Power generation and organics removal from wastewater using activated carbon nanofiber (ACNF) microbial fuel cells (MFCs)

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1. Introduction

Bioenergy is a renewable energy derived from biological sources. Production usually involves various biological processing strategies, primarily from biomass and organic contaminants associated with wastewaters. The most extensively studied bio-electrochemical system (BES) for generating electricity is the microbial fuel cells (MFCs), which is an innovative technology exploiting anaerobic bacteria to generate electricity from wastewater [1–7] and the organic matters stored in marine sediments [1,8]. MFCs hold a great capability to address the escalating concerns of energy demands and sustenance of current water infrastructure. The power generation in an MFC system is dependent on both...
biological and electrochemical processes. In the anode compartment, anaerobic bacteria degrade organic substances in wastewater and transfer the electrons to the anode surface. The electrons then flow through an external electrical circuit and combine with an electron acceptor (e.g., oxygen) at the cathode, and electricity is generated [6–9]. The driving force for the power generation process in MFCs is extracellular electron transport from the anode to the cathode conducted by anaerobic exoelectrogenic bacteria [10,11]. The MFC technology has multiple advantages of power production and simultaneous treatment of wastewaters along with sludge minimization [5–8]. Prior to the application of MFCs in wastewater treatment plants, the critical issues of low power density and the high cost of electrode materials need to be resolved.

Electron transfer from the biofilms to the anode is critical for contaminant removal and electricity generation in MFCs [12]. Electron transfer can occur directly via extracellular redox cofactors (e.g., c type cytochromes) and nanowires [13,14], or through soluble redox mediators [9]. Biofilm formation on the anode surfaces is governed by different factors including: substratum conditions, hydrodynamic characteristics of the aqueous medium and cell surface properties [15]. Previous studies have indicated the importance of large anode surface area to achieve high power generation [16,17]. Ideally, a greater extent of bacterial adhesion should assist in a higher transfer of electrons to the anode. However, due to the presence of diverse microbial consortia in wastewater, uncontrolled microbial growth could result in competition for the available organic substrates by non-electrogenic bacteria, which divert the MFC systems away from useful power generation [6,18]. Therefore, it is important to achieve optimal biofilm growth on anode surfaces for effective contaminant degradation, high bacterial electron transfer capacity, and power generation.

Extensive studies have been conducted to explore novel anode materials to enhance electron transfer and biofilm formation [5,15]. The anode materials need to be highly conductive, chemically stable, biocompatibility, with high ratios of surface area to volume, and a porous structure to allow internal colonization of microbial biofilms for a stronger interaction with the anode material [6–8,19,20]. Diverse carbon-based anode materials have been investigated for application in MFC systems, including plain graphite, carbon paper, carbon cloth (CC), reticulated vitreous carbon (RVC), granular activated carbon (GAC), and graphite granules [18,21–24]. CC type woven materials have been limited by their thick structures and small surface areas, which result in high electron transport resistance. GAC has higher surface areas than CC, but has the problem of poor granular interconnectivity and inefficient usage of their porous structure for biofilm growth. This caused the problems of diffusional limitations that severely affected the biofilm kinetics [5,23,25]. Most importantly, these carbon-based anode materials are normally expensive, and have high resistances for mass transfer and electron transfer, which hinder the scale up applications of MFCs [18].

Carbon-based nanofiber material could be the next stage of anode materials with enhanced electron transfer capabilities, owing to their high porosities and specific surface areas, high-temperature tolerance, and good electrical and thermal conductivity. Currently, nanofiber materials are being used in drug delivery systems, high-temperature filters and catalysts, nanoelectronics, and supercapacitors/batteries [19,26,27]. Polycrylonitrile (PAN) based electrospinning technique is a simple, effective and inexpensive technique to produce the electrospun nonwoven carbon nanofibers with a high carbon yield and thermally stable structure [26,27]. The production of electrospun nanofibers also involves the stabilization and carbonization with heat treatment to activate the nanofibers for better surface properties [26,28].

The objective of this study was to employ activated carbon nanofibers (ACNF) as the novel anode material in MFC systems. Compared with other activated carbon materials, the unique features of ACNF are its mesoporous structure, excellent porous interconnectivity, and high bioavailable surface area for biofilm growth and electron transfer. The performance of ACNF was compared with two commonly-used anodes: granular activated carbon (GAC) and carbon cloth (CC). Three aspects were analyzed in this study: the extent of bacterial adhesion on each anode, their performance in MFC systems and finally, the contaminant removal and Coulombic efficiency (CE) of the three anodes were compared.

