (ORR) on carbon based electrodes has been shown to proceed via the peroxide pathway leading to alkaline conditions in the cathode according to the overall reaction 2a. It leads to producing perhydroxyl (HO_2^-), a protonated form of superoxide and its further reduction to more OH^- [9,10].



The result is leading to rapidly increasing local pH levels at the cathode electrode [11] and poor transport of OH^- from the cathode catalyst layer to the bulk liquid, consequently increasing over-potential losses. Many approaches result in using buffering agents in the cathode to decrease the pH gradient and minimise losses [11–13], which might not be successful [11] and unsustainable. However instead of trying to overcome this limitation, the alkaline agent could be harvested and utilised in a useful manner [12]. EC is a rapidly growing area in wastewater treatment, where the conventional electrolytic treatment produces electroactive

coagulants (flocculants) such as hydroxide ion (OH^-), which precipitate heavy metals. When caustic compounds are added to water containing soluble heavy metal ions, a metal hydroxide solid or precipitate is formed. In contaminated wastewater with heavy metals or dyes, it is desirable to precipitate as much solid metal as possible so that it can be removed from the water.

In recent years it has been demonstrated that hydroxide compounds such as caustic soda can be produced using Microbial Electrolysis Cells (MECs), where the proposed systems require the input of electrical energy [14,15]. Microbial Fuel Cells are self sustainable electricity generating bioreactors, which demonstrated that the production of caustic catholyte ($\text{pH} > 12$) could be achieved with a net production rather than consumption of electricity both with the use of specific cation exchange membranes [16] and plain terracotta used as separator [17]. This is due to the ORR and electroosmotically generated catholyte via electroosmosis within the cathode half-cell, which is a phenomenon first reported by F.F Reuss in 1809 in a ceramic plug [18]. Also, MFCs have been previously demonstrated to remove heavy metal compounds such as copper when the polluting compound was recirculated in the cathode chamber and mineralised to pure copper on the cathode electrode [19].

This current study describes a Microbial Fuel Cell (MFC) system, which produces a hydroxide coagulant (flocculant) in the form of a catholyte, but with the important advantage of generating – rather than using electricity. The self-powered electro-coagulation can be used to precipitate heavy metals from a range of solutions. This work presents a MFC-driven electrolysis of wastewater and urine to produce electricity and an active coagulant formed in the cathode, and proposes an innovative self-powered electro-coagulation system for practical implementation.

Materials and methods

MFC assembly and operation

MFCs (used in triplicate) were assembled using 10 cm long, 3.6 inside diameter terracotta caves (Weston Mills Pottery, UK)

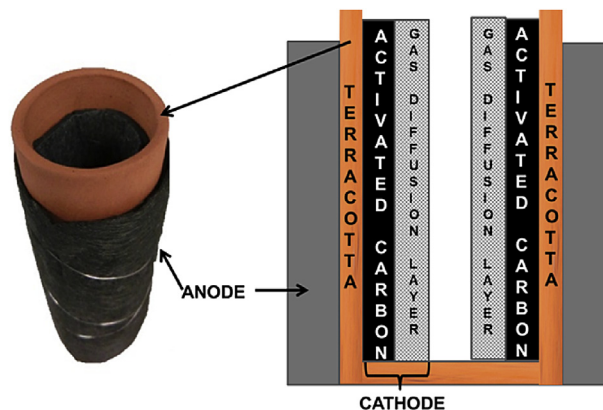


Fig. 1 – Terracotta based MFC reactor with anode and cathode configuration.

which were sealed at one end forming a hollow chamber. Fig. 1 shows one MFC reactor assembled with an outer anode and inner cathode configuration to allow the catholyte formation in the hollow cathode chamber. A carbon fibre veil (PRF Composites, UK) anode (carbon loading 20 g/m², total surface area 2430 cm²) was wrapped around the ceramic cylinder and activated carbon cathode was inserted inside the inner chamber. Activated carbon paste was prepared as previously described [17] and applied onto the 30% PTFE-treated carbon fibre veil substratum as gas diffusion layer. The cathode electrode surface area was 9 cm (length) by 10 cm (width) where the activated carbon side was facing the terracotta wall and gas diffusion layer was facing the air. The MFCs were placed in plastic containers (210 mL) and were inoculated with activated sewage sludge (Wessex Water, UK). The MFCs were further supplemented with a mixture of sludge and 0.1 M sodium acetate (pH 7) as an additional carbon source and kept in batch mode to evaluate the rate of performance. The MFC reactors were tested in triplicates under 100 Ω resistor. Following feedstock change, neat human urine was used as the substrate for the MFCs. Urine was collected anonymously from healthy individuals, pooled together and stored in a collection tank, at room temperature and used directly as the feedstock for the MFCs. The urine pH was ranging between: 8.6–9.4.

