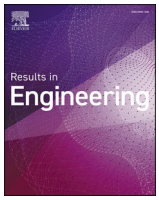
Comparative performance of sustainable anode materials in microbial fuel cells (MFCs) for electricity generation from wastewater

Results in Engineering 20 (2023) 101385

Contents lists available at ScienceDirect

Results in Engineering

journal homepage: www.sciencedirect.com/journal/results-in-engineering



Comparative performance of sustainable anode materials in microbial fuel cells (MFCs) for electricity generation from wastewater

A.K.M Khabirul Islam [a,*], Patrick SM. Dunlop [b], Gourav Bhattacharya [b], Md Mokim [a], Neil J. Hewitt [a], Ye Huang [a], Valentina Gogulancea [a], K. Zhang [c], Caterina Brandoni [a]

[a] CST, Belfast School of Architecture and the Built Environment, Ulster University, Northern Ireland, BT15 1AP, UK
[b] NIBEC, School of Engineering, Ulster University, Northern Ireland, BT15 1AP, UK
[c] EERC, North China Electric Power University, Beijing, China

ARTICLE INFO

Keywords:
Microbial fuel cells
Anodes
Recycled anode materials
Flexible graphite powder
Wastewater

ABSTRACT

Microbial fuel cells (MFCs) are a promising technology to generate electricity from wastewater and reduce the organic content. Whilst there has been a significant enhancement in MFC efficiency arising from the introduction of novel materials and cell designs, challenges remain with respect to the performance, cost, and sustainability of anode materials. This paper reports the development of single chamber MFCs with a focus on novel, cost-effective, and recycled carbon-based anode materials, including Recycled Water Filter Block/Powder (RWFB/RWFP), Recycled Chopped Carbon Fibre (RCCF), Carbon Felt (CF) and Graphite Flexible powder (GFG). Anodes prepared from GFG were shown to provide high power density (342.8 mW/m^2), followed by RCCF, CF, RWFP, RWFB and CF (77.6, 71.8, 59.0 and 57.9 mW/m^2, respectively). Chemical Oxygen Demand (COD) reduction was measured initially and at day 30, with GFG anodes observed to remove 83% of the initial load, compared to RCCF, RWFB, RWFP and CF anodes, where COD reductions of 69%, 61%, 65% and 73% were observed, respectively. Electrochemical analysis and biofilm imaging confirmed recycled materials were colonised by microorganisms and performed to high standards. GFG offers significant promise as an anode material, with excellent performance supported by a reduction in capital cost of up to 90% in comparison to CF. The use of recycled carbon material as MFC anodes shows promise, but requires additional work to improve the stability and durability of systems to permit scale-up.

1. Introduction

Wastewater treatment (WWT) is an energy-intensive process. Despite significant interest in reducing the energy required to drive conventional WWT processes, to help support carbon reduction targets and ensure affordability, energy usage within the sector is predicted to double by 2040 [1]. Microbial Fuel Cells (MFCs), which treat wastewater and produce electricity, are therefore seen as an attractive solution, with great scope for use in decentralised systems within developing nations where a significant proportion of wastewater is discharged to the environment without any treatment. In addition to energy production from wastewater, MFCs offer several practical solutions; they produce less sludge than traditional WWT, do not require oxygen for aeration, are easy to operate, have a compact footprint, and with the significant reduction in COD permit treated effluent to be discharged with lower risk of environmental pollution. Examples of novel and promising applications of MFCs include the combination of MFCs with constructed wetlands for the removal of antibiotics and electricity production [2], purification of urine [3] and application for a range of specialist industrial wastewaters [4], such as high strength brewing wastewater [5]. However, scaling up such systems continues to pose considerable challenges, including: (1) a low amount of energy is often produced - MFCs typically have lower power density than traditional batteries or fuel cells [6], and (2) large initial investment costs are required due primarily to the expense of electrode materials [7].

A typical MFC comprises an anode and cathode, with the optional inclusion of a membrane separating the electrodes. Systems can be single or double-chambered, with the anode chamber maintained in anaerobic conditions, whereas the cathode is usually aerobic [6]. A range of bacteria naturally found in wastewater act as a biocatalyst in a MFC, where they grow on an anode oxidising organic and inorganic matter to generate electrons [8], which are transferred via an external

* Corresponding author.
E-mail addresses: islam-akmk@ulster.ac.uk (A.K.MK. Islam), c.brandoni@ulster.ac.uk (C. Brandoni).

https://doi.org/10.1016/j.rineng.2023.101385
Received 29 June 2022; Received in revised form 9 June 2023; Accepted 27 August 2023
Available online 15 September 2023

circuit to the cathode for reduction via many potential reactions.

The anode is crucial to MFC performance, it serves as the support for the bioactive bacteria and a current collector – acting as the driving force of the reaction [9]. The anode should therefore have a large surface area and high porosity to facilitate and enhance biofilm formation [10], ideally, anode materials should be inexpensive, and widely available [11]. Given the biological nature of the system, suitable electrode material must be biocompatible, non-toxic to the bioactive species, and preferably prevent unwanted fouling [12]. The cost of the anode in MFCs has been estimated to be between 20% and 50% of the total capital cost [9], thereby appropriate selection of anode materials could significantly impact both performance and system cost.

Although there is significant effort to enhance the qualities of anode materials [13], costs are still high, with scientists frequently concentrating on cutting-edge, "exotic" materials, that may require energy-intensive treatment before being used. Carbon-based, metal--based, and mixed carbon-and-metal-based materials are often used, with a variety of physical and chemical treatments reported to improve conductivity, surface area, and biocompatibility for microbial growth, as well as enrich the electroactive microbial community, resulting in improved fuel cell efficiency [14]. For example, adding materials like activated carbon (AC) [15], carbon black (CB), and nanoparticles to the anode can enhance the specific surface area, allowing more interaction between the electrode and the microorganism [16]. Yaqoob et al. [9] recently reviewed a wide range of materials, highlighting the potential of waste-derived anode materials to decrease costs, while still maintaining good system performance. Carlotta-Jones et al. [17] used commercial recycled carbon fibre as the anode in cassette type Microbial Electrolysis Cell (MEC) to produce H_2 from real wastewater in a pilot project, reporting a significant reduction in anode cost without compromising the cell performance. By utilising a sustainable waste coffee-based anode (converting waste materials into valuable carbonised materials), Hung et al. [18] reported an improvement in the power density of MFCs (up to 3800 mW/m^2) which was much greater than that measured for conventional materials. Clauwaer et al. [19] developed a system based on a narrow hollow tube (1.5–3 mm diameter) filled with granular graphite (GG) and simply sealed with rubber stoppers to form an anode. Trials in a MFC indicated that during batch operation mode with sodium acetate-based medium, the GG anode achieved a power density of 83 mW/m^3.

The work in this paper extends the approach to develop sustainable and low-cost anode materials, exploiting low-cost and recycled materials to replace more widely used carbon-based anodes (such as carbon felt, carbon fibre, carbon cloth, carbon paper, carbon mesh, graphite fibre and felt). Utilising a compact single-chamber MFC with an air cathode, we report the implementation and performance of Graphite Flexible powder (GFG), Recycled Chopped Carbon Fibre (RCCF), Recycled Water Filter Block (RWFB), and Recycled Water Filter Powder (RWFP) to systems utilising Carbon Felt (CF) anodes, the industry-standard material possessing large specific surface area, excellent electrical conductivity, and biocompatibility [20]. The work contributes to the development of suitable, cost-effective anodes that will help MFC manufacturers to move the technology to a practical scale. Graphite flexible powder, typically used with paraffin, wood flour/high-density polyethene (WF/HDPE) matrix materials to make phase change materials for thermal energy storage, has good electrical conductivity, a high surface area, good mechanical strength, and can be purchased at high volumes at low cost (£13,000 per tonne [21]). We believe this to be the first time that GFG has been trialled for MFC anodes. Recycled carbon fibres have already been trialled in MECs, with successful results [17], and show potential for use in MFC systems. The authors chose RCCF as an anode material to aid in comparison to recycled carbon-based water filters. New water filter blocks, such as Sintered Activated Carbon (SAC), have previously been employed as cathodes in MFC [22], demonstrating a power density of 51 mW/m^2. However, to our knowledge, no work has been undertaken with spent (discarded) water filters, which do not require any treatment before formation into anodes – as such, they effectively form a zero-cost material. The novelty of the paper lies, therefore, in assessing the performance of commercially available low-cost (GFG) and recycled materials (RCCF, RWFB, RWFP) for anode fabrication, where these sustainably sourced products are compared with the industry standard carbon felt. The electrochemical behaviour of the novel anode materials was investigated using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements to gain insight into the performance data and highlight routes for further enhancement. Scanning Electron Microscopy (SEM) images were used to investigate the growth of biofilm on the anode surface constructed from these recyclable and inexpensive materials.