2. Materials and methods

2.1. Anode materials

Three anode materials with different morphologies were examined in this study. The first anode was carbon cloth (CC; non-wet proofed, Fuel Cell Earth; geometric area: 16 cm²), which has been widely used in MFCs [6–8]. The second was granular activated carbon (GAC, mesh size: 8 × 30, General Carbon, Paterson; anode working volume: 30 mL), which has been used in MFCs due to its high specific and interfacial surface areas [18]. GAC particles (diameter: 0.5–2 mm) were packed into a polypropylene mesh bag (length: 2.5 cm; width: 2.25 cm) to maintain a consistent distance to cathode. The third anode was activated carbon nanofibers (ACNF, geometric area: 16 cm²). This novel material was fabricated by heat-treatment of electrospun polycrylonitrile precursor and steam activation to produce carbon nanofibers in a nonwoven architecture [26,28,29]. Due to the light-weight of ACNF, it was sandwiched in a polypropylene mesh bag with the dimensions proportional to their geometric area in order to maintain its mechanic integrity and keep it fully submerged in MFC solution. Supporting information on the anode material construction is shown in Table 1.

2.2. Physical characterization of anode materials

Specific surface area (SSA) and pore size distributions of the anode materials were measured using ASAP 2020 Physisorption Analyzer (Micromeritics Instrument Corporation). Brunauer–Emmett–Teller (BET) model adsorption isotherms technique [30], owing to its easy of applicability, was employed for estimating the SSA. Barrett–Joyner–Halenda (BJH) model, which had been used for estimating the broad size distributions of medium to large mesopores [31], was employed for
estimating the pore size distribution of the anode materials. The specific conductivities of the anode materials were estimated based on the resistance measurements using electrochemical impedance spectroscopy (EIS) [24].

2.3. Single chamber MFC (SCMFC) setup and operation

Batch-mode single chamber MFCs (SCMFCs: effective working volume: 100 mL) were made with glass bottles (Wheaton Scientific) for use in this study. SCMFCs eliminated the proton exchange membrane (PEM) used in two-chamber MFCs. This lowered the internal resistance (R_int), and directly used oxygen present in air as the electron acceptor in the cathode [7]. The anode to be tested was placed inside the bottle, and the cathode (carbon cloth, 30% wet proofing, Fuel Cell Earth, MA; geometric area: 3 cm²) was placed in the extension arm of the bottle. The anode–cathode distance was maintained at 4 cm in all SCMFCs tested. The waterside of the cathode contacting with the solution in the SCMFCs was doped with platinum (10% by weight on carbon black) (0.5 mg/cm²), while the airside of the cathode was coated with 3 layers of polytetrafluoroethylene (PTFE) to prevent water seepage and evaporation from the anode chamber to air. The airside of the cathode only permits limited diffusion of oxygen to complete the reduction half reaction and generate a potential for MFCs.

The influent wastewater to the University of Connecticut Wastewater Treatment Plant that contained diverse anaerobic bacteria was used as inocula in the anode chamber. The wastewater had an initial chemical oxygen demand (COD) of 250–300 mg/L and a pH of 7–8. Sodium acetate was added to the wastewater as supplemental organic substrate to achieve the desired initial COD concentrations (1500–3000 mg/L) and stabilize pH (pKa 9.25) in the SCMFCs. The SCMFC reactors were thoroughly shaken after the addition of sodium acetate to ensure the uniform mixing of organic substrates in solution. The voltage over an external resistance (R_ext) of 100 Ω was recorded by a data log system (Keithley 2700) at intervals of 2 h. All analysis was conducted in duplicate SCMFCs which were operated at 30 °C in an incubator.

