Improved hydrogen gas production in microbial electrolysis cells using inexpensive recycled carbon fibre fabrics

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ABSTRACT

Growing energy demands of wastewater treatment have made it vital for water companies to develop less energy intensive processes for treating wastewater if net zero emissions are to be achieved by 2050. Microbial electrolysis cells (MECs) have the potential to do this by treating water and producing renewable hydrogen gas as a product, but capital and operational costs have slowed their deployment. By using recycled carbon fibre mats, commercially viable MECs can brought closer to reality, where recycled carbon fibre anode MECs treating real wastewater (normalised ~3100 L d^{-1}) were producing 66.77 L H_2 d^{-1} while graphite felt anode MECs produced 3.65 L H_2 d^{-1} per 1 m^3 reactor, anodes costing £5.53 m^{-2} and £88.36 m^{-2} respectively, resulting in a total anode cost saving of 93%. This could incentivise the development of larger pilot systems, opening the door for generating greater value and a more sustainable wastewater treatment industry.

1. Introduction

The need to move towards a circular economy is vital if human populations are to maintain a good standard of living while moving towards business models that promote economic and environmental sustainability (Green Alliance, 2017; Pan et al., 2015; United Nations, 2019). Standards of living are intrinsically linked to public health, and a key contributor towards this is wastewater treatment. This is achieved by protecting human populations from dangerous pathogens (Colwell et al., 2016; Hrudey et al., 2003) as well as protecting the environment from eutrophication (Garrido-Baserba et al., 2014) and preventing biodiversity loss (Bilotta and Brazier, 2008).

There is a particular need to improve on the standard of living in developing regions of the world, where a lack of wastewater treatment infrastructure causes environmental and public harm, with an estimated 2 billion people having to use drinking water contaminated with faeces (World Health Organization, 2019). The key requirement of a wastewater treatment asset therefore is that it is able to treat wastewater to a safe discharge standard.

The main reasons for a lack of effective wastewater treatment in developing nations are the capital and operational costs, largely attributed to energy use (Water, 2017). To help mitigate this, wastewater treatment must also recover as much value as possible from the wastewater with a low as possible capital cost and ideally, achieve energy

and financial neutrality (or a net gain) in order to achieve the three components of sustainability; social, environmental and economic (Bhamra and Lofthouse, 2007; Blackburn, 2007; Spellman, 2013).

Wastewater treatment contributes to climate change due to the high energy usage; 3% of all UK energy is used for wastewater treatment (Ainger et al., 2009) and is financially non-viable for multiple nations across the globe. One particular asset, the activated sludge pool (ASP), treats wastewater by using blowers to continuously aerate primary effluent, stimulating aerobic microorganisms to reduce the concentration of chemical oxygen demand (COD), biological oxygen demand (BOD) and nutrients such as phosphorous (de-Bashan and Bashan, 2004) and ammonia (Tchobanoglous et al., 2014).

These blowers can account for up to 60% of the overheads of a wastewater treatment plant (Severn Trent Water, 2019). Furthermore, the waste activated sludge (WAS) produced by an ASP is more difficult to process (compared to primary sludge) in an anaerobic digestor unit due to the lower solid content, resulting in a significant extra cost to the water company due to the pre-treatment stages required to reduce moisture content (Appels et al., 2008).

An alternative technology that has the potential of achieving the same outcome of the ASP but with a reduced impact is the microbial electrolysis cell (MEC), a subtype of the bio-electrochemical system (BES) (Butti et al., 2016). The MEC is a relatively complex device (compared to other wastewater treatment assets), which tends to share

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architectural similarities to other fuel cell systems, in that it has an anode and a cathode which can be separated with a membrane or separator; although there are examples where there is no separation (Escapa et al., 2015; Moreno et al., 2016). One (usually the anode) or both (Jafary et al., 2015) electrodes in the system are colonised by an electroactive biofilm which, is able to facilitate the oxidation of organic pollutants to carbon dioxide and H^+ ions (Logan et al., 2008), therefore treating the water by lowering the COD and BOD. With an external voltage, the H^+ can be reduced to H_2 gas, making the MEC a producer of renewable and potentially sustainable energy. Other compounds of value that are producible include caustic soda (Rabaey et al., 2010), ammonia (Zamora et al., 2017) and methane (Moreno et al., 2016).

