1	Ceramic MFCs with internal cathode producing sufficient power for practical applications				
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14	Highlights				
15 16 17 18 19 20 21 22 23 24	<ul> <li>Ceramic MFCs with inner cathode chamber show good performance to power practical applications</li> <li>Three MFC units connected in parallel could energise directly a DC motor continuously for over 6 days</li> <li>During MFC operation accumulation of catholyte improves performance</li> <li>A single MFC was shown to charge a mobile phone with the aid of energy harvesting electronics</li> <li>Inverted design shows the potential for MFCs to be directly immersed in wastewater extracting caustic catholyte</li> </ul>				
25	Abstract				
26	This communication reports on the powering of real world applications, whereby three				
27	interconnected MFCs directly power an external DC motor, and a single MFC recharges a				
28	mobile phone, via energy harvesting. The work is aiming to evaluate MFC performance				
29	based on low-cost, catalyst-free conditions, with an internal cathode to operate practical				
3U 21	applications. It presents the case for simple and easy-to-operate ceramic-based designs as a				
31 27	viable approach to larger-scale implementation in real-world conditions such as wastewater				
32 22	treatment plants. MIFUS hold great promise for sustainable wastewater treatment since they				
55	are the only technology that uncerty generates electricity from the break-down of waste.				

Key words: Microbial Fuel Cell (MFC), off the grid energy, wastewater treatment, activated
carbon, internal cathode

## 37 1. Introduction

Providing adequate sanitation and clean water to a global population is today's economic 38 challenge. Microbial fuel cells (MFCs) offer potential for direct biological conversion of 39 wastewater organic materials directly into electricity [1]. Significant improvements in power 40 performance have been achieved in the last 2 decades, so the successful, commercial real-life 41 42 MFC demonstration is closer than ever before. Recent advances in various fundamental areas can lead to practical applications [2] and subsequently to commercial use. Substantial 43 progress has been made towards enabling the implementation of this technology by replacing 44 expensive components such as platinum electrodes with carbon, membranes with ceramics 45 46 [3,4] simplifying operational conditions [5] and modifying reactor designs [6]. In recent review the design optimisation, improved harvesting and cost reduction have been identified 47 as main areas that require improvement towards the generation of practically usable power 48 [7]. A better understanding of the impact of reactor components on the performance of the 49 reaction system is an important step towards commercialisation of Bioelectrochemical 50 Systems (BES) [8,9]. The major hurdles are being recognised in design and engineering 51 rather than biology [10]. Understanding these phenomena can allow us to identify ways of 52 optimising reactor design, process conditions, and optimal outputs. The attempts to 53 implement the MFC technology into wastewater treatment plants have thus far been limited 54 by relatively low power densities, however, in recent study MFC was powering a pump 55 intermittently in the aerated lagoon treatment system improving organics removal [11]. At the 56 same time, attempts of scaling up have investigated various approaches such as a plate [12], 57 cassette [10] or tubular systems [13–15]. In general, the multiplication and miniaturisation 58 offers an alternative way of scaling up [16] that could be used to power mobile robots [17], 59 due to increased power density of miniaturised MFC units [18]. In this respect, a stack of 60 61 tubular MFCs provides a method of obtaining high surface areas in standard (inner anode, outside cathode) configurations and it has shown to power a commercial mobile phone 62 63 handset [19]. This work is aiming to present the inverted configuration where the anode is placed outside and the cathode inside the tube to emphasise the practicality of the internal 64 cathode design in the MFC. In this way, the proposed simple and cost effective design can be 65 used as a functional unit by directly immersing it in wastewater tanks. With a reversed 66 67 electrode set up, this work is leading further into simultaneous water recovery in the form of

68 catholyte [20] that could be collected from the internal cathode chamber, which is the reason why the energy-rich organic waste streams can be used as a high value fuel, increasing 69 70 energy recovery. This work also aims to present the essential component of catholyte accumulation (known in chemical fuel cells as "flooding") inside the cathode chamber 71 72 improving - instead of hindering - the performance. This work also aims to demonstrate the practical use of these MFCs, by (i) driving a motorised model windmill directly using 3 73 74 MFCs connected together and (ii) charging a mobile phone via energy harvesting electronics using a single MFC. 75