2. Materials and methods

2.1. MFC construction and anode fabrication

In keeping with the low-cost theme for this investigation, a 3.6 cm internal diameter Polyvinyl Chloride (PVC) pipe was used to create a single chamber membrane-less cube type MFC of 50 mL volume (Fig. 1). The chamber was sealed at one end with an acrylic support plate (6 cm by 6 cm) and a second acrylic plate (6 cm by 6 cm having a 3 cm hole at the centre) was used to support a polyester cloth forming the air cathode (Fig. 1). Rubber gaskets and mechanical support structure ensured the mechanical integrity of the system; no leakage of contents was observed. Four holes were drilled into the cylindrical surface of the reactor to enable the connection of the electrodes (anode and cathode), insertion of the reference electrode and a sample collection port. Rubber septa were utilised to ensure anaerobic conditions within the chamber. Using the methods described by Yang et al. [23], MFCs cathodes were prepared by mixing activated carbon (AC) powder, carbon black (CB) and a poly (vinylidene fluoride) (PVDF) binder (Redox, Sweden) to form a paste which was supported on Stainless-Steel Mesh size 60 (SSM60) - used as both the current collector and support material.

Regarding anode fabrication, water filter blocks are typically utilised in domestic water purification systems in developing nations. After around 2–3 months of use, this filter block needs to be replaced and is commonly rejected to waste. For this work, a used filter block was sourced from Bangladesh and utilised in two forms: as a block (designated RWFB) and, following manual crushing, as a powder (RWFP). To form the RWFB anode, a section of the filter block was manually removed (area 9 cm^2). A 1 mm hole was bored in the centre of the block and bound to stainless steel (SS) wire (diameter 0.5 mm). For the fabrication of RWFP anodes, recycled water filter powder was mixed with sodium alginate (SA) at a ratio of 90:10, respectively [24]. Deionised water was gradually added and with mixing a thick paste was formed. The paste was then applied with a spatula to pre-cut SSM60 support. A 0.95 g/L $CaCl_2$ solution was prepared as described by Ref. [25] and used to cross-link all SA-based electrodes. The RWFP anode was submerged into $CaCl_2$ to facilitate crosslinking for 15 min, followed by overnight drying at room temperature.

Graphite flexible powder (GFG) (SGL, Germany) and RCCF were also processed into anodes. GFG powder was combined with SA to form a paste prior to deposition on a SSM60 support as described above. For RCCF anode fabrication, the collected fibre was chopped into lengths of 0.5–1 cm, whereby the paste with SA was prepared prior to deposition into a SSM60 support.

2.2. MFC start-up and performance analysis

Wastewater (WW) was collected from a Belfast based WWTP (NI Water, Northern Ireland, UK) and used to inoculate all MFCs. Using standard analysis processes the following parameters were determined: Biochemical Oxygen Demand (BOD) (59.2 mg/L), COD (332 mg/L), Dissolved Oxygen (DO) (1.74 mg/L), pH (7.2), Total Suspended Solids (TSS) (231 mg/L), Total Dissolved Solids (TDS) (1.22 g/L) and Total

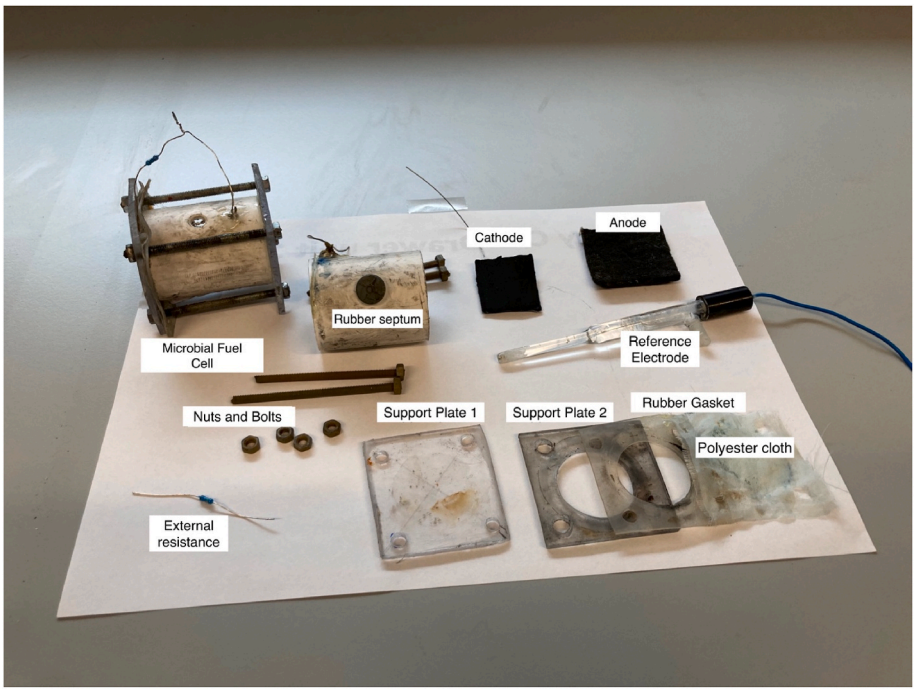


Fig. 1. Constructed PVC pipe-based MFC and components.

Solid (TS) (1.45 g/L). Synthetic wastewater (SWW) was prepared according to He et al. [26] and Angenent et al. [27] and mixed 50:50 with WW before addition to the MFCs, increasing the organic substrate available to the natural microorganisms. All MFCs were operated in batch mode at room temperature (18 °C–22 °C) for 30 days. Systems were set up and run in triplicate. On the first day of each experimental run, inoculation was performed by introducing 20 mL of wastewater into each MFC, followed by 20 mL of SWW. The system was sparged with pure N_2 for 20 min, and the headspace was filled with N_2 before sealing to ensure anaerobic conditions. Half the MFC content was emptied and refilled weekly, with the standard 50:50 ratio of SWW and WW. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were taken on Day 1, Day 15 and Day 30; anode surfaces were examined by SEM on Day 1 and Day 30. COD analysis was conducted on Day 1 and Day 30.

2.3. Electrochemical analysis

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) analyses were conducted using a three-electrode system controlled by a single channel potentiostat (PalmSense4, Netherlands), with anodes serving as the working electrode (WE), AC-based air cathodes as the counter electrode (CE) with an Ag/AgCl (BASi, UK) reference electrode (RE). Using the variable resistance method, polarization and power density curves were constructed using a multimeter and a variable resistor (RS Components, UK). This approach began in open circuit potential (OCP) mode, then in closed circuit mode through the selection of resistances ranging from 1 MΩ to 10 Ω. MFC current was determined using Ohm's Law. Measurements were acquired over 15-min periods to ensure a stable voltage reading. Eq. (1) and Eq. (2) were used to calculate the current density (CD) and power density (PD), respectively:

$$CD = I/A = V/RA\ (Amp/m2) \quad (1)$$

$$PD = VI/A\ \left(mW/m^2\right) \quad (2)$$

where I is the current generated by the MFC in Amp, V is the potential measured against a certain resistance (R), and A is the geometric surface area of anodes.

Closed-circuit voltage monitoring was carried out daily by connecting the anode and cathode of each MFC with a 638 Ω resistor with a digital multi-meter.

Cyclic voltammetry was undertaken across a potential window of −1 V–1 V (vs. Ag/AgCl) at a scan rate of 50 mV/s. The polarization and charge transfer resistance of the MFCs was monitored using EIS across a frequency range of 400 Hz–0.1 Hz, with a fixed anode potential of 10 mV (alternative current) versus Ag/AgCl. CV and EIS data were analysed using PSTrace 5.8 software (Netherlands), with Origin Pro 2021b used to plot the data.

To calculate the electrochemically active surface area (EASA) of the anodes, CV was measured using a 5.0 mM potassium ferricyanide redox couple $Fe(CN)_6^{4-/3-}$ in 0.1 M potassium chloride (KCl). A Pt mesh was used as the counter electrode and an Ag/AgCl reference electrode. Data were recorded at 20 mV/s steps ranging from 20 to 100 mV/s, with peak current recorded. The Randles-Sevcik relation was plotted and a linear fit was identified [28]. The EASA, defined as A within the Randles-Sevick equation (Eq. (3)), was subsequently calculated:

$$i_p = 2.687\text{x}10^5 n^{3/2} A\, D^{1/2} C\ v^{1/2} \quad (3)$$

where i_p is the peak current in amperes, A is the EASA in cm^2, D is the diffusion coefficient in $cm^2\ s^{-1}$, C is the concentration in mole, n is the number of electrons involved in the redox reaction and v is the scan rate in Vs^{-1}.