Lab scale testing has yielded some very high energy recovery efficiencies from hydrogen producing MECs, with up to 115–580% possible under ideal operating conditions such as controlled feed inputs, PBS catholyte, use of platinum etc. (Cheng and Logan, 2011, 2007; Selembo et al., 2010). Controlling the testing conditions such as temperature, acetate concentration etc. has been vital to understand the limiting factors of MECs, which include electrode spacing, material selection and membrane use (Call and Logan, 2011; Ribot-Llobet et al., 2013). However, the performances recorded in these lab scale experiments do not translate to larger scale (in terms of high performance) and conditions that replicate an industrial environment (Baeza et al., 2017; Cotterill et al., 2017; Heidrich et al., 2014).

There is also the issue of capital cost, which is arguably the largest area requiring improvement (Aiken et al., 2019). The *Heidrich* and *Cotterill* pilots demonstrated hydrogen production and wastewater treatment capabilities at larger scales, but both examples would be too expensive to replace the ASP, despite the lower operational costs and recovery of hydrogen gas (Cotterill et al., 2017; Heidrich et al., 2014). This was primarily due to the cost of the anode and current collector. There are examples suggesting alternative material use (Baudler et al., 2015), such as carbon based materials including graphite and carbon felt for the anodes in MECs. Though the carbon-based anodes are functional and, in many cases, can achieve good performances (in terms of hydrogen gas production), they are too expensive to be used in an MEC for larger applications. Aiken et al. (2019) reported that the Heidrich pilot scaled up to a 100,000 Population equivalent (PE) size could cost up to £42.37 million in materials alone, 99% of the overall total, whereas an equally scaled ASP cost just over £2 million, 4.7% of the price of the MEC.

There are also issues with the environmental implications of using graphite and virgin carbon felts, as both require large quantities of energy to produce, brining into question the positive environmental impact of an MEC (Marsh et al., 2006). Recycled carbon fibre, derived from the waste of carbon product manufacture in the automotive and aerospace industry, is less environmentally taxing compared to virgin carbon felts (ELG Carbon Fibre Ltd., 2017).

As they hold their structure in liquid environments and have been confirmed as conductors of electricity, recycled carbon fibres may present a viable alternative to virgin graphite and carbon felts, as they are significantly less expensive. To determine whether good performance can be achieved in real world conditions and at larger scales, mini-pilot MECs were deployed at a real wastewater treatment plant in the UK (Minworth sewage treatment works, UK) and operated for 3 months.

2. Methods

2.1. Materials

Four MECs were designed using AutoCAD Fusion 360 (v2.0.5790). The design was similar to the *Cotterill* pilot, in that the reactors were cuboid shape (Cotterill et al., 2017). Each reactor contained five modules (each with two anodes), using an Entek lead ion battery separator. The cathode was a 316 stainless steel weldmesh (PRW, UK)

with 13 mm apertures with 20 g 316 stainless steel wire wool weaved into the grid for each module. The current collector for the anodes was a CAD designed stainless steel grid, which was made by water jet cutting a 0.8 mm thick steel sheet. The reactors and module cassettes were manufactured from polymethyl methacrylate. Tedlar gas bags of both 1 and 3 L were used to collect the gas from the modules, using a Marprene tube, which was sealed in place using PTFE sealant. Four different anode materials were used for the MECs. Three MECs used variants of the recycled carbon fibre materials (rCF); MEC 1: ELG – M300 MnOx coated rCF, MEC 2: ELG – M100 MnOx coated rCF and MEC 3: ELG – M300 uncoated rCF. The manganese (IV) oxide coatings were achieved by placing each anode in a 4 L 0.25 M concentration of manganese (II) acetate, with an applied current of 0.72 A to the anode (using a power supply), using a stainless steel current collector and counter electrode (Zhang et al., 2015). MEC 4 used graphite felt (Sigracell GFD 4.6, SGL) which was used as a control material, as it is proven to work as anodes at larger scales and is one of the less expensive graphite felts available on the market (Cotterill et al., 2017).

2.2. MEC operation

The MECs were fed with settled sewage (wastewater that has been screened and treated by primary settlement tanks i.e. secondary wastewater), which at this site is normally treated by an activated sludge plant. The sewage was pumped from the Minworth lane separator tank to a reservoir that was continuously filled and emptied. Each MEC had its own pump supplying the wastewater.