2.4. Bacterial adhesion analysis of anode material

Bacterial adhesion on the anode materials was qualitatively observed using a field emission scanning electron microscope (FE-SEM) (Model: Joel 6335F). After 5 weeks of SCMFC operation, a small section of the anode material (0.25 cm²) was cut out and later fixed in a solution containing 2.5% paraformaldehyde, 1.5% glutaraldehyde and 0.1 M cacodylate buffer solution at 4 °C for 12 h. The samples were then triple washed in the buffer solution, followed by stepwise dehydration in a series of ethanol/water dilutions (volume proportions: 25, 50, 75, 95 and 100%) for 15 min each [32]. Subsequently, the samples were dried in a drying oven at 30 °C and sputtered with gold at 2.2 kV and 10 mA for 30 s before SEM observation.

Optical density (OD) and viable colony forming unit (CFU) plate counting measurements were employed to quantify the actual bacterial growth in the anode materials [33]. Two model biofilm strains of Pseudomonas aeruginosa (ATCC-97) and Shewanella oneidensis MR-1 (ATCC-BAA1096) were selected for the SCMFC bacterial growth tests. The anode materials to be tested were grown in the pure culture strains in the Laurie broth (LB) media and shaken at 35 °C for 48 h. The incubated anode materials were then transferred into the sterilized LB media (volume: 10 mL) and sonication for 1–2 min (Branson Sonicator, Model: 3510R-MT, 40 kHz ± 6%) to detach the adhered bacterial cells from the anode surfaces. The OD of the serial diluted solution containing the detached cells was measured at the wavelength of 600 nm (OD₁₅₀₀) using a spectrophotometer (HACH: DR2700). Viable CFU (CFU/mL) of the solution containing the detached cells was performed on LB agar plates using the surface spread method through serial dilution technique [34]. For both OD and CFU tests, sample controls (bacterial cell suspension solution) with only the pure cultures were analyzed to assure the consistency of the procedure. The analysis was conducted under sterile conditions in duplicates.

2.5. Electrochemical characteristics of SCMFCs with different anode materials

The volumetric power densities (W/m³) for SCMFC systems with different anode materials were calculated using the voltage results across different external resistors (R_ext) (46–1500 Ω) applied in the external circuit during the polarization curve measurement. The voltage over each R_ext was recorded by a multimeter (RadioShack, TX) [6,35]. The polarization curves record the current (mA) as a function of voltage [1]. The power and current densities were calculated according to Eqs. (1) and (2).

\[
\text{Power density} = \frac{V^2}{R_{\text{ext}} k}
\]

(1)

\[
\text{Current density} = \frac{V}{R_{\text{ext}} k}
\]

(2)

where V is the voltage across the external resistor (mV), R_ext is the external resistance (Ω), and k is the operating volume (125 mL) of the SCMFCs.

<table>
<thead>
<tr>
<th>Anode</th>
<th>BET SSA (m²/g)</th>
<th>Specific conductivity (S/m)</th>
<th>Mass of anode used (g)</th>
<th>Volume (10⁻³ m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>0.11</td>
<td>333</td>
<td>0.15 ± 0.06</td>
<td>1</td>
</tr>
<tr>
<td>GAC</td>
<td>843</td>
<td>748e</td>
<td>12.00 ± 0.93</td>
<td>40</td>
</tr>
<tr>
<td>ACNF</td>
<td>1159</td>
<td>19</td>
<td>0.04 ± 0.01</td>
<td>0.002</td>
</tr>
</tbody>
</table>

a BET specific surface area.
b Specific conductivity calculated by EIS.
c Ref. [19,24].
The electrode potential in open circuit conditions, termed as the open circuit potential (OCP) is an indicator of the maximum possible voltage under the operated thermodynamic limits. The electrode OCP was measured using a potentiostat (Gamry Reference 600) [7] with the target electrode (anode or cathode) as the working pole and an Ag/AgCl reference electrode as the counter and reference pole.

The internal resistance (Rin) in an MFC system is the primary source of voltage loss. The Rin for the whole cell was estimated using galvano electrochemical impedance spectroscopy (EIS), with CHI-601C electrochemical workstation (CH Instruments, USA) [24]. Data analysis was performed using EC Lab Software (BioLogic Science Instruments, V9.56) to obtain the Rin of SCMFCs based on impedance plots [36].

