Bioelectrochemical performance of microbial fuel cell powered electro-Fenton system (MFCⓅEFs) with composite PANI-Mn/CF anode

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ABSTRACT
Microbial fuel cell powered electro-Fenton system (MFCⓅEFs) is a self-sustainable energy conversion process to degrade refractory pollutants utilizing green biomass energy. Most previous works usually employed innovative cathode to minimize electron transfer losses but neglected the development of high-efficiency anode to enhance electron generation. The synergy of polyaniline (PANI) and MnO₂ on electrode could improve charge accessibility and facilitate rapid electron transfer due to its superior conductivity and capacitance, which had not been applied to MFCⓅEFs as anode so far. In this study, a PANI-Mn/C (carbon fiber loaded with polyaniline and MnO₂) composite anode was introduced into MFCⓅEFs to enhance interface activity and realize more efficient electricity generation and pollutant degradation. Experimental results showed that a higher power density (5.49 times that of the original CF) and lower ohmic resistance (7.17 Ω) occurred in the MFCⓅEFs with PANI-Mn/CF anode, which consumed more sewage sludge (37.14% of TCOD removal), leading to achieving more effective pollutant degradation (93.03% of tetracycline hydrochloride removal). Overall, this study provided an innovative way of thinking and approach to efficient utilization of biomass waste and degradation of refractory pollutants with the merits of environmental sustainability.

Keywords: In-situ electricity utilization, MFC-powered EF, PANI-Mn/CF composite anode, Sludge biomass recovery, Waste-to-energy conversion technology

Graphical Abstract

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1. Introduction

In recent years, microbial fuel cell powered electro-Fenton system (MFC\(\text{\textregistered}\)EFs) has garnered a growing amount of attention and developed as an ecologically friendly sustainable energy conversion technology capable of resource recovery and utilization [1-3]. The bio-electro-chemical reaction takes place in the anodic chamber of MFC\(\text{\textregistered}\)EFs, and electrochemically active bacteria oxidize organic substrates to generate bio-electrons and protons, which are transferred to the cathodic chamber via the external circuit and the proton exchange membrane, respectively [4-6], completing the conversion of biomass energy to electricity. The electro-Fenton oxidation reaction occurs in the cathodic chamber, and the electrons transferred from the anode are used to drive oxygen reduction to generate \(\text{H}_2\text{O}_2\) [Eq. 1], which can react with \(\text{Fe}^{2+}\) in situ to generate \(\cdot\text{OH}\) [Eq. 2] to oxidize organic matter in wastewater and complete the efficient utilization of the generated electricity [7-9]. Various types of wastewater can be used to generate electricity, such as slaughtering wastewater [10], landfill leachate [11], herbal wastewater [12], seawater brine, and industrial brine (saline wastewater) [13-15], and so on. Among them, sewage sludge can be utilized as an excellent biomass resource to generate electricity while self-degrading due to its rich organic matter [16,17]. Simultaneously, the MFC\(\text{\textregistered}\)EFs can use the electricity to directly treat various wastewater, including antibiotic wastewater [18], dye wastewater [19], coal gasification wastewater [20], and high salinity seawater [21], completing deep degradation to further purify water quality. MFC\(\text{\textregistered}\)EFs has evolved into a self-sustaining renewable bioenergy technology due to its ability to convert wastes (such as excess sludge from wastewater treatment plants) into clean energy that may be used to treat refractory organics (such as antibiotic wastewater) in situ.

\[
\text{O}_2+2\text{H}^++2e^\rightarrow\text{H}_2\text{O}_2 \\
\text{H}_2\text{O}_2+\text{Fe}^{2+}\rightarrow\cdot\text{OH}+\text{Fe}^{3+}+\text{OH}^- \tag{2}
\]