The MECs were powered in pairs by a power supply at 1 V (the power supplies had two sets of channels) (Tenma). Copper wiring was soldered so that each channel could be connected to the 5 anode and cathode current collector tabs. A 1 Ω resistor was soldered into the parent wire so that the current could be recorded in real time. After 10 days, this was exchanged for a 0.1 Ω resistor for all MECs.

2.3. Wastewater quality measurements

The following water quality consents were measured using HACH-Lange cuvettes.: 0–1000 mg L^{-1} COD (LCI400), COD 15–150 mg L^{-1} (LCK314), phosphates (TNT 845), nitrates (LCK 339), nitrites (LCK341), sulfates (LCK153) and sulfides (LCK653). COD was measured using two different ranges so that if lower concentrations of COD in the effluent were achieved, more accurate readings would be possible. All cuvettes have pre-measured chemical mixes, to which a sample of water is added (volume varies for each cuvette e.g. LCI400 requires 2 mL of sample, LCK 339 requires 1 mL). Each cuvette had different additional stages including heating in a reactor or the addition of other compounds, which were supplied with each cuvette test kit. Following the completion of the reaction, the cuvettes were read in a photometer and values recorded. A HACH-Lange reactor (LT 200) and photometer (DR 3800) were used for the digestion and readings respectively. The COD measurements were taken twice a week and the other nutrients once a week.

Total Suspended solids (TSS), pH and temperature were also monitored. TSS was monitored by filtering 100 mL samples of effluent through a pre weighed (when unused) glass filter paper discs using an air pump. The solids on the disc were then heated in a microwave for 3 min, to evaporate the water. The discs were then weighed, with the original weight then subtracted to provide the mass. This was then multiplied by 10 to provide the value in mg L^{-1}.

pH was spot checked using a HACH-Lange HQ40D and PHC20101 pH probe. Temperature was measured from day 36, using a Picotech temperature data logger with miniature 0.25 mm diameter mineral insulated thermocouples with a Pot Seal (TC Direct). This was only measured from day 36, due to issues with the equipment (probe unavailability) and laptop – these were not resolved until this time point.

Table 1
Total hydrogen gas production for each MEC.

MEC	Anode material	Total volume of H_2 (L)	Average daily volume of H_2 (L d^{-1})	Peak daily hydrogen volume for best month (L d^{-1})	Normalized daily volume of H_2 (L d^{-1} m^{-3})
1	M300 MnOx	12.21	0.16	0.15 (May)	19.82
2	M100 MnOx	0.00	0.00	0.00	0.00
3	M300 Plain	41.13	0.53	0.70 (May)	66.77
4	Graphite felt	2.25	0.03	0.03 (June)	3.65

2.4. Hydrogen gas monitoring

Hydrogen gas collected in the gas bags was transported from site to the University of Warwick on every site visit for gas chromatography using an Agilent, Micro GC (with a micro thermal conductivity detector and Molsieve 5A and PoraPlot 10 m columns, Agilent 490, Agilent Technologies) and calibrated against a standard curve of pure hydrogen (99.99% Calgaz) diluted with air, following the 5-point calibration method, as used by Cotterill et al. (2017). The method for GC analysis was adapted from *Chen et al.* differing only in the injection time for the Molsieve column which was at 20 ms (backflush time remained the same at 9 s).(Chen et al., 2019) The volume of gas was measured using a 100 mL borosilicate glass syringe (Fortuna, Poulten & Graf).

2.5. Statistical analysis

Statistical significance tests (T test to generate P-Values) were applied for wastewater treatment (COD, TSS % and mg removal) and hydrogen production. The T test compared each rCF material variant to the SGL graphite felt, as it served as the control. A 95% confidence was used, meaning that the P values generated had to be < 0.05% to be considered as having a significant difference. Correlation coefficients were also determined for performance (hydrogen gas production) relative to temperature, current generation, COD input and pH.