2.4. COD analysis

To determine COD reduction during MFC operations, effluent samples were analysed periodically via the standard HACH-based potassium dichromate oxidation method using spectrophotometry at 420 nm, with high-range COD vials (HACH, UK), a COD digester (DRB 200), and colourimeter (DR/2500, UK). Effluent samples (2 mL) were added to COD vials, heated at 150 °C in the COD digester for 2 h, and cooled before spectrophotometric analysis.

2.5. Scanning Electron Microscopy

Microscopy images of the anodes were acquired to assess biofilm formation/coverage. Anodes were removed from MFC at Day 1 and Day 30 and stabilised by established procedures [29], whereby samples were immersed in 2.5% glutaraldehyde and 0.1 M phosphate buffer solution, followed by dehydration with progressive ethanol concentrations (10–100%). Samples were dried before sputter-coated with gold (approx 3 nm). The Hitachi SU5000 FE-SEM was used, with a 10 kV accelerating voltage and high vacuum of 10^{-8} bar; images were acquired at a working distance of 10 mm.

3. Results and discussion

3.1. Voltage and power generation

The polarization curve can be determined by the relationship formed between the voltage and current density, which has been validated with various external resistances [30]. Polarization curves for MFCs using each of the 5 anode materials are shown in Fig. 2. Generally, polarization curves are understood to have three primary features, an initial rapid voltage loss zone, a linear voltage drop region, and a subsequent rapid voltage drop region. Initial rapid voltage loss is caused by the need for energy to initiate biological and chemical processes, often known as oxidation or reduction reactions [31,32]. The bell-shaped PD curves indicate the presence and activities of exo-electrogenic bacteria within the MFC reactors and subsequent redox reactions. It is evident from the data that when current density increased, the value of power density also increased to a maximum. Power density subsequently decreased at higher voltage. Consequently, electron mobility in the circuit is reliant on the external resistance, resulting in a high current density as opposed to high power density [33,34]. GFG anodes produced the highest power density (59.21 mW/m^2), with all materials bar RWFB (2.25 mW/m^2), outperforming CF (5.44 mW/m^2).

The voltage generation pattern over time in closed-circuit mode was also monitored (Fig. 3(a)). All MFCs produced increasing voltage during the 30-day experiment, with renewed generation following the replacement of influent WW. The maximum power density was measured on day 25, where the GFG anode MFC produced 342.8 mW/m^2. MFC based upon RWFB anodes, again gave the lowest value (57.92 mW/m^2), closely followed by RWFP. GFG and RCCF outperformed CF-based systems (71.8 mW/m^2) (Fig. 3(b)). System performance decreased after 32 days when the electrode stability issues began to dominate.

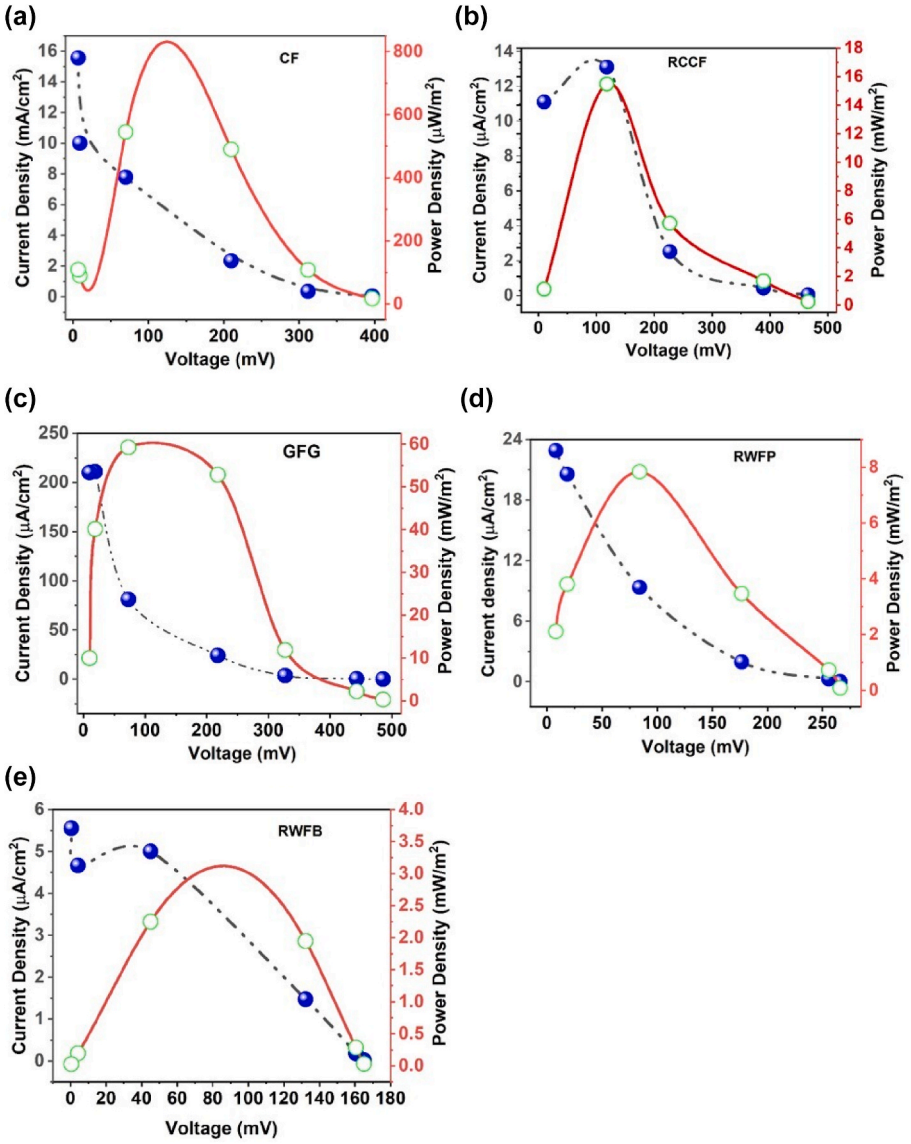


Fig. 2. Polarization and power curve of MFCs with anodes prepared from (a) CF, (b) RCCF, (c), GFG, (d) RWFP and (e) RWFB.

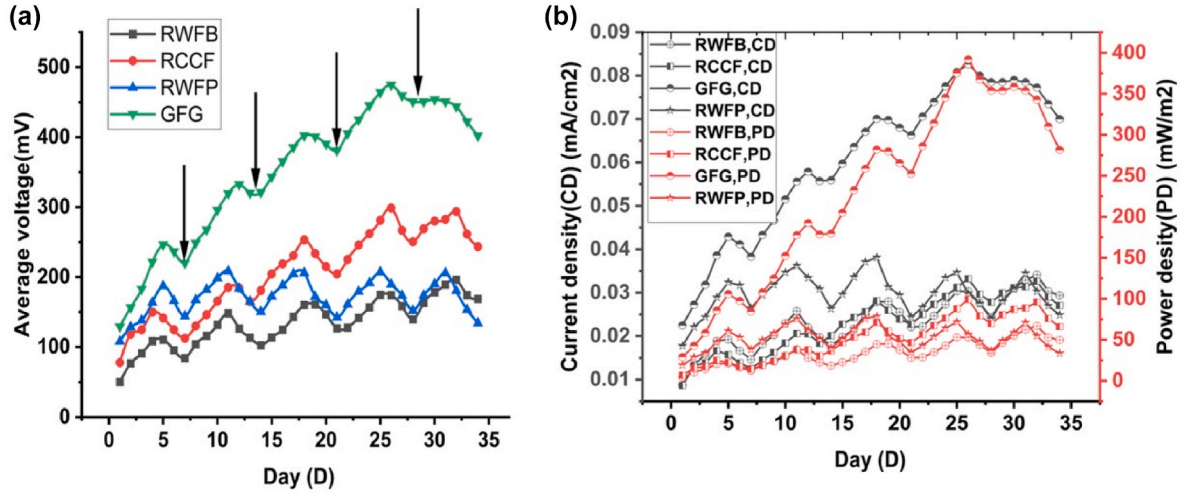


Fig. 3. Time-dependent comparative (a) voltage generation of all MFCs, black arrows indicate substrate renewal, (b) Current density (CD)/power density (PD) curve for GFG, RCCF, RWFP, RWFB and CF.