Despite owning a number of advantages, such as no additional external power supply required, in-situ generation of \(\text{H}_2\text{O}_2\), and mild operating conditions [22], there are still some constraints that need to be addressed. The primary limiting factors for high-efficiency electricity generation are the formation of high-efficiency external electrical biofilms and a decrease in electron transfer loss [23,24], which lead to stricter operating conditions and limited application and development. To improve the system performance, previous studies typically focused on the preparation of novel cathodes with high catalytic performance [25,26], optimization of operating modes and circuit conditions [27], coupling to other advanced oxidation processes [28], replacement of anode substrates, and directional culture inoculum [29]. Wang et al. [30] synthesized a novel Fe–Mn–Mg/CF cathode by utilizing the excellent polymerization function of Mg, Fe, and Mn, which promoted the generation of reactive oxide products (\(\cdot\text{OH}\) and \(\text{O}_2\)). Ernestien et al. [31] verified that a higher norfloxacin (NOR) removal rate could be obtained if marine sludge was inoculated with \(\text{Fe}_3\text{O}_4\) composite electrode. As the key to electron transfer, the correct selection of electrode materials is the primary critical aspect of successfully constructing MFC\(\text{\textregistered}\)EFs among these improvement measures [32]. Because it provides essential surface area for microbial growth and serves as a source of electron circulation, the anode is a crucial component of bio-electrochemical system. Nevertheless, the majority of previous studies only paid more attention to cathode materials when constructing MFC\(\text{\textregistered}\)EFs, and merely a few investigated the influence of anode electrode properties on the performance of bioelectrochemistry system.

Manganese (Mn) has been actively explored as a catalyst and electrode material because of low cost, outstanding environmental compatibility, and high theoretical capacitance of its oxides [33,34]. Its poor electrical conductivity is the major drawback for a range of applications [35,36]. In this respect, many attempts have been made by coupling with other substances to play synergistic roles, such as metal elements and carbonaceous materials [37]. Mn was frequently coupled to conducting polymers because of their excellent electrical conductivity, which improved their poor cycle stability and low electrochemical capacitance [38-40]. Conducting polymers such as polyaniline (PANI) and Mn composite electrodes are commonly employed as supercapacitors, capacitive air cathodes, and bioanodes to ameliorate the mismatch between MFC power generation and demand. The fibrous PANI-MnO\(_2\) nanocomposites prepared by Sajid et al. [41] provided a high surface area for the contacts of electrode/electrolyte and electronic conduction channels, as well as exhibited pseudocapacitive behavior, which ultimately resulted in a 0.0588 W/m\(^2\) increase in power density. However, Mn-containing composite anodes have never been applied to MFC\(\text{\textregistered}\)EFs to improve the electricity generation performance and complete the efficient degradation of target pollutants. In this study, high-performance and low-cost Mn was coupled with conductive polymer PANI on carbon fiber (CF) anode in an attempt to recover and utilize more electrical energy from waste.

Based on the above, this study constructed a MFC\(\text{\textregistered}\)EFs introducing PANI-Mn/CF composite electrode as anode to simultaneously improve the performance of electricity generation and in-situ utilization to degrade target pollutants. The objective and scope were: (1) to analyze the electrochemical and structural characteristics of PANI-Mn/CF; (2) to investigate the effect of PANI-Mn/CF composite anode on the performance of system electricity generation; (3) to assess the utilization and generation of bioelectricity in systems with different anodes; and (4) to evaluate the advantages of MFC\(\text{\textregistered}\)EFs in terms of energy consumption.
2. Materials and Methods

2.1. Preparation of the Composite PANI-Mn/CF Anode

The composite PANI-Mn/CF anode was fabricated as follows: the MnO2 layer was firstly deposited on the carbon fiber (CF) brush by electrochemical method. Electrochemical deposition of the MnO2 layer was operated in a three-electrode system in a mixed solution containing 0.1 mol/L MnSO4 and 0.01 mol/L Na2SO4 with a continuous voltage of 1 V for 2000 s, with CF as the working electrode, platinum plate as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. The sample was rinsed and dried at 80 °C for 10 h and used as a substrate for the overlay of PANI. The PANI electrode was fabricated as follows: the MnO2/CF prepared was submerged into 50 mL 1 mol/L Na2SO4 (with supporting electrolyte solution 0.1mol/L APS in 50 mL of 1 mol/L HCl), was added drop-wise to the mixture slowly, and then kept shielded from light for 12 h. The CF was dried at 60 °C for 10 h to obtain the PANI-Mn/CF composite anode. The PANI/CF composite anode was prepared by the same method without depositing the MnO2 layer.