2.6. Efficiency calculations

Electrical energy recovery, coulombic, substrate and total efficiencies were calculated for each MEC using the calculations below and are described in detail (Logan et al., 2008). η_E = Electrical energy recovery, W_{out} = energy output, W_E = Energy in, *CE = coulombic efficiency,* N_{CE} = moles of hydrogen, S_E = Substrate efficiency.

$$\eta E = \frac{W_{out}}{W_E} \times 100 \tag{1}$$

$$CE = \frac{\eta_E}{N_{CE}} \tag{2}$$

$$S_E = \frac{Moles\ H_2\ recovered}{Theoretical\ moles\ of\ H_2\ in\ the\ substrate\ removed} \tag{3}$$

3. Results and discussion

3.1. Hydrogen gas production

3.1.1. Start-up

Hydrogen gas was first detected in two of the modules of MEC 3 (plain 300 gsm rCF) on day 13 with all five modules eventually producing gas throughout the experiment. MEC 1 (MnOx coated 300 gsm recycled rCF) started producing gas on day 18, with a total of 4 modules eventually producing gas (the other three modules did not start producing gas until the 87th day). MEC 4 (graphite felt) first began to produce detectable hydrogen gas on day 42 with a total of 4 hydrogen producing modules. MEC 2 failed to produce any gas at any point during the three months of operation.

The faster start up time of MEC 3's modules relative to the modules of MEC 1 (same base M300 material with the manganese (IV) oxide coatings) can be attributed to the lower resistivity of the plain carbon fibre anodes. Manganese (IV) oxide increases the resistance of the material to which it is coated (Zhang et al., 2015) and resistance increases have been shown to correlate negatively with hydrogen recovery. This reduced internal resistance means that a greater proportion of the applied voltage from the power supply can be used for the reactions at the site of the electrodes (e.g. hydrogen gas production via the reduction of H_+ ions at the site of the cathode) (Kadier et al., 2016). The materials with the higher resistances needed more time to start producing gas, as an increased amount of electrogenic microorganisms were required to reduce the overall resistance of the system to produce enough collectable gas for measurement.

The lowest resistance material was the graphite felt (used in MEC 4) and its use in an MEC would normally be expected to be one of, if not the earliest to start producing gas. As explained previously, MEC 4 was over 2 weeks later than both MECs 1 and 3 in terms of the start-up date for gas production.

3.1.2. Gas production comparison

MEC 3 produced the most hydrogen gas (41 L) with MEC 1 s (12 L). MEC 4 using graphite produced significantly less (2 L) which was statistically significant when compared to both MEC 1 and 3 (P = 0.001). Assuming linear performance with scale to normalise (unlikely based on *Cotterill et al*) (Cotterill et al., 2017) the maximum hydrogen gas production per day when using the M300 is 66 L (determined by normalising the reactor volumes to a 1 m^3) (Table 1).

The *Cotterill* pilot had maximum hydrogen productions of 0.86 L d^{-1} (average over the course of the highest gas producing month) using an MEC which had an anodic volume of 175 L (unclear if the volume of the cathodic components has been deducted from this value or not) (Cotterill et al., 2017). The peak daily hydrogen production from MEC 3 produced 0.70 L d^{-1}, 0.16 L less than the *Cotterill* Pilot, but with an anodic volume that was 21 times smaller than the larger aforementioned pilot. This is significant for the potential of the use of recycled carbon fibre as anodes for MECs, as the 21 times smaller MECs used in this experiment (relative to the *Cotterill* example) demonstrate comparable performance. If the systems used in this experiment were enlarged to an equal size, it is very likely that they would outperform the *Cotterill* MECs. This is supported by the significant difference in the hydrogen gas recovery from the MECs using the same graphite felt against the MECs using the M300 rCF in this experiment.

An additional argument for the use of the recycled carbon fibre anodes in MECs over virgin graphite and carbon materials can be made when comparing the performance of the M300 MEC to the *Heidrich* pilot (Heidrich et al., 2014). This pilot produced an average of 0.43 L d^{-1} H$_2$ during the April-June period (same period of operation as this experiment), which is 0.1 L d^{-1} less than MEC 3. The *Heidrich* pilot had a volume of 100 L, over 12 times larger than these MECs, using an Olmec carbon felt, which is significantly more expensive than the recycled carbon fibre. The operating conditions between these MECs were very different (the efficiencies of the *Heidrich* plant were significantly better, suggesting reduced Ωic resistance), but the comparable hydrogen production from the MEC using the M300 anode suggests significant potential for this material for improving the production of hydrogen production of MECs while significantly reducing the price of MECs.

Table 2
COD removal percentages for the MECs.