Data analysis and polarisation experiments

MFC performance was monitored using a multi-channel Agilent 34972A DAQ unit, recording output in Volts. Current (I) was calculated using Ohm's law ($I = V/R$), where R is the known external resistor value and V is the recorded voltage value, and power (P) was calculated as the product of voltage and current ($P = V \times I$). The quality of wastewater and formed catholyte was analysed using a 8424 pH meter (Hanna Inst., UK) and Jenway conductivity meter (Camlab, UK). Polarisation experiments were performed on single MFC units by applying a range of resistance values from 30 kΩ down to 11 Ω using an automated variable resistor every 3 min during which time, data were recorded every 30 s [20].

Precipitation tests

The catholyte collected from the MFCs was immediately used *ex situ* as the precipitating agent in separate metal/salts-based solutions. Catholyte was used for precipitation of water soluble salts such as iron chloride, copper sulphate and zinc chloride. A 0.1 g sample of the subject salts was dissolved in 20 mL of tested catholyte and deionized water (control) in glass universal bottles (Fisher, UK).

Results and discussion

MFC power performance

The polarisation experiment showed that all three tested MFCs have reached a power performance above 1 mW per MFC (actual power) with the maximum performance for MFC3 at 1.71 mW, 1.47 mW for MFC1 and 1.37 mW for MFC2 (Fig. 2).

The fluctuations shown in the power curve during the 30 s sampling intervals (6 samples per each resistance value), shows the genuine MFC behaviour during the experiment, and are the result of how the resistorstat apparatus operates. This is due to the stabilisation period that the MFC performs when the resistance is applied.

Following the polarisation experiments, the MFCs were kept under fixed load conditions, over 31 days. The performance reached steady states, during the operational period, under batch fed conditions with acetate/wastewater (Fig. 3). Due to the batch mode operation, the power performance was diminishing with time in each feeding cycle, and the recovery of power levels was recorded after the feeding with fresh feedstock. It is worth noting that the real-time performance of the MFCs (ca. 1.2 mW average) was on par with the power output levels recorded during the polarisation experiments.

Cathode electrode morphology

During the MFC operation, the formation of clear liquid was observed as previously described [17,21] and collected in the inner chamber where the accumulation of the liquid actually improved the performance. The catholyte formation mechanism has been discussed in detail in previous publications and it is due to the electroosmotic drag and passive diffusion where the more power the system generates the more catholyte can be produced in the cathode chamber [17,21].

The mobility of water molecules was due to the clay particles acquiring a surface charge when in contact with an electrolyte. The immobile surface charge attracts free ions of the opposite charge creating a Debye layer of mobile charges next to it. The thickness of an electrical double layer depends on the intensity of thermal fluctuations and the strength of the electrostatic attraction (charge density) [22]. Advances in fluid mechanics show that electroosmosis is a very efficient transport mechanism through very narrow capillaries [23]. The main advantage of electroosmotic flow is that it is a useful means of transporting analytes in a microfluidic circuits [24] which seems suitable for the terracotta built-MFC reactors and water recovery from waste. Moreover the current dependent transport of cations such as Na⁺, K⁺, Ca²⁺, Mg²⁺,

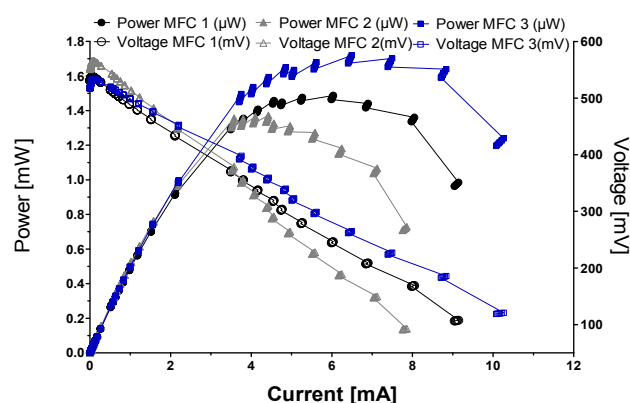


Fig. 2 – Power and polarisation curves from the 3 MFCs.