2.2. Configuration and Operation of the MFC-EFs

The MFC-EFs reactor containing two chambers was constructed with plexiglass. The anode chamber (Φ160 mm×80 mm, 1440 mL) equipped with Ag/AgCl electrode (+0.195V vs. SHE) and the cathode chamber (80 mm×80 mm×80 mm,512 mL) were separated with proton exchange membrane (PEM, Nafion 117, DuPont) to increase H+ diffusion. The two electrodes were connected via a copper wire by passing through a variable external resistor.

In the start-up phase, the anode chambers were inoculated with excess sludge obtained from the anaerobic tank of a municipal wastewater treatment plant (Harbin, China) to enrich bacterial consortia, the cathode chambers were filled with solution containing potassium ferricyanide, and connected through the 1000 Ω resistor. All anode were original CF, PANI/CF, and PANI-Mn/CF, while only CF was placed in the cathode anode chamber, respectively. The system was started up successfully once a stable voltage had been achieved.

In the experimental phase, the cathode chamber was employed to treat antibiotic wastewater (tetracycline hydrochloride, TC), with FeMnOx/CF composite electrodes being transferred as cathodes to strengthen electron-Fenton (EF) process. The operating settings were based on earlier research [42]: an initial concentration of the target pollutant (TC) was 40 mg/L (with supporting electrolyte solution 0.1mol/L Na2SO4) and the pH was adjusted to 3 with H2SO4 solution and an aerator was placed in the cathode chamber to provide sufficient oxygen supply. FeMnOx/CF was fabricated using a previously reported method [43]. All experiments were performed in triplicate.

2.3. Methods and Analysis

2.3.1. Characterizations and Measurements

Scan electron microscopy (SEM) (Zeiss, Gemini SEM 500, Germany) and Optical contact angle & interface tension meter (SL150, SOLON TECH, China) were employed to characterize the surface microstructure and degree of hydrophilicity. The element distribution and structure composition were represented by Energy dispersive X-ray detector (EDS) (OXFORD, X-Max, UK) and Fourier infrared spectroscopy (Waltham, MA, USA). Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) were determined using an electrochemical workstation (CHI660E, Chenhua, China) in 0.5 mol/L H2SO4 solution. The Cyclic voltammetry (CV) experiments were studied at a scan rate of 5mV/s over a potential range of -0.1 V to 1 V (vs. SCE), and EIS experiments were carried out in a frequency range from 100 k Hz to 0.01 Hz by applying 5 mV.

2.3.2. Electrochemical Measurements

The output voltage of the system was continuously monitored using a multi-channel voltage collector (PCI1713U, Advantech, Taiwan) and linked to a desktop PC for data display and storage. The current density (I=U/RA) and power density (P=UI) were measured by declining the external resistance from 9000 Ω to 10 Ω gradually, which was normalized to anode chamber volume. CV and chronocoulometry (CA) of the system were tested with a three-electrode system using an electrochemical workstation (CHI660E, Chenhua, China), with the anode as the working electrode, the Ag/AgCl (+0.195 V vs. SHE) electrode as the counter electrode and the cathode as the reference electrode. After open circuit reached steady state, the CV curves were tested at 5 mV/s in a potential range of -0.6 V to 0.2 V. The CA tests investigated capacitance characteristics by causing the anode to discharge by supplying -0.1 V to the system.