#### 76 2. Experimental

MFCs were assembled using 10 cm long, 3 mm wall thickness terracotta caves (Orwell 77 Aquatics, UK) serving both as the MFC casing and a separator between the anode and the 78 cathode. Anode electrodes were 2430 cm<sup>2</sup>; 20 gsm carbon fibre veil (PRF Composites, UK) 79 wrapped around the ceramic cave and pressed against the wall with nickel chromium wire 80 (0.45 mm diameter). Cathode electrodes were made of activated carbon and PTFE paste 81 applied on the same carbon fibre veil substratum (90 cm<sup>2</sup>; 20 gsm) as previously described 82 [21] and placed inside the cylinder so the activated carbon was facing the ceramic wall. A 83 stainless steel crocodile clip and Ni-Chr wire was used for connecting the cathodes. The 84 terracotta MFCs were placed inside plastic containers, inoculated with 200 mL of activated 85 sludge provided by Wessex Water Scientific Laboratory (Cam Valley, Saltford, UK) and 86 operated in batch conditions to assess its performance and catholyte accumulation. The 87 anolyte was periodically supplemented with a mixture of activated sludge and 20 mM sodium 88 acetate at pH 6.7 - 7.9. A total of three MFCs (units labelled as T1-T3) were tested under an 89 external resistor load of 53  $\Omega$  and a further 3 MFCs were tested under open circuit conditions 90 (units labelled as T4-T6). All tests were performed under room temperature, 22 °C, without 91 pH control or any platinum catalyst. 92

A model windmill equipped with a DC electric motor (RF-300CA-11440 DC/2.0V 11303,

94 HSC Motors) was used as practical demonstrator of the usable power from the three parallel

95 connected MFCs. A 300F 2.7 V max. super-capacitor (XW3550/2R7307/R, Cooper

96 Bussmann) was also used to store excess energy in addition to powering the windmill.

Furthermore, a mobile phone Samsung GT-E2121B was connected via a Texas Instruments
energy harvester (TI BQ25504EVM-674, Farnell, UK). The output voltage from the single
ceramic MFC was insufficient to meet the voltage requirements of the phone battery and

100 charge it directly, hence the energy harvester was used. Data logging was performed via

101 multichannel DAQ Agilent 34972A (Farnell, UK). Current and power output levels were

- 102 calculated as previously described [18].
- 103 3. Results and Discussion

# 104 3.1. Performance

Tubular MFCs were tested in closed circuit conditions, under 53  $\Omega$  external resistor (T1, T2, 105 T3) and open circuit conditions (T4, T5, T6). A stable power output was recorded over a 106 period of 7 days with an average of 805 µW, 458 µW and 880 µW, for T1, T2 and T3 107 respectively, whilst the open circuit MFCs produced open circuit voltages of T4 649 mV, T5 108 638 mV and T6 656 mV. To demonstrate the useful power levels of the tested units, T1, T2 109 and T3 had their external resistors removed and connected in parallel directly to power the 110 111 windmill motor. The substrate was replenished by fresh sludge+20 mM sodium acetate at pH 7.9 and conductivity of 17.7 mS/cm. Figure 1 illustrates the energising of the windmill DC 112 motor. As can be seen, the voltage output was steadily increasing over a period of 3 days, 113 from 245 mV to 265 mV, after which period a current probe was connected to measure the 114 current directly, which was shown to be approximately 9.6 mA throughout. The test also 115 included connecting a 300F super-capacitor to the circuit, whist the motor was still running, 116 showing excess amounts of electricity that could be stored in a system during continuous 117 operation. This shows that the additional energy stored in the capacitor would make the 118 system more efficient. At the end of the  $6^{th}$  day, the motor stopped when the voltage level 119 dropped below 200mV. It was observed that during this practical demonstration catholyte 120 was produced and accumulated in the internal cathode chamber. On average, as shown in 121 Figure 1B, MFCs powering an external circuit generated 44 mL of catholyte whilst the open 122 circuit MFCs produced only 9.6 mL, which is significantly less volume. This suggests that 123 some passive diffusion through the terracotta material was occurring primarily for the open-124 circuit MFCs, but when under load, anolyte was transported via electro-osmostic drag [13]. 125 126 Catholyte properties include a significantly higher pH and an almost two-fold increase in conductivity values in comparison with the catholyte formed from the open circuit MFCs. 127 This might be one reason why MFC operation was improved [22]. Similar caustic catholyte 128 formation in MFC has been previously reported [20] and this could be one method of 129 recycling wastewater and generating caustic solutions. (See Supplementary Information for a 130 video clip of the windmill running with only 1 MFC). 131



Figure 1.A- T1, T2 and T3 connected in parallel continuous operation of the DC motor
operating a model windmill; B- Amount of the catholyte collected after a 7 day continuous
operation; C-pH and conductivity under open and closed circuit conditions.