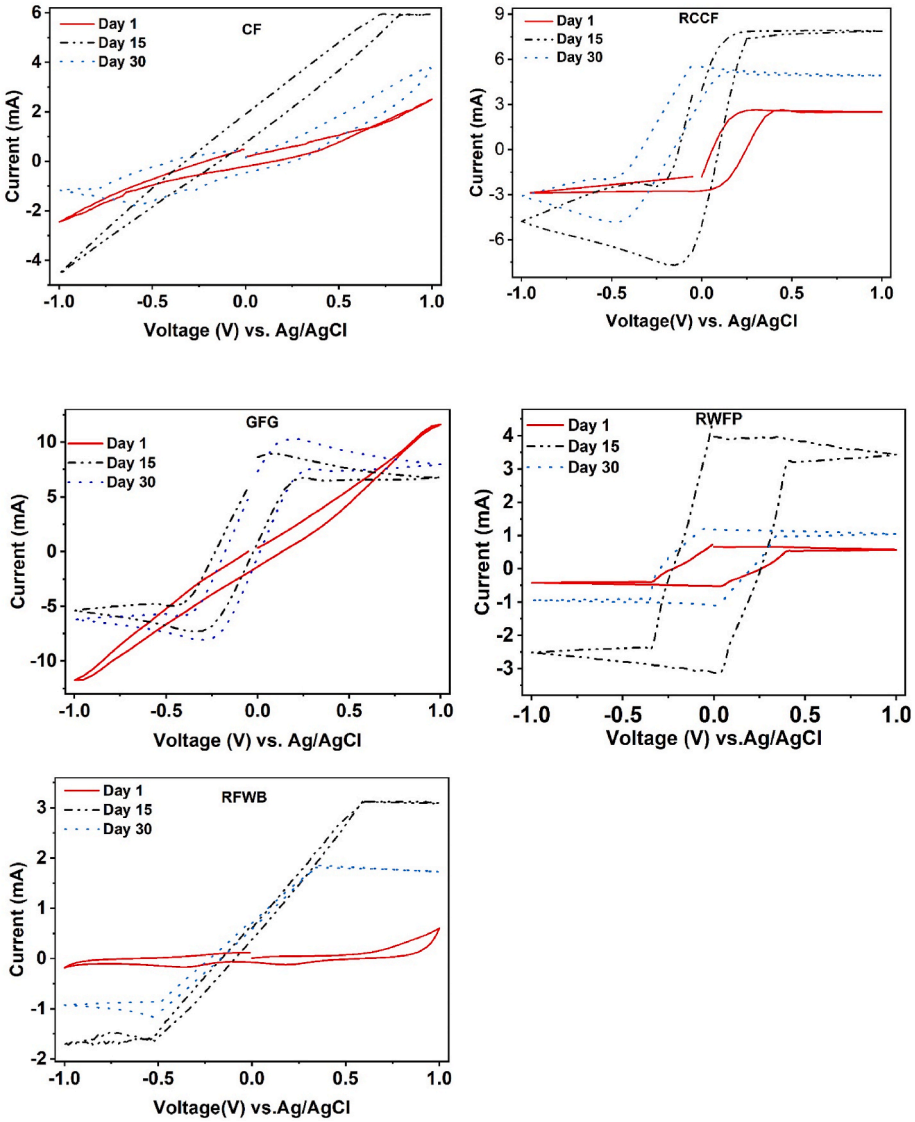


Fig. 4. CVs recorded for anode materials used in MFCs with CF a), RCCF b), GFG c), RWFP d) and RWFB e) anodes, at Day 1, Day 15 and Day 30.

3.2. Cyclic voltammetry analysis

Cyclic voltammetry was employed to determine changes in electrical conductivity and electron transfer kinetics arising from biofilm formation [35]. To gain an accurate view of anode performance, wastewater was used as the electrolyte during acquisition of CV data at various timepoints during the 30-day MFC trial of novel anodes. The initial current density was found to be greatest for the GFG anode, which signifies the highest electrical conductivity of the five electrodes. Low current density was observed for the RWFB anode, confirming poor electrical conductivity. The enhanced current densities and appearance of redox peaks, along with higher area under the curve, observed at day-15 for all the electrodes implied anode colonisation and biofilm formation [36]. Redox activities and current densities for all MFCs gradually decreased on day 30 (D30), which we speculate is due to the low mechanical stability of the anodes (some physical disintegration was visually observed). The increase in peak current values and capacitive behaviour of the GFG anode, when compared to RWFP, RCCF and CF anodes, suggests superior bio-catalytic activity, corresponding to good organic matter degradation and power generation (Fig. 4) [37].

3.3. Electrochemical impedance spectroscopy analysis

Along with the cyclic voltametric study, EIS was carried out to aid in understanding charge transfer and ohmic limitations within the MFCs. The Nyquist plot for each electrode is shown in Fig. 5. The lowest impedance can be observed in the data for the GFG electrode which signifies high electrical conductivity - in agreement with the CV studies. A simplified Randles equivalent circuit model (ECM) (Fig. 5 (f)) was further used to extract data for ohmic resistance (R1), charge transfer resistance (R2) and the interfacial capacitance (C1) (Table 1). The trends in resistive and capacitive components on day 15 (D15) indicate that biofilm development had occurred in all MFCs, with capacitance increased substantially. The observed enhanced resistivity over time was likely due to a thicker and aged biofilm, which reduced the efficiency of electron transport to the electrode. Coupled with cathode cloth fouling, this may account for the variation observed by day 30 (D30), demonstrating the complex relationship between the mature biofilm and the electrode surface [38].

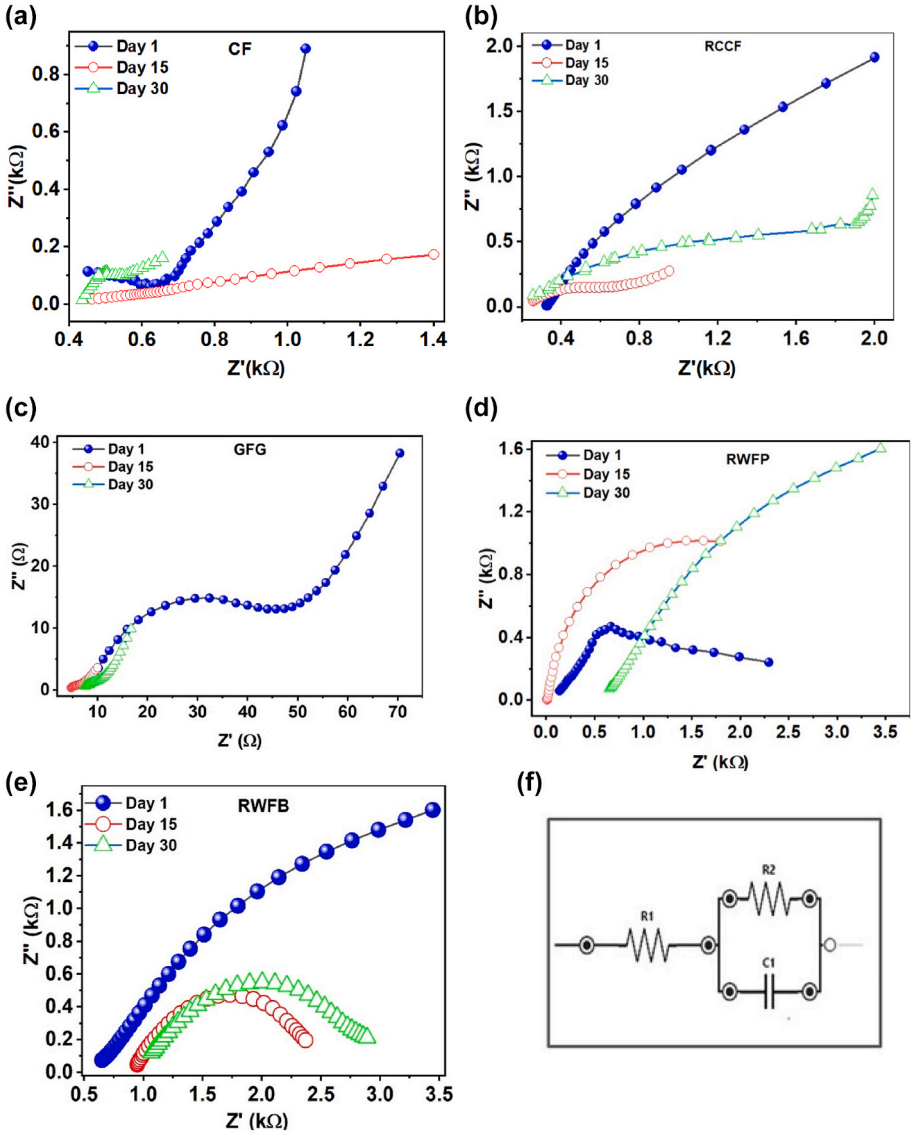


Fig. 5. Nyquist plots of the single-chamber MFCs measured at D1, D15 and D30 with anodes comprised of (a) CF, (b) RCCF, (c) GFG, (d) RWFP (e) RWFB and (f) Randles simplified equivalent circuit. Z': Real impedance, Z'': Imaginary impedance, R1: ohmic resistance, R2: charge transfer resistance and C1: double-layer capacitance.

Table 1
ECM fitted data for anode materials recorded on days 1, 15 and 30 of MFC operation.