Linear sweep voltammetry (LSV) analysis is a powerful approach to study the electron transfer kinetics in MFCs. Specifically, LSV measured the current response at the anode electrode as a function of an applied potential [6,37,38]. The LSV analysis of the anode materials in SCMFCs was performed weekly using a potentiostat (Gamry Reference 600) in a three-electrode electrochemical cell setup, with the current density at the working electrode (anode) being measured, while the potential between the anode electrode and reference electrode (Ag/AgCl) was swept linearly over time under no convection. The platinum spiral was served as the counter pole. A scan rate of 0.1 mV/s, from the anode OCP to the anodic limit.

2.6. Wastewater characterization and Coulombic efficiency (CE) calculation

The chemical oxygen demand (COD) of the substrate was measured using HACH COD vials for high range measurements (0–15,000 mg/L) and a DR 220 spectroscopy (HACH, Loveland, CO, USA) according to the HACH analysis protocol.

The Coulombic efficiency (CE, ε) is defined as the ratio of actual charge generated to the maximum theoretical charge attainable (Eq. (3)). It is a critical parameter used to evaluate the performance of an MFC system.

$$\epsilon = \frac{\int_0^t I dt}{\Delta \text{COD} \times \frac{4}{32} F}$$

where $M = 32$ is the molecular weight of oxygen (g/mol), $I$ is the current (mA), $F$ is the Faraday constant (96,485 C/mol), $b = 4$ is the number of electrons exchanged per mole of oxygen, $v$ is the reactor working volume (mL), and ΔCOD is the change in COD concentrations between the influent and effluent streams (mg/L).

3. Results and discussion

3.1. Characterization of the anode materials

The specific surface area (SSA) of the anode materials was analyzed using the BET model. The results showed that CC had the lowest SSA value (0.11 m²/g), GAC had the medium (GAC: 830 m²/g) and ACNF had the highest value (1159 m²/g) (Table 1). The analysis gave an estimate of the SSA available for bacterial adhesion and biofilm growth, with ACNF having the highest surface area as a result of steam activation step. CC anode material pore size distribution is predominantly macropores (>0.3 μm), but the significance of their large pore size was diminished by their low SSA. The BJH analysis of GAC and ACNF anode materials indicated that about 65% of the SSA for GAC had a pore size distribution in the mesoporous range (<0.3 μm), whereas only 35% of the SSA for ACNF was in the mesoporous range, with the remaining primarily being macropores. Since typical bacterial size is about 0.5–3 μm, the pore size distribution greater than 0.3 μm would greatly contribute to the bioavailable surface area for the bacteria to access and colonize. More than half of GAC surface areas were not be accessible by bacterial cells, while the architecture of ACNF could establish an effective biofilm structure where it was easier for microorganisms to access the wastewater nutrients and better transfer electrons.

3.2. Bacterial adhesion analysis on anode materials

The extent of bacterial adhesion varied with the properties of the anode material, as represented in the SEM images (Fig. 1). CC had the lowest surface area (<0.11 m²/g, Table 1) (Fig. 1a), while GAC (~850 m²/g) (Fig. 1b) and ACNF (~1200 m²/g) (Fig. 1c) had much higher surface areas. The interconnected and nonwoven structure of ACNF was expected to promote biofilm growth and enhance electron transport. The SEM images show the extents of biofilm formation on CC (Fig. 1d) and GAC (Fig. 1e) were limited, due to the SSA and BET pore size. On the contrary, a more extensive biofilm formed on ACNF (Fig. 1f), which could be the result of relatively easy diffusion of organic substrates through the material. The random interconnectivity of the ACNF nanofibers enabled more accessibility for biological interactions, which resulted in more widespread biofilm formation.

The biofilm thickness is often limited by the substrate diffusion resistance inside biofilms [39,40]. These diffusion resistances are further increased by the lower pH/redox conditions inside biofilms and the reduced cytochromes on the outer biofilm layers, which may not support additional bacterial layers [39–41]. The substrate transfer resistances could be partially solved in the continuous flow MFCs treating wastewater, since it would enable a constant biofilm thickness and sufficient buffer capability of wastewater to prevent pH decrease.