2.3.3. Other Chemical Analysis

Tetracycline hydrochloride (TC) was purchased from Aladdin Reagent (Shanghai). Other reagents were analytic grade. TC was used as the target contaminated in cathode chamber to evaluate the micro-electric utilization of the system, and the concentration of cathodic water samples was measured using a TOC analyzer (Shimadzu Co., Japan). Throughout the treatment procedure, UV-Vis absorption spectra (Shimadzu Co., Tokyo, Japan) of the TC solution was performed to analyze TC degradation degree and changes in molecular structure based on variations in absorbance. The H2O2 concentration was determined by the iodination method at 352 nm [41]. The properties of the anode target pollutant sludge including TS, VS, TCOD, and SCOD were determined by standard methods [42], soluble carbohydrates and soluble proteins were measured by the Lowry method and the Phenol-sulphate acid method [43], respectively. VFAs were obtained using a gas chromatograph (GC7890, Agilent, USA) equipped with a hydrogen flame ionization detector and an HP 19095N-123 capillary column.
2.3.4. Analyses of microbial communities
The microorganisms on the anode surface of reactors were taken for DNA extraction, data evaluation and quality control, splicing and assembly, binning and other operations to obtain gene abundance and gene functional annotation. Based on the gene abundance and annotation information, species abundance and functional abundance were obtained. Multi-directional statistical analysis and exploration such as species and functional composition analysis, species and functional difference analysis, and comparative sample analysis were conducted.

2.4. Data Analysis and Calculation
The coulombic efficiency (CE) was calculated as (Eq. 3) for investigating electron utilization.

\[
CE = \frac{M \cdot \int i \, dt}{F \Delta COD} \times 100\% 
\]

(3)

where \( M \) is molecular mass of oxygen (32 g/mol), \( i \) is the current (C/s), \( F \) is Faraday's constant (96485 C/mol), \( Z \) is number of electrons required at the anode (4), \( \Delta COD \) is the removal of COD from substrate to generate electricity (g).

The removal efficiencies of TCOD for sludge in anode chamber and TC in cathode chamber were estimated using (Eq. 4) and (Eq. 5), respectively.

\[
\text{TCOD removal efficiency} = \frac{C_{C0} - C_{Cf}}{C_{C0}} \times 100\% 
\]

(4)

\[
\text{TC removal efficiency} = \frac{C_{T0} - C_{Tf}}{C_{T0}} \times 100\% 
\]

(5)

where \( C_{C0} \) and \( C_{Cf} \) denote the TCOD concentrations before and after sludge degradation in the anodic chamber (mg/L), \( C_{T0} \) and \( C_{Tf} \) were the TC concentrations before and after EF oxidation in the cathodic chamber (mg/L), respectively.

Fig. 1. SEM images of CF (a), PANI/CF (b), PANI-Mn/CF (c); and the EDS images of composite PANI-Mn/CF anode for O (d), N (e), Mn (f).
3. Results and Discussion

3.1. Characterization of PANI-Mn/CF

SEM and contact angle analysis were carried out to clearly characterize the microstructure and hydrophilic properties of the composite anode surface. In contrast to the smooth surface of CF, overlays could be observed on the surface of carbon fiber of PANI/CF and PANI-Mn/CF, which displayed agglomerates adhering to the surface of carbon fiber (Fig. 1a-c). The PANI-Mn/CF electrode had more loadings and formed a tighter cross-linked interface, which reinforced the easily broken chain structure of PANI polymer and facilitated the interaction between electron acceptor and donor [47], thereby making the electron transfer inside the electrode more convenient and stable. Greater specific surface areas allowed for increased interaction between microorganisms and anode [48], forming more attachment sites and dwelling regions for microorganisms. Based on the characterization results of EDS mapping of PANI-Mn/CF (Fig. 1d-f), the homogeneous distribution of O, N, and Mn elements on the surface of the PANI-Mn/CF electrode might suggest the successful loading of PANI and Mn on the carbon brush surface.

PANI loaded on the outermost layer of the electrode made CF appear super hydrophilic (Fig. S1). This result was attributable to the fact that the material surface of PANI with sulfuric acid as doped acid was rich in hydrophilic groups such as carboxyl and sulfonic acid [54], which significantly enhanced the hydrophilic properties of the electrode material and provided a more suitable living and adhesion environment for electrogenic bacteria [49]. Therefore, the composite anode was more conducive to improving the MFC's power production performance.