COD removal value	MEC 1	MEC 2	MEC 3	MEC 4
Anode material	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
Total average %	24.55	24.63	27.40	13.05
Average from onset of gas %	27.90	N*	31.42	15.37
Peak % removal (single measurement)	43.53	49.29	51.46	33.89

3.2. Wastewater treatment efficacy

Average COD removal from all of the MECs was too low to meet the regulatory requirements for discharge to the environment (125 mg L^{-1}), as stipulated by the 1994 wastewater treatment directive (Table 2) (HMSO, 1994). MEC 3 had the highest percentage removals for both average calculations and the peak removal (27, 31 and 51%). MEC 1 and 3 both had performances that were significantly better than the graphite felt anode MEC, with a P values of ≤ 0.05 for both % removal and actual mg COD removed.

Over time, the COD removal performance deteriorated after a period of continued improvement. It was hypothesised that this was due to a build-up of sludge inside the reactor which was negatively affecting the COD concentration of the effluent. Upon decommissioning, large volumes of concentrated black sludge was found inside the reactors. Future reactors will need sludge removal (similar to conventional wastewater treatment assets ASPs, Humus tanks or PSTs), longer HRTs or improved architectures and operation, including recirculation, to avoid sludge build up and deterioration of wastewater treatment performance (with particular reference to organic compound removal).

TSS removal % was also significantly better for MEC 3 relative to MEC 4 with a P value ≤ 0.002 (Table 3). Secondary wastewater treatment assets are expected to remove an average of 50% of solids, which all MECs achieved (Tchobanoglous et al., 2014). MEC 4 performed poorly compared to the MEC 3, removing 30% less suspended solids. There was a large amount of solid build up in all the reactors by the close of the trial. Different mass particles have a different settling times (i.e. the heavier the particle are the faster it settles), therefore; the flow of wastewater, the length and width of the reactor have a significant impact on the settling rate of particles and have to be designed to ensure that any wastewater treated has the time to settle/be treated before it leaves the reactor (Mihelcic and Zimmerman, 2010). Sludge removal via pumps or gravity is used in all wastewater treatment assets (i.e. humus tanks, primary settlement tanks etc) and therefore, this will need to be considered for any future MECs reactors. Sludge build up in the tank will have negatively impacted the wastewater treatment performance (in terms of organics removal).

The other nutrient tests indicated that there were no significant differences between the different MECs (Table 4). Increases to the concentration of nitrate can be explained by the oxidation of nitrate to nitrate by Nitrobacter genus, which are prevalent in wastewater

Table 3
TSS removal performances for MECs.

	MEC 1*	MEC 2	MEC 3	MEC 4
Anode material code	M300 MnOx	M100 MnOx	M300 Plain	SGL 4.6
Total removed (mg)	975	1055	1530	985
Average removal (mg)	54.17	58.61	85.00	54.72
Average percentage removal (%)	56.18	61.47	88.24	57.94
Peak percentage removal (%)	90.00	88.89	100.00	84.62

* MEC 1 had a pump issue which introduced a high dose of sludge mid-operation (day 54).

treatment environments. Sulfates would have been reduced to hydrogen sulfide by sulfate reducing bacteria (SRB), which like the *Nitrobacter* and *Nitrosomonas*, are common taxa in wastewater treatment environments (Hao, 2003; Spring et al., 2019) also explaining the sulphide increases in some of the MEC effluents (Table 5).

There was an average phosphorous increase for all of the MECs, likely to be attributed to solids build up within the reactor. In wastewater treatment plants, phosphorous removal is usually achieved via the dosing of chemicals (i.e. ferric sulphate) to chemically precipitate the solids and remove them in the form of a sludge (Tchobanoglous et al., 2014). Biological phosphorous removal is possible, but not at high levels from traditional secondary wastewater treatment assets (i.e. trickling filters or ASPs), therefore phosphorous removal by the MECs was not expected. Organic acid removal varied little between the MECs (standard deviation of the averages of 2.16). A low removal of organic acids suggests poor performance in anaerobic digestors, so it is possible that the low removals observed in the MECs is suggesting a similar failure, potentially due to the anoxic nature of the operation.