Microbial biofilm growth quantified on the three anode materials well corresponded with the SEM observations. Indirect spectroscopy measurements (OD600 results, Fig. 2a) and direct viable dilution spread plate count technique (CFU results, Fig. 2b) of the pure culture strains (P. aeruginosa and S. oneidensis MR-1) indicated that ACNF had a higher amount of bacterial biomass than GAC and CC. The OD results demonstrated that a higher amount of biomass attached on the anode materials (ACNF) led to higher turbidity in the cell suspension and higher absorbance values. The log10 normalized, CFU/mL, accounted for the average number of viable bacterial cells.
present in the anode material biofilms, indicating that they were metabolically active. Although these two tests were conducted using pure cell cultures to obtain the clear trend and avoid the interference of mixed cultures and particles in wastewater, it was expected that the same trend could be followed in the MFC systems treating wastewater containing diverse microbial consortia.

3.3. Power generation with different anode materials

The comparison of power density curves showed that SCMFCs with GAC and ACNF as anodes achieved the power density values of $3.09 \pm 0.33 \, \text{W/m}^2$ and $3.5 \pm 0.46 \, \text{W/m}^2$, respectively, while SCMFCs with CC had a lower power density of $1.1 \pm 0.21 \, \text{W/m}^2$ (Fig. 3a). As a biofilm-based process, the power

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**Fig. 1** — Scanning electron microscopy (SEM) images of the anode materials, after 5 week operational period: carbon cloth (CC) (1000×) (a); granular activated carbon (GAC) (2400×) (b); activated carbon nanofibers (ACNF) (6000×), Inset (2400×) (c); CC with biofilm (2400×) (d); GAC with biofilm (2700×) (e); ACNF with biofilm (6000×), Inset (2400×) (f).
generation in MFCs is affected by the interactions between bacterial cells and the anode surface [19,42,43]. Although ACNF qualitatively and quantitatively showed a greater extent of biofilm growth over GAC, which might lead to higher power generation, GAC being more conductive over ACNF (Table 2) served to facilitate lower $R_{in}$ for the SCMFC systems and had power outputs similar to ACNF [44]. CC had low surface areas and less biomass growth, resulting in less electron generation and hence lower power generation.

The polarization curves represent the relation between voltage and current (Fig. 3b). The cell voltage for the current above zero exhibited a steep drop for CC, while maintained a gentle drop for GAC and ACNF. The likely reasons could be: (i) activation overpotentials and the morphology of the anode materials play a vital role in attaining higher voltages over a long range of current values [24]. Overpotential is an essential loss of cell voltage in the form of activation, metabolic and mass transfer losses. In the SCMFCs with three anode
materials to be tested, the determining factor was the electron transfer between the bacteria cells and the anode surfaces, since the proton transport resistance was minimized with pH buffering capacity by replenishing sodium acetate and wastewater at the end of each batch cycle, and (ii) the current densities are a function of the electron generation and the electron transport capacity. Even though the three anode materials had the similar starting points (a high voltage at a low current densities, Fig. 2b), the ACNF exhibited the slower voltage decrease with current increase, perhaps due to a higher electron output. The distinct advantage of ACNF over the other anode materials is the higher bioavailable surface area, which resulted in a more extensive biofilm formation (Fig. 2). This benefit is critical for MFC systems, since an efficient biofilm growth leads to the prominence of electro-active bacteria and the electron transport to the anode electrode [24,45].

Power generation at different stages of biofilm growth on ACNF was also studied. The results showed that the power densities for ACNF increased with biofilm growth on anode surfaces, with $0.9 \pm 0.32 \text{ W/m}^3$ in the 3rd week and increasing to $3.5 \pm 0.46 \text{ W/m}^3$ in the 4th week (Fig. 4a). The increase in power density with biofilm growth was caused by the increased electron transport of the electrogenic bacteria growing on the well-connected ANCF fibers. Previous studies indicated that a higher bioavailable anode surface area could enhance biofilm formation and result in more electron transfer and higher power density generation [43,44,46]. With mature biofilms growing on anode surfaces, the SCMFCs developed stable voltage generation and maintain a steady and linear voltage–current correlation [47]. The benefits of biofilm growth for power generation were also indicated in the polarization curves (Fig. 4b). The voltage of the ACNF with biofilm growth in the 9th week had more stable voltage trend with current changes than the ACNF in the 3rd week, which is concurrent with previous studies [37,48].

### 3.4. Electrochemical characteristics of SCMFCs with different anode materials

The electrochemical characteristics for SCMFC systems with these three anode materials were compared (Table 2). In an MFC system, a greater difference between the negative anodic potential and the positive cathode potential leads to a higher power generation. A higher anode potential implies electrons are likely to be consumed by alternate electron acceptors, indicating that the bacteria do not use the anode and lower energy recovery for the MFC system [5]. Thereby, the anode potential should be lower in conjunction with the anaerobic environment and the generation of negative charges (electrons) by the degradation of the organic substrates in wastewater [6,9].