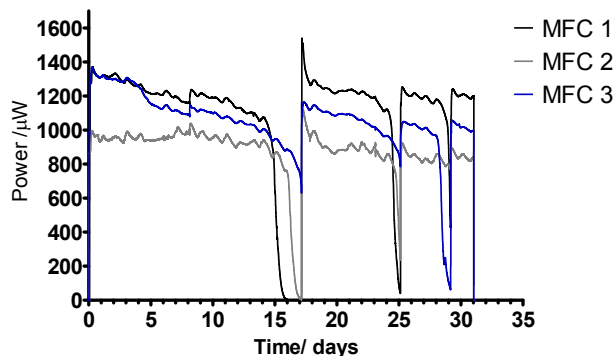


Fig. 3 – Power performance of the three tested MFCs over 31 days of operation.

NH_4^+ [17] from the anode through the ceramic and to the cathode chamber allows for the electrokinetic ion separation and active electrolytic filtration of wastewater including urine [25] which was used for electrolysis in previous studies [26]. It is the current induced active filtration that is perhaps responsible for the high levels of power. In chemical fuel cells, the proton flux through a proton specific membrane leads to water transport in the same direction due to the hydration of the protons. This leads to additional water transport through the membrane. In the wastewater operated MFC conditions it would additionally benefit the system by dewatering contaminated waste (sludge, urine).

The morphology of the activated cathode electrode has not been studied so far. To investigate the mechanism of catholyte formation directly on the surface of the cathode, the electrodes were observed using the electron scanning microscopy as functionalising the cathode surface is essential for the achievement of improved current generation and production of catholyte. The cathode morphology (Fig. 4) shows that activated carbon is the preferred catalytic area for ORR due to the

microporous surface creating high specific surface area while the gas diffusion layer is full of void spaces where carbon fibres are partially clustered by the PTFE. This is similar to nano particles of carbon black in microporous layers (MPL) forming the active area and PTFE treated carbon cloth forming the gas diffusion layer (GDL) [27,28]. Analogous to the aforementioned carbon cloth, here carbon veil fibre GDL was treated with PTFE to achieve hydrophobicity and to improve the robustness of the carbon fibre veil material. In this way it effectively supplies the AC layer with oxygen and allows effective accumulation and transport of catholyte away from the active zone. This shows that the oxygen freely diffuses through the hydrophobic gas diffusion layer to be readily available at the AC layer which is in direct contact with the membrane and electrolyte. The mass transport process is dependent upon the adsorption of oxygen on the cathode and removal of water molecules from cathodes [29] which can be achieved through the hollow surface of the hydrophobic GDL (Fig. 4).

Catholyte use for heavy metal precipitation

The MFCs produced on average 0.89 mW of electric power over a 7-day period while the formation and accumulation of catholyte was observed in the cathode chamber (data not shown). The electrochemically produced catholyte (11.23 pH, conductivity 24 mS/cm) was collected and used as the coagulant to precipitate iron (III) chloride, copper (II) sulphate and zinc (II) chloride from the solution in comparison with deionised water, for the same period of time. As shown in the images of Fig. 5, precipitation, which suggests flocculation (left hand side universal bottles), is clearly evident. $\text{Fe}(\text{OH})_3$ is the precipitate that was settling at the bottom of the iron chloride bottle.