The chemical composition and molecular structure characteristics of composite anodes were identified with FTIR spectroscopy (Fig. S2). PANI/CF composite anode contained apparent characteristic peaks of PANI at 1562 cm⁻¹ (the aromatic C=C stretching of the quinonoid ring), 1487 cm⁻¹ (the aromatic C=C stretching of the benzenoid ring), 1297 cm⁻¹ (C-N stretching vibration), 1131 cm⁻¹ (the N=Quinoid=N stretching) and 801 cm⁻¹ (C-H in the benzenoid ring), indicating successful coverage of anode with PANI [54]. The new band of PANI-Mn/CF around 597 cm⁻¹ was ascribed to the Mn-O stretching adsorption of MnO₂. Compared with PANI, the corresponding characteristic peaks of PANI-Mn/CF presented the red shift and widening, which was ascribed to the progress of Mn-N coordination bonding between Mn²⁺ and the PANI polymer chain [51]. Low electron density on the main chain of polyaniline was generated by the conjugation interaction, which strengthened the polymer chain and promoted delocalization of conjugated electrons for enhanced electron transport [50].

To fully understand the synergistic effects, electrochemical performances such as CV and EIS were examined (Fig. 2). Obvious redox peaks were observed for the PANI-Mn/CF and PANI/CF, owing to the reversible transition and pseudocapacitive behavior of PANI between oxidized, eigen, and reduced states [52]. However, the stronger peak intensity and larger current response were exhibited in the PANI-Mn/CF composite electrode, while the electron transfer resistance (0.001 Ω) and the double-layer capacitance (70750 μF) (Table. S1) were decreased to near insignificance and distinctly increased, respectively. The results demonstrated that the synergistic impact accelerated the redox reaction on the electrode's surface, boosting electrochemical activity performance, electrode capacitance, and electron storage and transmission. The reduced transfer resistance of the PANI-Mn/CF composite electrode could be attributed to the substitution of O ions in manganese dioxide and the pair of anions in the PANI chain to form conducting holes, a certain amount of electron holes and free electrons caused the polyaniline macromolecular chain to form a certain potential gradient [53], thus promoting electron transfer to reduce internal resistance.

3.2. Electrical Performance of the MFC with PANI-Mn/CF Anode

The variations in biomass electricity generation could be graphically displayed by recording and analyzing the system's
voltage output during the whole process from start-up to steady phase. At beginning of the start-up phase (Fig. S3), the voltage of the systems with PANI-Mn/CF and PANI/CF grew at a similar rate and faster than CF, indicating the rapid proliferation and adhesion of electrogenic bacteria owing to hyper hydrophilic and large surface area [54]. The voltages were stable after around 400 h. The largest average voltage of the system with PANI-Mn/CF achieved 0.74 V, higher than PANI/CF (0.7 V) and CF (0.63 V), demonstrating significant electricity generation. These might be explained by the addition of MnO2 caused electrons to accelerate while passing through the polyaniline molecular chain, hence promoting electron transfer [55]. Compared with the MFC fed with the thermophiles-acidogens pretreated sludge (MFC AB) [56], the systems with PANI-Mn/CF owned higher and more stable voltage output, which evidenced that outstanding electrode materials were the primary factor for efficient system operation.