3.3. Current generation

All of the current generations oscillated over time, but there was a general increase in current generation for MECs 1 and 3, both of which produced significantly more gas than MEC 4 which exhibited a drop in current over time (Fig. 1). Over time, the biofilms would be increasing in thickness which would increase microbial activity and therefore, increase the overall current generation, observed in MECs 1 and 3. MEC 4 appears to have experienced a reduction in current between day 10 (lower resistor installation) to the final day of operation (day 90), indicating that the resistance of the system increased, likely due to membrane fouling by microorganisms and chemical build-up (sulfur/FOGs) (Ding et al., 2018; Zhou et al., 2013). MEC 2 also did not increase its overall current generation over the period of operation, and given its lack of hydrogen gas production, this suggests a failure to maintain a suitable biofilm with fouling on the membrane resulting in an increase to the resistance of the system.

The anode material (recycled carbon fibre) is less conductive than the graphite, with a higher resistance and less density (M300 has 300 gsm and graphite felt has 465 gsm), explaining the initial superior current production of MEC 4 relative to the other MECs using recycled carbon fibre anodes. However, the higher current of MEC 4 did not translate to superior COD/TSS removal or hydrogen gas production, suggesting a lower abundance of electrogenic microorganisms. Therefore, the difference in performance (hydrogen gas production) could be due to the reduced density of the fibres relative to the graphite felt, which will increase the exposed surface area of the anode material available for biofilm growth. This suggests that a higher conductivity does not always correlate to better performance in MECs.

3.4. Correlation coefficients

Pearson correlation coefficient values indicated that current correlated strongly and positively with increasing temperature for MECs 1 and 3 and a small positive correlation for MEC 2 (Table 6). Higher temperatures increase the rate of microbial activity and proliferation (so long as the bacteria can survive the temperature increase), explaining the strong correlation between temperature and current generation observed in MECs 1 and 3 (Jadhav and Ghangrekar, 2009).

MEC 4 appears to exhibit no correlation between current and temperature, which is supported by the continuing decline in the overall current production throughout the experiment with an increasing temperature from April to July.

Temperature also had a strong positive correlation for H$_2$ production for MEC 1 and 4, but not a strong correlation positively or negatively, for MEC 3. A positive correlation between hydrogen production and temperature was expected, as similarly to the reasons explained for

Table 4
Average nutrient change in %.

MEC	Anode	Nitrate %	Nitrite %	Phosphorous %	Sulfide %	Sulfate %	Organic acids %
1	M100 MnOx	+140.98	−44.67	+7.12	−0.93	−58.70	−21.89
2	M300 Plain	+158.79	−45.05	+8.66	−5.56	−60.05	−19.05
3	SGL 4.6	+178.44	−40.63	+10.96	−7.41	−63.29	−19.34
4	M300 MnOx	+156.48	−38.54	+7.44	−13.32	−62.86	−17.13

Table 5
Correlation coefficient (R) values for temperature against current and moles of H_2.

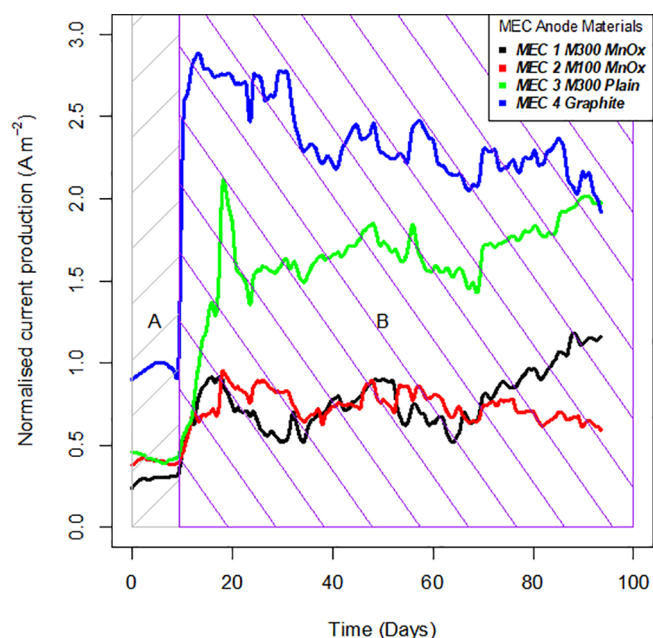|	MEC 1	MEC 2	MEC 3	MEC 4
Anode material	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
Current v Temp	0.67	0.19	0.71	−0.01
Temp v Moles H_2	0.75	N/A	0.09	0.72

Fig. 1. Current generation over time. Period A: period where a 1 Ω resistor was used to measure the current generation. Period B: period from which the 1 Ω resistor was replaced with a 0.1 Ω resistor.

current, the increase in temperature will increase microbial activity and proliferation will result in an increase of hydrogen production. MEC 1 and 4 were therefore far more sensitive to temperature, relative to MEC 3.