Hydroxide precipitation makes use of the fact that the solubility of many metal compounds diminishes with an increasing pH. Therefore, a very common precipitant for this

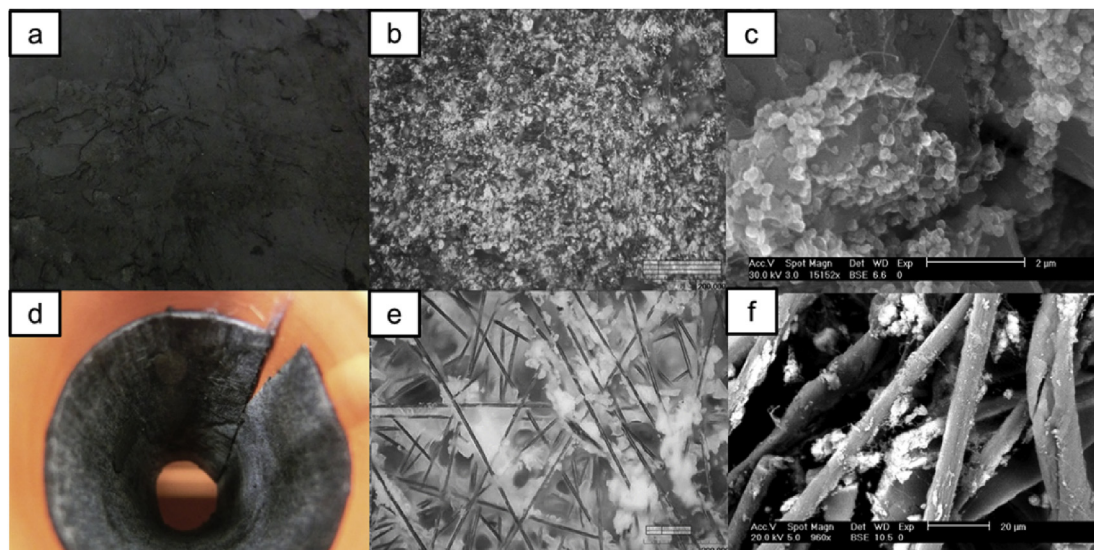


Fig. 4 – Cathode electrode morphology. (a) Photograph illustrating AC layer; (b) digital microscope image using 400× magnification of AC; (c) ESEM image of AC under high (15,152×) magnification; (d) photograph illustrating GDL on the air side; (e) digital microscope image at 400× magnification of GDL; (f) GDL under 960× magnification.

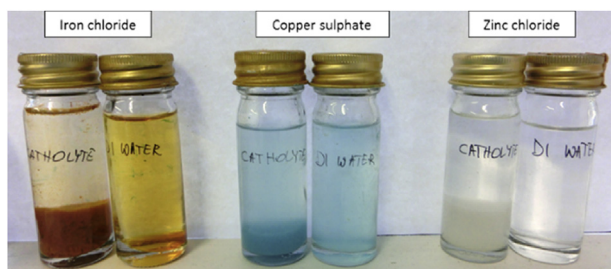


Fig. 5 – Precipitation of heavy metals from the exposure of samples to MFC-generated catholyte.

process is caustic soda (NaOH). The produced liquid by the same type of terracotta MFC has been recently shown to actively lyse algae [30]. Wastewater that contains dissolved pollutants can be treated with OH^- ions that react with metal ions to form insoluble hydroxide compounds. Industrial wastewater can contain toxic compounds such as heavy metals, which are normally present in the form of ions and can be removed from the wastewater by ion exchange. These terracotta cylinders have demonstrated that they could be employed as cost effective MFC membranes [31] employed in direct production of electricity from urine in pilot field trials [25]. MFCs were able to produce stable power at FeCl_3 concentrations likely to be found where the wastewater treatment technique for coagulation is practised [32], however their mode of operation is not completely understood. Moreover, cathodic ORR production of chemically reactive hydroxyl OH^- and superoxide HO_2^- radicals causes precipitation of hydroxides of heavy metals and breakdown of many soluble organic molecules [12]. Because of the reason that the OH^- was electrochemically produced by the MFC without an external electrical input the proposed mechanism might serve as an example of electrocoagulation.