### Table 2 – OCP, internal resistance ($R_{in}$), COD removal, and Coulombic efficiencies (CE) of three anodes. Mean data for duplicate MFC systems operated under similar conditions with standard deviation, after 9 week operational period.

<table>
<thead>
<tr>
<th>Anode</th>
<th>Anodic potential vs. Ag/AgCl (mV)</th>
<th>Internal resistance ($R_{in}$) (Ω)</th>
<th>COD removal efficiency (%)</th>
<th>Coulombic efficiency (CE, %)</th>
<th>Peak power densities (W/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC</td>
<td>$-460 \pm 8$</td>
<td>$65 \pm 13$</td>
<td>$70 \pm 2$</td>
<td>$11 \pm 1$</td>
<td>$1.10 \pm 0.21$</td>
</tr>
<tr>
<td>GAC</td>
<td>$-480 \pm 13$</td>
<td>$50 \pm 17$</td>
<td>$75 \pm 5$</td>
<td>$15 \pm 4$</td>
<td>$3.09 \pm 0.33$</td>
</tr>
<tr>
<td>ACNF</td>
<td>$-495 \pm 10$</td>
<td>$103 \pm 8$</td>
<td>$85 \pm 4$</td>
<td>$8 \pm 2$</td>
<td>$3.50 \pm 0.46$</td>
</tr>
</tbody>
</table>

**Fig. 4** – Power generation (a), and polarization curves (b) for ACNF during the operational periods (Week 3–Week 9). Mean values (standard deviation not included) of two independent runs, performed on duplicate MFC systems operated under similar conditions.
The anode OCP (the maximum voltage that can be obtained at infinite resistance) varied between −450 and −500 mV for the three materials, with ACNF having the most negative value. The results indicated that ACNF had the lowest anodic OCP (−495 ± 10 mV), followed closely by GAC (−480 ± 13 mV), and CC exhibited the highest OCP (−460 ± 8 mV). The difference in anodic OCP was predominantly a function of the anode materials, the microbial communities inside biofilms, and the biofilm thickness. Since most anaerobic microorganisms rely on similar electron transport chains for their metabolic requirements, reduced form of electron carriers (e.g. NADH) were generated when these microorganisms degrade the organic substrates [5,9,24]. The accumulation of these reductive byproducts in biofilms caused the decrease in the anodic potential.

The \( R_n \) in an MFC can be attributed to three major components: charge transfer activation (or kinetic losses), ion and electron transport (or Ohmic losses), and substrate concentration (or mass transfer losses) [8,24,36]. Given that bacterial metabolic losses are inevitable, the activation and mass transfer losses at the electrode can be reduced by changing electrode morphological properties and by enhancing substrate flux to the electrode surface. The \( R_n \) as estimated from EIS (Table 2) for the whole SCMFCs indicated that \( R_n \) of the SCMFC with ACNF was higher (103 ± 8 \( \Omega \)) (Table 2) than those of GAC (50 ± 17 \( \Omega \)) and CC (65 ± 13 \( \Omega \)), even as ACNF demonstrated more biofilm growth and lower negative anodic OCP. This may be explained based on the EIS specific conductivity (S/m) measurements, where ACNF showed lower conductivity (19 S/m) than CC (333 S/m) and GAC (748 S/m) [19] (Table 1). The low conductivity of ACNF could be ascribed to the activation process during fabrication. Although all the anodes tested have the same carbon-based material, the steam activation step essentially hydrophilized the ACNF material, which may have resulted in the addition of some hydroxyl (OH\(^-\)) groups to the nanofibers and given it an overall negative surface charge [49–51]. Other studies have indicated the importance of surface modifications to promote biofilm adhesion and enhance performance of MFCs [18,52], which could be employed for further enhancing the ACNF conductivity. Despite the lower conductivity of ACNF, its performance was better than that of GAC and CC.