136 3.2.Catholyte effect

To explore the effect of the accumulated catholyte on the MFC performance, the catholyte 137 was removed from all 3 working MFCs (T1, T2 and T3; Figure 2 inset), whilst connected and 138 running the windmill. During this process, when the whole catholyte was removed, the motor 139 stopped working, and only started again when the catholyte was reinstated in the inner 140 cathode chamber. This was repeated as marked by the (\*\*) on the Figure 2, after feeding the 141 MFCs with fresh feedstock (f). As before, the motor stopped when the cathode chamber was 142 143 emptied and started working normally when the same catholyte was returned into the cathode. This procedure was repeated a third time, leaving the cathode empty for a day, 144 during which the windmill had once again stopped working. After this period, only half of the 145 catholyte was reinstated into the cathode, which resulted in a slower windmill operation - see 146 Table 1. When the full catholyte volume was added back into the cathode, the MFC 147

- 148 performance once again stabilised and the windmill reached full speed and continued for the
- 149 next three days. Catholyte provides a moisture bridge and sufficient hydration for the oxygen
- reduction reaction (ORR). In previous work, ceramic MFCs with the cathode outside,
- demonstrated improved performance following manual hydration and in addition showed
- 152 higher rates of anolyte dissipation when the cathode was intentionally not supplied with water
- 153 [4]. In a further previous study, where inner cathodes were tested, forced air flow through the
- 154 cathode tube was shown to decrease power generation, therefore it can be assumed that the
- 155 cathode in such a configuration could be drying out [5].



156

157 Figure 2. Effect of accumulated catholyte during MFCs powering a motor, "f"-feeding with

fresh feedstock, \*\*- repeated catholyte removal resulting in the same behaviour as shown in
the inset. Table 1. Detailed performance of the stack powering the dc motor as shown in

160 Figure 2.

	Catholyte average [mL]	Voltage [mV]	Motor performance [rpm]
day 0 cathode emptied	0	164	0
day 0 catholyte put back in	16.6	238	88
day 3 before feeding	53	246	108
day 3 after feeding	53	260	144
day 3 cathode emptied	0	167	0
day 4 half of the catholyte in	26.5	226	96

	day 4 whole catholyte in	53	243	132
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- 162 Figure 3 shows the single tubular MFC as a power source for charging a mobile phone, using
- an energy harvesting system. Previously it has been demonstrated this could be done directly
- via a stack of 12 MFCs [19], here the inverted configuration (cathode inside) of one single
- 165 MFC enabled charging through smart electronics.



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Figure 3. Charging cycles of the commercial mobile phone via single MFC and an energyharvesting system.

The current study also demonstrates that the capital cost of the system could be substantially 169 reduced through system designs that use less expensive electrodes (carbon veil cost is only 170  $\pounds 6.70/m^2$ ), ceramic membranes and simple design for optimised operation. A recent report 171 showed that in clayware cylinders (inner anode, outer cathode) with multiple electrodes 172 exposed to the same liquid, maximum power can be extracted using parallel circuit 173 connection [14]. Therefore, the MFCs operated as individual units in the present study, would 174 perform equally well when immersed in one common feedstock tank but kept in parallel as 175 recently demonstrated at the Reinvent the Toilet Fair in Delhi, India, in March 2014 under the 176 177 the Bill & Melinda Gates Foundation [23] or indeed when kept in fluidic-electrical isolation as part of a cascade stack designed to treat the same feedstock [24]. This study is contributing 178 179 new knowledge in the area of MFC based wastewater treatment, but further research is still required for MFC stacks in this application scenario, especially when the level of energy 180 output (i.e. driving a real world device such as a pump) becomes the governing factor of 181 treatment efficiency and catholyte recovery. 182

## 183 Conclusions

Microbial Fuel Cell which is representing a bioconversion technology, serves as a standalone power source for practical applications. This work is presenting ready to implement MFCs by simply immersing the units directly in the wastewater. The development of ready to use MFCs in different stages of real wastewater treatment plants would help to lower the consumption of energy for wastewater treatment and consequently establish a more stable energy network.

## 190 Acknowledgements

- 191 This work was funded by the Engineering and Physical Sciences Research Council United
- 192 Kingdom EPSRC CAF EP-I004653/1 and EP/L002132/1. Parts of this study have contributed
- to the Urine-tricity++ project, funded by the Bill & Melinda Gates Foundation, grant no.
- 194 **OPP1094890**.

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