Catholyte generation from other substrates such as urine

To investigate if this process would occur with real wastewater (instead of sodium acetate as carbon source), the

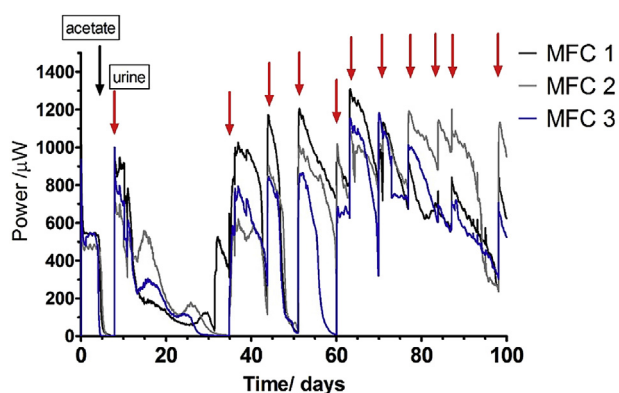


Fig. 6 – Change of feedstock to neat human urine and long term performance. Red arrows indicate feeding points with neat urine. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

substrate was changed to neat human urine. Fig. 6 shows the feedstock change from wastewater supplemented with acetate to neat human urine. The performance was reaching the levels obtained with the use of acetate (max power 1.2 mW) and long term operation of over 100 days was sustained with the addition of fresh feedstock.

The catholyte once again was collected from the inner chambers and used to investigate the suitability of the effluent for precipitation. The pH analysis of the 4 days treatment showed that once again urine used as a feedstock was treated by the electrochemical process and the pH splitting could also be observed as shown in Fig. 7.

The MFC treatment of urine was presented previously where electrochemical operation induced pH splitting and ion separation was indicating the anolyte pH to stabilise towards neutral values, where natural urea hydrolysis (without MFC treatment) would increase the pH of urine [25]. At the same time it was observed that pH of the newly generated catholyte is increasing with power and in time of MFC operation which is in agreement with these results.

Catholyte was collected and used for further tests and the pH level was in the range of 10–11, therefore it was assumed that the alkaline agent is present and is ready to use for the precipitation test. This was performed *ex situ* in order to avoid possible cathode contamination, where the precipitating agent (catholyte) was mixed with the heavy metals outside the MFC reactor. Fig. 8 now shows the mixing of iron (III) chloride, copper (II) sulphate and zinc (II) chloride with (i) collected catholyte (test), (ii) collected anolyte (positive control), (iii) fresh urine and (iv) deionised water; the latter two as negative controls. It may be observed that the precipitation occurred mostly in the mixture where the catholyte was used. As the catholyte had the highest pH therefore the highest amount of hydroxide ions available to perform the reaction with soluble metal ions to form iron hydroxide (Fig. 8a) and zinc hydroxide (Fig. 8c). Copper in this case did not precipitate, however the colour change was quite evident. This implies that a different type of reaction was taking place in this particular mixture, which is the subject of ongoing investigation. One of the possible reactions in this case is between copper (II) sulphate and ammonium hydroxide that would be present in the obtained urine-based MFC catholyte. This would be similar to the process whereby a small amount of ammonium hydroxide is added to a solution of copper sulphate, which then results in a precipitate of copper (II) hydroxide being formed. The addition of more ammonium hydroxide dissolves the copper (II) hydroxide precipitate leaving the vivid blue solution of complex ions and possibly $\text{Cu}(\text{NH}_3)_4$.

Producing the acid and alkali compounds for mineral sequestration at sufficiently large scale requires energy, the production of which would generate more carbon dioxide. The MFC technology appears to be a promising avenue for sustainable, carbon-neutral alkali production. The correlation between the electrical conductivity and salinity is proportional to the concentration of electrolyte ions where urine is a very conductive substrate that could serve as an ideal electrolyte due to the high concentration of mineral ions and metabolites. Ceramics have been shown in previous studies as ideal structural materials in the MFC architecture in both outer cathode designs [21,22] and inner cathode configurations as shown in