MFC Type	Resistance & Capacitance based on ECM								
	Day 1 (D1)			Day 15 (D15)			Day 30 (D30)		
	R1(Ω)	R2(Ω)	C1 (nF)	R1(Ω)	R2(Ω)	C1 (nF)	R1(Ω)	R2(Ω)	C1 (nF)
RWFB	649	3445	2.8×10^4	647	2370	1.6×10^5	1068	2890	3.0×10^4
RWFP	158	2523	1.8×10^5	9.63	1723	1.9×10^5	649	3434	1.7×10^5
RCCF	300	2002	1.7×10^5	239	957	2.2×10^5	244	1995	2.5×10^5
GFG	9	70	1.2×10^5	4.75	10	1.0×10^6	7	16	1.1×10^5
CF	452	1050	1.8×10^5	436	656	2.3×10^5	463	1402	2.0×10^5

3.4. Electrochemical active surface area analysis

In order to determine the EASA, the electrochemical behaviours of all the electrodes as a function of scan rate were further probed using the Randles-Sevcik equation. Fig. 6 demonstrates the CV plots using anodes comprised of each material as a function of scan rate, with the EASA calculated via the Randles-Sevcik equation. The highest EASA was observed for the RCCF anode (0.484 cm^2) followed by GFG (0.375 cm^2), RWFP (0.203 cm^2), CF (0.151 cm^2) with the lowest for the RWFB (0.063 cm^2). The less porous structure of the GFG likely correlated with the EASA being lower than RCCF.

3.5. COD reduction analysis

Samples were collected from each MFC at D1 and D30 for COD analysis, with the reduction in COD shown in Fig. 7. The MFC containing the anode prepared from GFG was shown the highest COD reduction (82%), outperforming CF (73%). Good levels of COD reduction were attained by all systems, 69%, 65% and 61% for RCCF, RWFP, and RWPB, respectively. The high COD reduction observed in the GFG system can be correlated to the superior current density and enhanced bio-electrochemical performance.

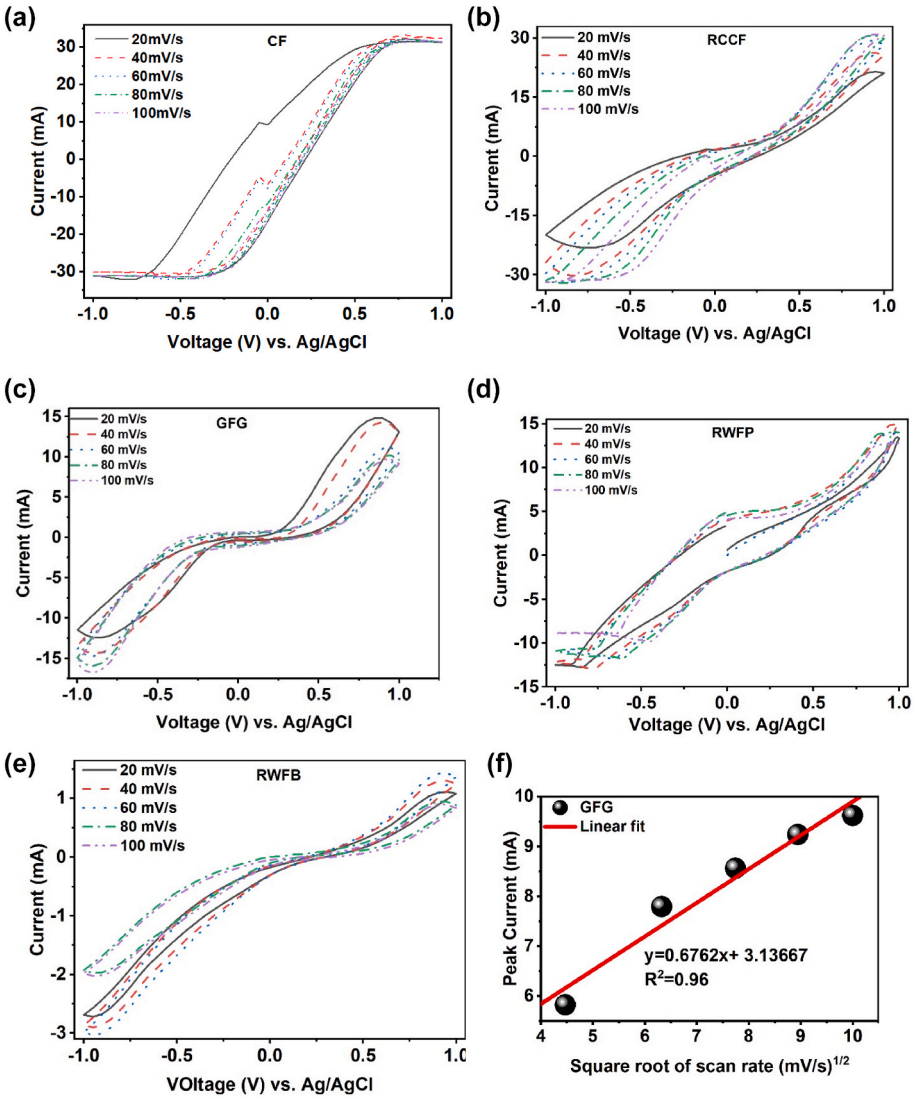


Fig. 6. Cyclic voltammetry at different scan rates of (a) CF, (b) RCCF, (c) GFG, (d) RWFP and (e) RWFB anode in 5.0 mM [Fe(CN)6]4- 3- solution containing 0.1 M KCl. Randles- Sevick plot (f) exhibiting the dependency of anodic peak current on the square root of scan rate for GFG electrode.

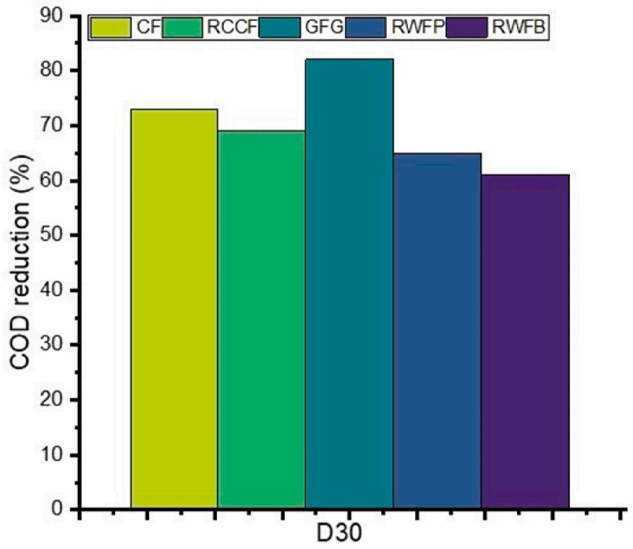


Fig. 7. Comparative COD reduction for MFC prepared from low-cost/recycled materials.

3.6. Morphology of biofilm on the anode surfaces

SEM images of all anodes were acquired at D1 and D30 (Fig. 8). SEM was used to analyse the structure and morphology of the anodes at D1 (Fig. 8 (b), (d), (f), (h) and (j)). For the GFG anode, the initial granular structure is subsequently coated by bacterial cells (some evident as rods) forming biofilm. Biofilm was also confirmed to be present on the surface of other electrodes at D30. GFG-based anodes exhibited increased surface coverage of a thick biofilm (Fig. 8 (f)), perhaps resulting from the hydrophilic nature of the GFG and good electrical conductivity of the GFG-based anode, whereas RWFB anodes demonstrated low surface coverage (Fig. 8 (j)).

3.7. Cost analysis

The cost of the anode in MFCs ranges from 20% to 50% of the total capital cost [9], suggesting that using recycled and cost-effective materials can potentially reduce the cost of MFC significantly.

The performance of GFG based anodes offers significant potential and from a cost perspective, anodes can be fabricated with the use of a stainless-steel mesh support material and sodium alginate (SA) at a total manufacturing cost of £65/m^{2}-approximately an order of magnitude (90%) lower than the cost of a standard carbon based MFC, e.g. CF ranges in price from £635 to £794/m^2 [21]. Recycled, biocompatible and conductive materials, such as recycled chopped carbon fibres or recycled water filters may be available at low/no cost, but preparation or pre-treatment can be required before anode fabrication. Fig. 9 shows the normalised cost (per m^2) of anodes for MFC, with RCCF demonstrating a cost reduction of up to 87% when compared to CF. The cost associated with RWFP is solely the anode support and preparation cost, demonstrating a 93% cost reduction vs CF.