In order to further evaluate the catalytic activity of the anode and its contribution to electricity generation from the system, the power density curves and polarization curves were compared (Fig. 3). The power density of the MFCs with PANI-Mn/CF anode achieved the maximum (2.14 W/m²) (Fig. 3a), which was 1.98 and 5.49 times higher than the system with PANI/CF (1.22 W/m²) and CF (0.39 W/m²), respectively. Higher open circuit voltage (OCV) usually tends to represent higher electrode activity, and lower ohmic resistance generally means easier electron transfer. The OCVs and the ohmic resistances of the MFCs were in the order of PANI-Mn/CF (0.77 V) > PANI/CF (0.75 V) > CF (0.49 V), and PANI-Mn/CF (7.17 Ω) < PANI/CF (24.75 Ω) < CF (58.05 Ω) (Fig. 3b), respectively. The formation of Mn-N coordination bonds leads to conjugation interactions, which strengthen the molecular chain structure and decrease the electron density of the PANI main chain [57]. The particularly conjugated structure of Mn-N enhances charge accessibility, provides a better channel for ion transport, effectively reduces anode reaction resistance [58], and reduces electron transfer loss. As well-known redox catalysts, the interaction between the modified layer of PANI and MnO2 improves the conductivity of the electrode, increases the active catalytic site [59], and accommodates more microorganisms [60], thereby accelerating the electron transfer kinetics and ultimately resulting in increased power generation.

Electrochemical tests such as CV and CA analyses were performed to further investigate the electron transfer and storage mechanism at the anode interface (Fig. 4). The closed area and

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**Fig. 3.** The power density curve (a) and polarization curves (b) of MFCs with different anodes.

**Fig. 4.** Electrochemical performance of MFCs with different anodes: CV curves at 5 mV/s (a) and CA curves with -0.1 V (b).
peak current of the system with PANI-Mn/CF were larger than those of the other two systems for the CV curve (Fig. 4a), indicating that the PANI-Mn/CF anode owned stronger electron adsorption capacity and redox activity. The PANI-Mn/CF anode covered by electroactive biofilm exhibited an obvious anodic peak centered around -200 mV, attributing to the interaction between cytochrome C proteins [61] and the coating. The varieties thereby facilitated direct electron transfer by microorganisms through adventitious conduits and improved electron transfer mechanism, which was consistent with the impressively enhanced power output. The CA curves were recorded while charging for 10 min and discharging for 20 min (Fig. 4b). The higher the peak current (0.148A) and stable current (0.006A) in the PANI-Mn/CF anode, the more electrons were gathered from the metabolism during the open circuit phase. The improved capacitive behavior could be attributed to the addition of PANI and MnO₂, which advanced the electrode to complete both biological and abiotic reactions during the charging process, as well as utilizing electrons to form reduction products for faster abiotic reactions and promoting the storage of more electrons.

3.3. Electricity Utilization and Generation of the MFC-PES with PANI-Mn/CF Anode

3.3.1. In-situ utilization of electricity to oxidize cathodic refractory pollutants

The electrons generated from organic degradation on the anode can be directly used after their being transferred to the cathode to complete the oxidation of target pollutants. Thus, the effect of composite anodes on MFC-PES performance was explored to understand in-situ utilization of electricity in cathode chamber.

Previous studies discovered that the contribution of H₂O₂ was more significant than that of Fe²⁺ to form •OH, which was considered to be the most critical ingredient in the Fenton reaction [62]. During MFC-PES operation, H₂O₂ concentration first increased rapidly and then decreased gradually. The maximum H₂O₂ productivities were in the order of (Fig. 5a) PANI-Mn/CF (21.78 mg/L) > PANI/CF (18.85 mg/L) > CF (15.51 mg/L), showing that the MFC-PES with PANI-Mn/CF owned greater demand and utilization degree for H₂O₂ due to excellent electrons supply. These results contributed to the biocapacitor of PANI-Mn/CF anode, which could store more electrons generated by microbial oxidation of substrates and release the accumulated charges simultaneously [63]. The coupling structure of PANI and MnO₂ provided high capacitance, which acted as an ion buffer pool to promote more actively the Faradaic reaction during charge and discharge and slowed down the change of anode potential. In addition, both electron transfer resistance and energy consumption to overcome activation energy were reduced [64], thereby maintaining higher voltage output and adaptability to adverse conditions.