MEC 3 (using the plain M300 recycled carbon fibre anodes) produced hydrogen gas during the colder and warmer periods of operation, with more of its modules consistently producing gas. The structure of the materials used in MEC 1 and 3 are the same, differing only in that the MEC 1 anodes have an increased resistivity due to the electro-deposition of manganese (IV) oxide. This indicates that the Mn (IV) oxide coating has contributed to increasing the sensitivity of the performance of the MEC to temperature. As the addition of manganese (IV)

oxide increases the overall price and decreases the performance, it is preferable to use the plain recycled carbon fibres as anodes.

3.5. Efficiency calculations

MEC 3 (Plain M300) had the highest peak and average energy efficiency recovery (ηE_{mec}), with MEC 1 (manganese (IV) oxide coated M300) in second. MEC 2 produced no hydrogen so was the worst (with 0% recovery), but MEC 4 (graphite) was significantly lower than MECs 1 and 3. MECs 1 and 3 had steady increases in ηE_{mec} from start-up (day 18 and 13 respectively) until day 49 with a peak of 20% for MEC 3. Following this time point, a drop in ηE_{mec} was observed, which coincided with a drop in current generation and temperature (from both the input wastewater and internal MEC temperature).

Coulombic efficiencies (CE_{mec}) were also low but still had the same hierarchy of average performance; MEC 3 = 4.9%, MEC 1 = 3.2%, MEC 4 = < 0.01% and MEC 2 = 0%. Average substrate efficiencies (S_{Emec}) were also low; MEC 3 = 12.1%, MEC 1 = 4.08%, MEC 4 = 0.01% and MEC 2 = 0%. This indicates that the recycled carbon fibre anodes are superior to the graphite in terms of cathodic product recovery, with the overall architecture and operation of the system being very inefficient.

There have been clear improvements to performance in the form of better efficiencies between the recycled carbon fibre anodes and the graphite felt anodes, with MEC 3 being the best performing unit. However, the best periods of performance were still unable to achieve close to the 100% energy efficiency recovery from the energy supplied by the power supply, in the recovered hydrogen gas. The coulombic and substrate recovery efficiencies were low in all MECs, suggesting that significant hydrogen losses were occurring in all systems, especially when considering the increasingly high current generations from MEC 1 and 3.

The losses would have been from leakage and hydrogenotrophic microorganisms, suggesting an issue with the architecture, but this could be improved by refreshing the catholyte on a regular basis, in order to reduce the proliferation of hydrogen scavenging bacteria (Cotterill et al., 2017). Furthermore, the input voltage of 1 V means that the maximum energy recovery efficiency would be 123% (assuming no loses of any kind). There is a high likelihood that the input energy was too high, and that a lower energy input would have produced the same performance in terms of gas production but improved the efficiency (Logan et al., 2008).