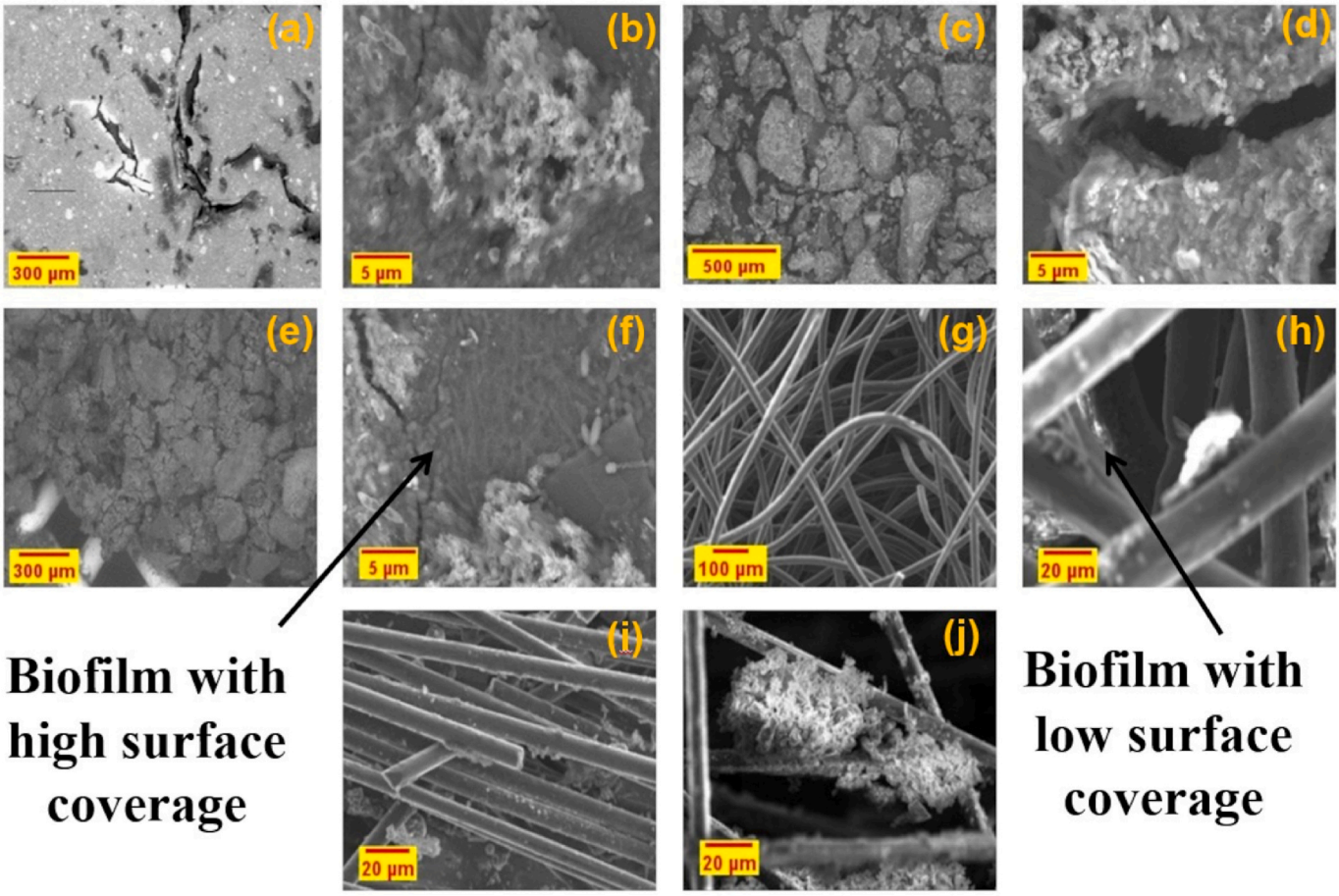


Fig. 8. SEM image of different anode material of MFCs RWFP (a)–(b), RWFB (c)–(d), GFG (e)–(f), CF (g)–(h) and RCCF (i)–(j). Images at D1 (a), (c), (e), (g) and (i); images at D30 (b), (d), (f), (h) and (j).

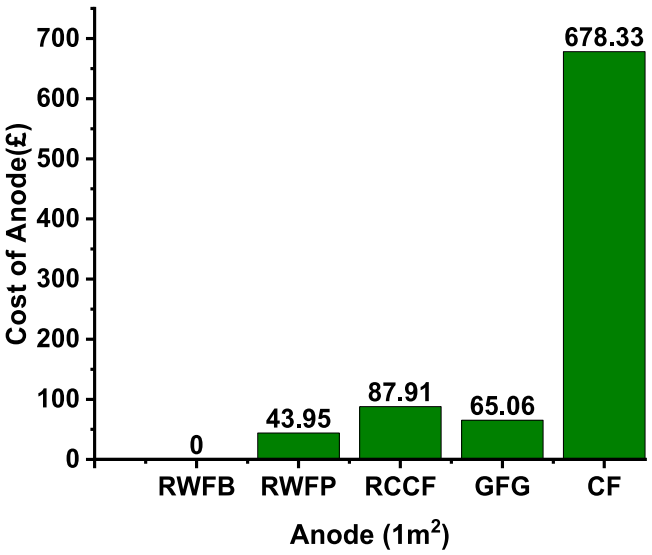


Fig. 9. Comparative normalised cost of different anodes used in MFCs.

3.8. Comparison of experimental results with available literature and future work

Table 2 compares the results obtained from the present study to published works to validate and better understand the potential for application of recycled carbon materials. The complexity of the MFC systems and the mix of biotic and abiotic controlling parameters prevents direct comparison, however, several trend can be observed.

The power density and the COD reduction attained with the MFC containing CF are comparable to equivalent systems studied in literature employing treated CF with a 30 mL chamber [39]. Given perhaps the changes in influent characteristics, the power density reported above is slightly higher than similar MFCs with CF anodes [40–42], nonetheless, this confirms the rational of the use of CF as the baseline material. Whilst increasing the environmental temperature or including a platinum-coated cathode could deliver increased energy production with carbon felt, such approaches incur additional costs and resources, paraphs outweighing the gain. The performance of the GFG-based MFCs against studies reporting the use of graphite granules (GG) shows significant promise for this material. The power density of the GFG-based MFC analysed in the present paper is 343.8 mW/m^2, which is well above MFC with GG anodes, even characterised by bigger volumes of the MFC [19,43–45]. The 82% reduction of the COD identified in the present paper is in line with the literature [45]. Better performances can, furthermore, be obtained with physical and chemical surface modification, as demonstrated by Kim et al. [43].

The performance of RCCF is aligned with studies using carbon-based anodes in single and double-chamber MFCs [39,46], further demonstrating the potential to use recycling carbon fibres for anode fabrication in MFCs. Whilst researchers such as Yuan et al. [47] and Karuppiah et al. [48] reported superior performance for some carbon-based anodes, the substrate, inoculum, and operational parameters of such systems were different to the present study. Given that the performance of spent RWFP and RWFB as anodes for MEC has not been previously reported, Table 2 compares the result with the work of Walter et al. who implemented a pristine water filter block with urine as the substrate, achieving a power density of 71.83 mW/m^2 [22]. The value is 18% higher than the reused filter tested in the present study. The COD reduction is above 60%, in line with the performance of the RCCF. Theodosiou et al. [49]

Table 2
Comparative summary of MFC performance, with focus on anode materials.

MFC type & size (mL)	Anode treatment, (if any)	Cathode & catholyte (if any)	Membrane	Substrate	Temp (^{0}C)	Power density (mW/m^2)	COD reduction (%)	Ref
Carbon Felt (CF)								
SC (30)	CF treated with GO	SSM with Pt catalyst	PEM	SWW	33–37	77.82	83.7	[39]
DC (25)	CF treated with hot H_2O_2	CF, 0.1 M PBS + 50 mM $C_6N_6FeK_3$	CEM	SWW	30	0.18	–	[40]
DC (200)	CF treated with HCl	NP, 0.02 M PBS + 50 mM K_3	Nafion	0.1 M Glucose + 0.1 M PBS	25	3.2	–	[41]
DC (220)	Untreated CF	CF	PEM	13.6 g/L Gucose	35	45–67	45–67	[42]
SC (50)	Untreated CF	AC + CB SSM	–	SWW & WW	18–22	71.8 73		This study
Graphite granules (GG)								
DC (600)	GG in SSM cylinder	CF, K_3	Nafion	SWW	30	900[a]	–	[43]
DC	GG	GG with Pt catalyst	CEM	SWW	22 ± 2	8[a]	–	[44]
DC (1000)	GG	CF with MnO catalyst	CEM	SWW	22 ± 2	83 ± 11[a]	–	[19]
DC (672)	GG	GG	CEM	SWW	25	137.4	82	[45]
SC (50)	Untreated GFG	AC + CB SSM	–	SWW & WW	16–20	343.8	82	This study
Carbon fibre/cloth/mesh/brush/Veil (CF/CC/CM/CB/CV)								
DC (112)	CBr	CC with Ti catalyst	AEM	–	25–30	4.25	–	[46]
DC (550)	Carbon paper (CP)	CP	PEM	Hydrolysate WW	20	123	–	[47]
DC (1100)	Carbon Veil (CVe)	CVe with PBS	PEM	Electroplate WW	27 ± 3	260–364	79–87	[48]
SC (50)	Untreated RCCF	AC + CB SSM	–	SWW & WW	16–20	77.6	69	This study
Activated carbon (AC) powder/filter								
SC	CFV	WFB	–	Urine		71.83	–	[22]
SC (15)	CFV	SCBF	–	TYE & AS	–	10–15[b]	–	[49]
SC (50)	RWFB RWFP	AC + CB SSM	–	SWW & WW	16–20	57.9 59	61 65	This study