The degradation of target pollutant (TC) in cathode chamber was studied as an intuitive parameter of MFC-PES running performance. The TC removal efficiencies followed the order (Fig. 5b) of PANI-Mn/CF (93.02%) > PANI/CF (83.3%) > CF (78.9%), indicating that the MFC-PES with PANI-Mn/CF had better utilization of electric energy due to a higher voltage output and H₂O₂ production. Excellent electron storage and release mechanism of the MFC-PES ensured the relatively smooth transfer of electrons for providing more H₂O₂. To further understand the high TC removal in the MFC-PES with PANI-Mn/CF anode, the UV-Vis absorption of TC solution at different time intervals was analyzed (Fig. 5c). There are distinct absorption bands at 275 nm and 360 nm, corresponding to four different ring structures of TC [65]. Tetracycline hydrochloride has three functional groups, including double bonds, phenolic, and amine groups with high electron density that are vulnerable to assault by •OH radicals during electrochemical oxidation. The peak at 360 nm faded quickly as the reaction continued, and the peak at 275 nm vanished with a baseline lift in the UV region, demonstrating a rapid degradation of TC and a rapid disruption of the conjugated structure.

3.3.2. Electricity generation from degradation of anodic sludge

In order to generate bio-electrons from the MFC-PES, biocatalyst plays a vital role in efficient utilization of substrates.

![Fig. 5. The concentration of H₂O₂ (a) and TC removal efficiency (b) in cathode chamber of MFC-PES with different anodes during operation phase.](image)
To investigate how microorganisms on the anode surface improved electricity generation by promoting organic matter degradation, the changes in sludge properties in anode chamber and the microbial community structure on anode surface were analyzed to reveal the reason for high energy conversion efficiency of the system with PANI-Mn/CF. Excess sludge is a complex substrate containing microbial cells, extracellular polymers, inorganic ions and other substances, and the amount of total pollutant in sludge can be reflected by TCOD concentration. TCOD removal improved constantly as the reaction progressed (Fig. 6a) with the highest TCOD removal efficiency of 37.14% obtained with PANI-Mn/CF, which was 11.43% and 37.35% higher than those of PANI/CF (33.33%) and CF (27.04%), respectively. The organic substrates in anodic chamber with PANI-Mn/CF were utilized rapidly, thereby enhancing the rate of oxidation, which promoted electricity generation when delivering more reducing equivalents via extracellular electron pathway required for facilitating redox re-

Fig. 6. TCOD removal efficiency (a), VS/TS value (b), the concentration of SCOD (c), the concentration of soluble carbohydrates (d), the concentration of soluble protein (e) and the concentration of TVFAs (f) in anode chamber of MFC©EFs with different anodes during operation phase.
actions [66]. The composite PANI-Mn/CF electrode possessed excellent capacitive properties, allowing it to store electrons as well as promote electron generation. Furthermore, the MnO₂ coupling alleviated the insufficiency caused by ion doping and dedoping in the PANI polymer chain [50], maintaining the stability of the electrode structure and lowering the difficulty of electron transfer. As a consequence of an efficient storage and a more accessible transfer mechanism, bacteria could continuously generate new electrons by decomposing organic matter in sludge.

The VS/TS value of the sludge represents the proportion of degradable organic matter to the total matter in the sludge. The decrease in VS/TS in each reactor (Fig. 6b) was in an order of PANI-Mn/CF (47.9%) > PANI/CF (37.99%) > CF (21.16%), illustrating the accordance of biodegradable organic matter with TCOD consumption of sludge. High TCOD and VS removal efficiencies can enhance electricity generation while simultaneously having significant implications for sludge treatment and subsequent disposal. The degradation of complex organic matters to soluble organics is an essential step for anode electricity generation, therefore, an efficient release of intracellular organic matter has been identified as a prominent process. The concentration variations of various soluble substances (SCOD, soluble carbohydrates, soluble protein, and TVFAs) during the system operation behaved similarly, all accumulated rapidly to maximum and then decreased gradually. The SCOD concentration in the system with PANI-Mn/CF anode increased quickly from 525.2 mg/L to 727.2 mg/L (by 38.46%), while those with PANI/CF and CF were increased only by 26.67% and 21.21% (Fig. 6c), respectively, which evidenced PANI-Mn/CF could promote the release of intracellular and extracellular polymers into solution. As is known, soluble carbohydrates (Fig. 6d) and proteins (Fig. 6e) are important components of soluble organic matter in sludge, which are more easily decomposed and utilized by electricity-generating microorganisms. The order of their accumulation and consumption was PANI-Mn/CF > PANI/CF > CF. VFAs are electron donors and excellent carbon sources which can be directly utilized by microorganisms (Fig. 6f). Their changing patterns were comparable to those of the soluble compounds listed above.