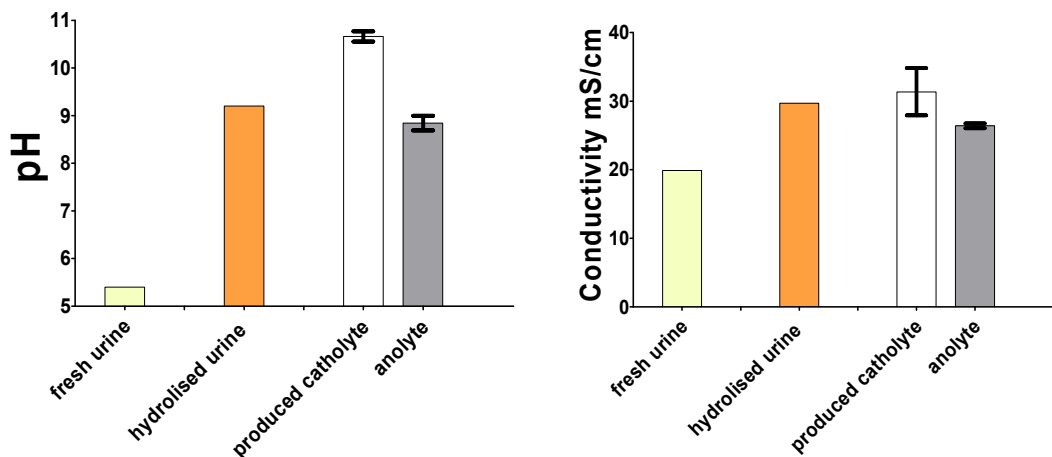


Fig. 7 – Physico-chemical properties of the anolyte and produced catholyte after the MFC treatment.

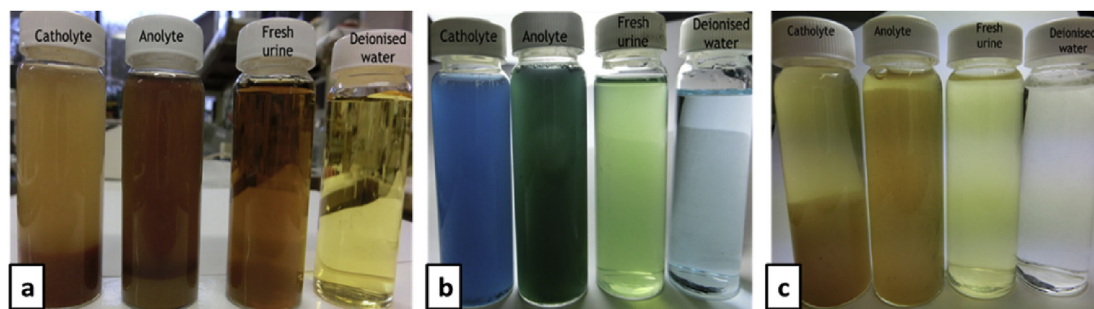


Fig. 8 – The use of anolyte, catholyte, neat urine and deionised water as precipitating agents for iron chloride (a), copper sulphate (b) and zinc chloride (c).

this work [17,21,23]; moreover it is used in many electrochemical applications such as microfiltration or electrolysis. This is due to the robustness and physico-chemical stability of the ceramic material that could be a good, cost effective material for the technology advancement [33]. Moreover, wastewater electrolysis systems could be used for toilet water disinfection [34] and with the development of electricity producing MFCs, the combined electrolytic function would be particularly attractive for autonomous and decentralised wastewater treatment. Future investigation will include metal polluted waste streams where the MFC system would extract the cations transported from the anode to the cathode [35] and precipitate them into insoluble compounds within the cathode chamber with the help of the system proposed here. This then allows for the potential to extract the heavy metal compounds from the wastewater and collect these in solution. Further studies will include quantitative analysis of the ions that could be recovered from polluted waste streams and the *in situ* precipitation testing.

This paper reports on the innovative MFC driven electrocoagulation that can be used for removing metal pollutants, such as copper, zinc and iron from aqueous solutions. A chemical reaction between the catholyte may produce a solid or semisolid precipitant that can be easily collected. This could give an important advantage of self-driven MFCs treating polluted wastewater and removing heavy metals *in situ* which will be investigated further. Furthermore, the

production of such value-added chemicals will support the sustainable production of renewable materials, which is one of the most promising biotechnological approaches.

Conclusion

This work presents a Microbial Fuel Cell that is generating electricity and at the same time produces active electrolyte in this process as a product of wastewater electrolysis. The produced *in situ* active solution by the MFC electrokinetic function and harvested in the terracotta based MFC reactor is highly caustic and can be used for flocculation and precipitation of heavy metals. Further studies should be implemented to explore this feature for *in situ* electrocoagulation and precipitation of toxic pollutants.

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