Notes.
SC: Single chamber; DC: Double chamber; SWW: Synthetic wastewater; WW: Wastewater; TYE: Tryptone yeast extract.
GO: Graphene oxide; CM: Carbon mesh; CBr: Carbon brush; CC: Carbon cloth; CSP: Coconut shell based powder; CFV: Carbon fibre veil.
SCBF: Sintered carbon block filter; WFB: Water filter block; AC: Activated carbon; CB: Carbon black; SSM: Stainless steel mesh.
PEM: Proton exchange membrane; AEM:Anion exchange membrane; CEM: Cation exchange membrane.
[a] Values indicated mW/m^3 normalised to anode chamber volume.
[b] Result indicated as micro Watt/m.^{3}.

demonstrated that sintered carbon block when used as a cathode in MFC with carbon fibre veil as an anode, produces negligible power (10–15 μW), encouraging use of recycled sintered activated carbon filter (RWFB/RWFP) as anodes. The idea of using existing RWFP and RWFB has potential, having the advantage of addressing the problem of waste disposal of water filters abundantly used in developing countries. The comparison suggests, however, the need to improve the performance of RWFP or RWFB by investigation into low-cost surface treatments or addition of a small amount of AC or CB with RWFP, to increase the conductivity and subsequently enhance the overall performance. The use of recycling/waste material is an interesting opportunity for anode fabrication that can help resources to be kept in the market for a longer period of time, in line with the circular economy philosophy [40], diverting waste disposal from landfill and creating new markets for recycling materials.

The main issue with the experimental approach employed was the decrease in anode stability following day 30, primarily due to the binder used. Anode integrity and stability are key for long-term performance, and in keeping with the sustainability theme, there is potential for the application of various biobased binder materials to be examined. Secondly, increasing the power density could be realised via design of circular/cylindrical/tubular MFCs, in which the electrode surface area to volume ration can be increased via use of concentric structures whereby the distance between the anode and cathode can be reduced.

4. Conclusion

Four cost-effective and recycled anode materials (GFG, RCCF, RWFB and RWFP) were compared to the research standard anode material (CF). All materials achieved a reduction in the COD of wastewater of at least 60%. The power density of the MFC with a GFG anode outperformed CF by a factor of 4.4, with a reduction in the manufacturing cost of 90%. The use of RCCF confirmed the potential of recycled carbon fibres, with a power density 7% higher than CF and costs up to 87% lower. The power density of recycled water filters was lower than that of CF, and 18% lower than the power density derived from novel water filters. Considering the environmental impact of reusing existing water filters, the cost savings, and the high availability of this waste material, future work will be directed towards improving the performance of recycled water filters with low-cost surface treatments, modified MFC architectures and sustainable binders to extend their integrity and stability for long-term performances.

Credit author statement

A K M Khabirul Islam: Writing-Original draft preparation, Methodology, Software. **Patrick SM Dunlop:** Supervision, Reviewing and Editing. **Gourav Bhattacharya:** Investigation and Validation. **Md Mokim:** Data curation. **Neil J Hewitt:** Supervision, Conceptualization. **Ye Huang:** Conceptualization. **Valentina Gogulancea:** Data curation. **K. Zhang:** Visualization and **Caterina Brandoni**: Supervision, Reviewing Editing and Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

The authors are thankful to Horizon 2020 ALICE project for the financial support provided. ALICE project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 734560. This publication reflects only the authors' view and the Research Executive Agency, REA, is not responsible for any use that may be made of the information it contains. This research work was also carried out as part of the Royal Society and National Natural Science Foundation of China (IEC\NSFC\201070).

References

[1] International Energy Agency, WEO Special report: Water-energy nexus, March 2017. Page 37. Available at: https://www.iea.org/reports/water-energy-nexus (Last access: September 2023).
[2] I. Maldonado, E.G.M. Terrazas, J.M. Mamani, F.Z. Vilca, Removal of tetracycline and chloramphenicol through constructed wetlands: Roles of plants, substrates, and microbial fuel cells, Results in Engineering 17 (2023), 100982.
[3] T.O. Ajiboye, O.D. Ogunbiyi, E.O. Omotola, W.J. Adeyemi, O.O. Agboola, D. C. Onwudiwe, Urine: Useless or useful "waste", Results in Engineering 16 (2022), 100522 https://doi.org/10.1016/j.rineng.2022.100522 (urine can be used as substrate for electricity production from MFCs).
[4] O. Sahu, Sustainable and clean treatment of industrial wastewater with microbial fuel cell, Results in Engineering 4 (2019), 100053.
[5] Haris Nalakath Abubackar, İnci Biryol, Azize Ayol, Yeast industry wastewater treatment with microbial fuel cells: effect of electrode materials and reactor configurations, Int. J. Hydrog. Energy. 48 (2022) 12424–12432, https://doi.org/10.1016/j.ijhydene.2022.05.277.
[6] B.E. Logan, M.J. Wallack, K.Y. Kim, W. He, Y. Feng, P.E. Saikaly, Assessment of microbial fuel cell configurations and power densities, Environ. Sci. Technol. Lett. 2 (2015) 206–214, https://doi.org/10.1021/acs.estlett.5b00180.
[7] C. Munoz-Cupa, Y. Hu, C. Xu, A. Bassi, An overview of microbial fuel cell usage in wastewater treatment, resource recovery and energy production, Sci. Total Environ. 754 (2021), 142429, https://doi.org/10.1016/j.scitotenv.2020.142429.
[8] S. Malekmohammadi, S.A. Mirbagheri, A review of the operating parameters on the microbial fuel cell for wastewater treatment and electricity generation, Water Sci. Technol. 84 (2021) 1309–1323, https://doi.org/10.2166/wst.2021.333.
[9] A.A. Yaqoob, M.N.M. Ibrahim, S. Rodríguez-Couto, Development and modification of materials to build cost-effective anodes for microbial fuel cells (MFCs): an overview, Biochem. Eng. J. 164 (2020), 107779, https://doi.org/10.1016/j.bej.2020.107779.
[10] B.E. Logan, Microbial Fuel Cells, 2007. ISBN 9780444531933.
[11] M. Zhou, M. Chi, J. Luo, H. He, T. Jin, An overview of electrode materials in microbial fuel cells, J. Power Sources 196 (2011) 4427–4435, https://doi.org/10.1016/j.jpowsour.2011.01.012.
[12] K. Guo, A. Prévoteau, S.A. Patil, K. Rabaey, Engineering electrodes for microbial electrocatalysis, Curr. Opin. Biotechnol. 33 (2015) 149–156, https://doi.org/10.1016/j.copbio.2015.02.014.
[13] A. Aghababai Beni, H. Jabbari, Nanomaterials for environmental applications, Results in Engineering 15 (2022), 100467, https://doi.org/10.1016/j.rineng.2022.100467.
[14] M. Rahimnejad, A. Adhami, S. Darvari, A. Zirepour, S.E. Oh, Microbial fuel cell as new technol ogy for bioelectricity generation: a review, Alexandria Eng. J. 54 (2015) 745–756, https://doi.org/10.1016/j.aej.2015.03.031.
[15] D. Bose, R. Bhattacharya, M. Gopinath, P. Vijay, B. Krishnakumar, Bioelectricity production and bioremediation from sugarcane industry wastewater using microbial fuel cells with activated carbon cathodes, Results in Engineering 18 (2023), 101052.
[16] Y. Fan, S. Xu, R. Schaller, J. Jiao, F. Chaplen, H. Liu, Nanoparticle decorated anodes for enhanced current generation in microbial electrochemical cells, Biosens. Bioelectron. 26 (2011) 1908–1912, https://doi.org/10.1016/j.bios.2010.05.006.
[17] D.I. Carlotta-Jones, K. Purdy, K. Kirwan, J. Stratford, S.R. Coles, Improved hydrogen gas production in microbial electrolysis cells using inexpensive recycled carbon fibre fabrics, Bioresour. Technol. 304 (2020), 122983, https://doi.org/10.1016/j.biortech.2020.122983.
[18] Y.H. Hung, T.Y. Liu, H.Y. Chen, Renewable coffee waste-derived porous carbons as anode materials for high-performance sustainable microbial fuel cells, ACS Sustain. Chem. Eng. 7 (2019) 16991–16999, https://doi.org/10.1021/acssuschemeng.9b02405.
[19] P. Clauwaert, D. Van Der Ha, N. Boon, K. Verbeken, M. Verhaege, K. Rabaey, W. Verstraete, Open air biocathode enables effective electricity generation with microbial fuel cells, Environ. Sci. Technol. 41 (2007) 7564–7569, https://doi.org/10.1021/es0709831.
[20] Y. Zhao, Y. Ma, T. Li, Z. Dong, Y. Wang, Modification of carbon felt anodes using double-oxidant HNO3/H2O2 for application in microbial fuel cells, RSC Adv. 8 (2018) 2059–2064, https://doi.org/10.1039/c7ra12923h.
[21] Thermo Fisher Scientific Quotation- Web Date 31 Oct 2021, ALFA AESAR WEB QUOTATION, 2021.
[22] X.A. Walter, J. Greenman, I. Ieropoulos, Binder materials for the cathodes applied to self-stratifying membraneless microbial fuel cell, Bioelectrochemistry (2018), https://doi.org/10.1016/j.bioelechem.2018.04.011.
[23] W. Yang, W. He, F. Zhang, M.A. Hickner, B.E. Logan, Single-Step fabrication using a phase inversion method of poly(vinylidene fluoride) (PVDF) activated carbon air