The anode polarization results clearly showed that anodes had a significant influence on the SCMFC performance (Fig. 5), while the cathode polarizations (not shown) were similar for all the SCMFCs tested, since the cathode structure, size and configuration were the same for all the SCMFCs tested. The LSV polarization scans of the anode material after the 5-week operational period indicated that ACNF superseded CC and GAC as the anode material. The scan started at the cell potential under open circuit conditions, and then was carried out from left to right of the current density and potential plot, the anode potentials were corrected for \( R_n \) obtained from EIS measurements. The current density increased linearly with the potential at low overpotentials, and then increased more rapidly at higher potential and reached a maximum stationary region before it began to drop. This current increase under voltage sweep from its initial electrochemical kinetic equilibrium region was a function of the availability of organic substrates and the reactivity for electron transfer. The region of stationary current was influenced by the diffusional limitations for the substrate mass transport to the electrode surface, as a result of the microbial biofilm growth. Thereby, the flux of the organic substrates was not fast enough to satisfy the Nernstian conditions, and was dominated by mass transfer [53–55]. The LSV curves showed that ACNF reached the diffusional limited current region much later than GAC and CC (Fig. 5), and corresponded with the results obtained at the fixed \( R_{\text{ext}} \) (Fig. 3b) [56]. This ascertained our hypothesis that the novel architecture of ACNF promoted a better biofilm growth and an efficient substrate transfer on ACNF surfaces to achieve higher power densities. However, the power generation of SCMFCs with ACNF as the anode was only 20–40% higher than those with CC and GAC as anodes. The possible reason could

![Fig. 5 — Linear sweep voltammetry (LSV) scans for the anode materials (ACNF, GAC, and CC) after 5-week operational period. Mean values (standard deviation not included) of two independent runs, performed on duplicate MFC systems operated under similar conditions.](image)
be the heterogeneity of electronic active biofilms, which were composed of more or less active fractions of microbial consortia and their distance from the electrode surfaces. This reveals that novel MFC configurations should be developed to fully bring out the advantages of ACNF as anodes.

3.5. COD removal with different anode materials

The SCMFCs with ACNF exhibited higher COD removal efficiency (85 ± 4%) than those of GAC (75 ± 5%) and CC (70 ± 2%) (Table 2). Previous studies using carbon-based electrodes (such as CC and GAC) had the COD removal efficiencies of 65–75% [38,41,43]. ACNF had a better performance due to the good contact between the biofilms and the nanofiber network, which resulted in the better access of the organic substances to the microbial consortium and more efficient degradation.

The SCMFCs with the ACNF had lower CE values (8 ± 2%) than those with GAC (15 ± 4%) and CC (11 ± 1%) (Table 2). CE and COD removal are inversely related (Eq. (3)). Previous studies showed that higher COD removal efficiencies (%) and lower CE values (%) were potentially caused by the consumption of organic substrates by non-electrogenic bacteria which divert the electron flow toward other metabolic processes [39,41,42,56], so that electrogenic bacteria were unable to effectively obtain organic substrates. The high COD removal efficiency with relatively higher power densities but lower CE values of ACNF might indicate that even though organic substrates were degraded in the wastewater by the microbial communities including methanogens and fermentative microorganisms [25], the presence of electrogenic microorganisms was constrained. It can be attributed to the fact that domestic wastewater in the anode compartment is heterogeneous in chemical composition and comprise diverse microbial consortia, where numerous biochemical reactions govern the bacterial metabolic pathways [25,40,42]. The relationship between COD removal and CE values is of potential significance for further research, since the degradation of organic substrates in MFCs is a biochemical process dependent on microbial consortia, biofilm growth, and functioning.

4. Conclusions

This study compared the three anode materials (ACNF, GAC and CC) with different morphologies, in terms of power generation and COD removal in MFCs. As a good biofilm support material, ACNF possessed high bioavailable surface area and an interconnected network, which substantially reduced the mass transfer resistance and in turn enhanced electron transport. The results clearly demonstrated the distinct advantages of ACNF for biofilm growth, power generation, and COD removal. The significant findings include (i) higher extents of biofilm growth on ACNF than GAC and CC; (ii) higher power densities for ACNF and GAC than CC; and (iii) higher COD removal efficiency for ACNF than that of GAC and CC. Overall, the performance of ACNF as an MFC anode in comparison to the other anode substrates has shown a potential to develop and upscale novel MFC systems for treating wastewaters.

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References