3.6. Cost benefit of using recycled carbon fibre anodes

In terms of cost benefit, there are large differences in the anode cost compared to reported examples when using rCF. The SGL material that was used in this study (MEC 4) was the same in the *Cotterill et al.* pilot
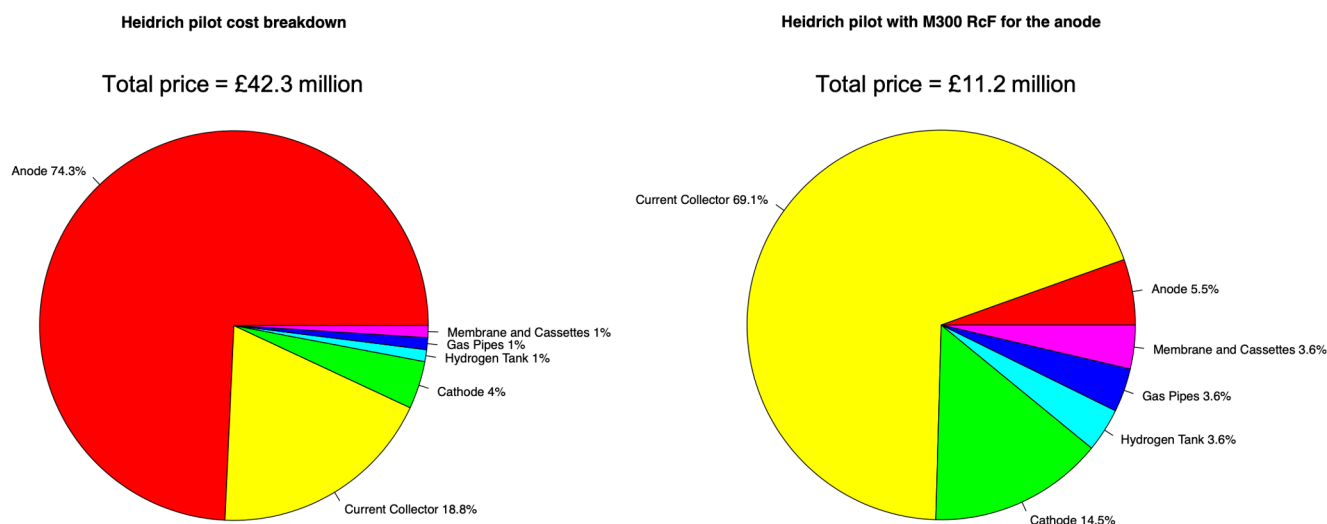
Table 6
Average and peak electrical energy recovery efficiencies.

	MEC 1	MEC 2	MEC 3	MEC 4
Anode Material	M300 MnOx	M100 MnOx	M300 (plain)	Graphite Felt
Electrical energy recovery for the whole MEC % (ηE_{mec})	5.00	0.00	7.89	0.00
Peak electrical energy recovery for the whole MEC %	12.00	0.00	20.00	1.87

Heidrich pilot cost breakdown

Total price = £42.3 million

Anode 74.3%

Membrane and Cassettes 1%
Gas Pipes 1%
Hydrogen Tank 1%

Cathode 4%

Current Collector 18.8%

Heidrich pilot with M300 RcF for the anode

Total price = £11.2 million

Current Collector 69.1%

Anode 5.5%

Membrane and Cassettes 3.6%

Gas Pipes 3.6%

Hydrogen Tank 3.6%

Cathode 14.5%

Fig. 2. Break down costs for Heidrich pilot with the Olmec and the RCF M300 anodes.

and has been shown to be inferior in terms of performance to the M300 and is costing £82 m^{-2} more. The *Heidrich* pilot anode was more expensive still and has been reported as requiring a 90% reduction in cost of anode/current collector assembly (Aiken et al., 2019). Due to the low cost of the recycled carbon fibre, the concerns for the cost of periodically replacing the anode (e.g. every 10, 20 years) are reduced.

By using the scenarios developed by Aiken et al. (2019) it possible to demonstrate the impact to the material costs that the recycled carbon fibre has, in terms of the break down. The use of the M300 means that the anode is no longer the cost barrier to deployment and instead, the current collector is now the main barrier to deployment from a cost perspective. If the scaled *Heidrich et al.* MEC has a cost of £42.3 million the anode would cost £32.1 million. By using the M300, the anode cost is reduced to £640 K (a saving of £31.46 million) and the total cost of the MEC to £11.2 million (Fig. 2). Assuming that the performance shown in the Heidrich pilot would be the same with the M300, this would automatically save approximately 75% of the total costs by changing one component.

4. Conclusion

MECs require an inexpensive anode if they are to be industrially deployed, and the recycled carbon fibre anodes are a potential solution. rCF has demonstrated statistically significant performance improvements (in terms of COD/TSS removal, hydrogen production and efficiencies) over a previously tested graphite felt material at 93% reduction in cost. The use of rCF contributes to creating a circular economy by valorising a waste product and then producing renewable energy from waste and potentially treating wastewater with a lower energy requirement. Improvements to the operation and architecture of the system will still be required to deploy MECs at larger scale.

CRediT authorship contribution statement

Daniel Indiana Carlotta-Jones: Conceptualization, Methodology, Investigation, Formal analysis, Writing - original draft. **Kevin Purdy:** Methodology, Resources, Writing - review & editing. **Kerry Kirwan:** Funding acquisition, Writing - review & editing. **James Stratford:** Methodology, Writing - review & editing. **Stuart R. Coles:** Conceptualization, Project administration, Supervision, Writing - review & editing.

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