cathodes for microbial fuel cells, Environ. Sci. Technol. Lett. 1 (2014) 416–420, https://doi.org/10.1021/ez5002769.
[24] B. Neethu, G.D. Bhowmick, M.M. Ghangrekar, Improving performance of microbial fuel cell by enhanced bacterial-anode interaction using sludge immobilized beads with activated carbon, Process Saf. Environ. Prot. 143 (2020) 285–292, https://doi.org/10.1016/j.psep.2020.06.043.
[25] G. Zhao, Z. Wang, C. Wei, H. Zhao, Y. Wu, Y. Fu, J. Yang, Effect of CaCl2 and glycerol on response performance of biological gel electric actuator, Mater. Res. Express 5 (2018), https://doi.org/10.1088/2053-1591/aac809.
[26] Z. He, S.D. Minteer, L.T. Angenent, Electricity generation from artificial wastewater using an upflow microbial fuel cell, Environ. Sci. Technol. 39 (2005) 5262–5267, https://doi.org/10.1021/es0502876.
[27] L.T. Angenent, S. Sung, Development of anaerobic migrating blanket reactor (AMBR), a novel anaerobic treatment system, Water Res. 35 (2001) 1739–1747, https://doi.org/10.1016/S0043-1354(00)00447-4.
[28] S. Choudhury, S. Roy, G. Bhattacharya, S. Fishlock, S. Deshmukh, S. Bhowmick, J. McLaughlign, S.S. Roy, Potentiometric ion-selective sensors based on UV-ozone irradiated laser-induced graphene electrode, Electrochim. Acta 387 (2021), 138341, https://doi.org/10.1016/j.electacta.2021.138341.
[29] J. Li, H. Li, J. Zheng, L. Zhang, Q. Fu, X. Zhu, Q. Liao, Response of anodic biofilm and the performance of microbial fuel cells to different discharging current densities, Bioresour. Technol. 233 (2017) 1–6, https://doi.org/10.1016/j.biortech.2017.02.083.
[30] V.J. Watson, B.E. Logan, Analysis of polarization methods for elimination of power overshoot in microbial fuel cells, Electrochem. Commun. 13 (1) (2017) 54–56.
[31] I. Gajda, O. Obata, M.J. Salar-Garcia, J. Greenman, I.A. Ieropoulos, Long-term biopower of ceramic microbial fuel cells in individual and stacked configurations, Bioelectrochemistry 133 (2020), 107459, 2020.
[32] P. Choudhury, B. Bhunia, T.K. Bandyopadhyay, R.N. Ray, The overall performance improvement of microbial fuel cells connected in series with dairy wastewater treatment, J. Electrochem. Sci. Technol 12 (1) (2021) 101–111.
[33] S.V. Mohan, G. Mohanakrishna, G. Velvizhi, V.L. Babu, P.N. Sarma, Bio-catalyzed electrochemical treatment of real field dairy wastewater with simultaneous power generation, Biochem. Eng. J. 51 (1–2) (2010) 32–39.
[34] K.J. Yoon, P. Zink, S. Gopalan, U.B. Pal, Polarization measurements on single-step co-fired solid oxide fuel cells (SOFCs), J. Power Sources 172 (1) (2007) 39–49, 2007.
[35] F. Harnisch, S. Freguia, A basic tutorial on cyclic voltammetry for the investigation of electroactive microbial biofilms, Chem. Asian J. 7 (3) (2012) 466–475.
[36] E. Marsili, J.B. Rollefson, D.B. Baron, R.M. Hozalski, D.R. Bond, Microbial biofilm voltammetry: direct electrochemical characterization of catalytic electrode-attached biofilms, Appl. Environ. Microbiol. 74 (23) (2008) 7329–7337.
[37] M.Á. López Zavala, O.I. Gonzalez Pena, H. Cabral Ruelas, C. Delgado Mena, M. Guizani, Use of cyclic voltammetry to describe the electrochemical behavior of a dual-chamber microbial fuel cell, Energies 12 (18) (2019) 3532.
[38] A. Nandy, M. Sharma, S.V. Venkatesan, N. Taylor, L. Gieg, V. Thangadurai, Comparative evaluation of coated and non-coated carbon electrodes in a microbial fuel cell for treatment of municipal sludge, Energies 12 (2019), https://doi.org/10.3390/en12061034.
[39] D. Paul, M.T. Noori, P.P. Rajesh, M.M. Ghangrekar, A. Mitra, Modification of carbon felt anode with graphene oxide-zeolite composite for enhancing the performance of microbial fuel cell, Sustain. Energy Technol. Assessments 26 (2018) 77–82, https://doi.org/10.1016/j.seta.2017.10.001.
[40] Z. Lv, D. Xie, X. Yue, C. Feng, C. Wei, Ruthenium oxide-coated carbon felt electrode: a highly active anode for microbial fuel cell applications, J. Power Sources 210 (2012) 26–31, https://doi.org/10.1016/j.jpowsour.2012.02.109.
[41] U. Mardiana, C. Innocent, H. Jarrar, M. Cretin, Buchari, S. Gandasasmita, Electropolymerized neutral red as redox mediator for yeast fuel cell, Int. J. Electrochem. Sci. 10 (2015) 8886–8898.
[42] L. Fu, S.J. You, G. quan Zhang, F.L. Yang, X. Fang, Hong Degradation of azo dyes using in-situ Fenton reaction incorporated into H2O2-producing microbial fuel cell, Chem. Eng. J. 160 (2010) 164–169, https://doi.org/10.1016/j.cej.2010.03.032.
[43] M. Kim, Y.E. Song, S. Li, J.R. Kim, Microwave-treated expandable graphite granule for enhancing the bioelectricity generation of microbial fuel cells, J. Electrochem. Sci. Technol. 12 (2021) 297–301, https://doi.org/10.33961/jecst.2020.01739.
[44] P. Clauwaert, K. Rabaey, P. Aelterman, L. De Schamphelaire, T.H. Pham, P. Boeckx, N. Boon, W. Verstraete, Biological denitrification in microbial fuel cells, Environ. Sci. Technol. 41 (2007) 3354–3360, https://doi.org/10.1021/es062580r.
[45] Y. Mu, K. Rabaey, R.A. Rozendal, Z. Yuan, J. Keller, Decolorization of azo dyes in bioelectrochemical systems, Environ. Sci. Technol. 43 (2009) 5137–5143, https://doi.org/10.1021/es900057f.
[46] B. Zhang, C. Feng, J. Ni, J. Zhang, W. Huang, Simultaneous reduction of vanadium (V) and chromium (VI) with enhanced energy recovery based on microbial fuel cell technology, J. Power Sources 204 (2012) 34–39, https://doi.org/10.1016/j.jpowsour.2012.01.013.
[47] Y. Yuan, T. Liu, P. Fu, J. Tang, S. Zhou, Conversion of sewage sludge into high-performance bifunctional electrode materials for microbial energy harvesting, J. Mater. Chem. A 3 (2015) 8475–8482, https://doi.org/10.1039/c5ta00458f.
[48] T. Karuppiah, U. Uthirakrishnan, S.V. Sivakumar, S. Authilingam, J. Arun, R. Sivaramakrishnan, A. Pugazhendhi, Processing of electroplating industry wastewater through dual chambered microbial fuel cells (MFC) for simultaneous treatment of wastewater and green fuel production, Int. J. Hydrogen Energy 47 (88) (2022) 37569–37576.
[49] P. Theodosiou, J. Greenman, I.A. Ieropoulos, Developing 3D-printable cathode electrode for monolithically printed microbial fuel cells (MFCs), Molecules 25 (2020), https://doi.org/10.3390/molecules25163635.