The fluctuation in the concentration of soluble substances demonstrated a more substantial need for organic compounds and increased metabolic activity among the microorganisms in the system with PANI-Mn/CF. This could be due to the PANI and MnO₂ modified layers acting as a support structure to increase interfacial activity, improve the effective attachment area, and provide good biocompatibility. Additionally, prior research has demonstrated that polyaniline can enhance interactions between electrogenic bacteria [67,68] and can enter the electrolyte to participate in the reaction to improve the electrode’s catalytic activity while adding manganese dioxide better promotes the catalytic activity of the electrode [61]. A co-reaction of biotic and abiotic processes results in the enhanced usage of organic substrates by anodic biofilms that improve power generation by supplying more protons and electrons.

To explore the impact of composite anodes on microorganisms and reveal their effects on pollutant degradation and power generation, the microbial community structure of MFC/EFs with different anodes was analyzed. The diversity of bio-community on the surface of PANI-Mn/CF anode (Shannon’s index = 13.48) was smaller than those of PANI/CF anode (13.62) and CF anode (12.53), demonstrating that the composite electrode selectively preferred particular microorganisms which were favorable to the functioning of the system, hence enhancing the overall efficacy.

At the phylum level (Fig. 7a), the anode biofilms of MFC/EFs possessed rich microbial diversity, with Proteobacteria, Bacteroidetes, and Chloroflexi dominating. Compared with CF, the addition of PANI increased the abundance of Proteobacteria in the biofilm, whereas the addition of MnO₂ interlayer did not. Bioelectricity generation is a complex synergistic antagonism, which requires simultaneous attention to the mutual cooperation of diverse species. In PANI-Mn/CF, the abundance of Bacteroidetes and Chloroflexi increased to 15.93% and 11.08%, respectively. Bacteroidetes could better adapt to changes in the micro-ecological environment, and as-

![Fig. 7](image_url) Fig. 7. The relative abundances of the predominant biofilm microorganism at phylum (a) and genus levels (b) of MFC/EFs with different anodes.
sure the stability of system performance by playing a significant role in degrading organic substrates. Studies showed that high enrichment of *Bacteroides* in glucose-rich MFC biofilms could be achieved [69]. *Chloroflexi* could utilize various carbohydrate and organic acids as electron donors and electrodes as electron acceptors to facilitate the breakdown of complicated organic substances while also transferring electrons [70]. In addition, the presence of *Actinobacteria* could also promote the degradation of organic matter, which was more abundantly distributed on the surfaces of PANI-Mn/CF electrodes and PANI/CF electrodes [71]. The various dominant populations of the microbial community could play better synergistic roles when those owned an optimal distribution ratio to accomplish the optimal resource and energy utilization of organic matter.

At the genus level (Fig. 7b), in PANI-Mn/CF, the relative abundances of *Nitrospira* as the dominant species were 9.17% higher than others. *Nitrospira* belonged to *Nitrospirae* [72], an autotrophic nitrite oxidizing bacterium which was reported to be found in denitrifying biocathodes [73-75], capable of utilizing NH₃ and nitrite.

### 3.3.3. Energy conversion efficiency of the MFC EFs

CE can reflect the proportion of the electrons used to generate electricity out of the total electrons supplied by degrading substrate. Generally, the CE in MFC EFs showed a tendency of initial decrease and then increase over time (Fig. S5). The CE of the MFC EFs with PANI-Mn/CF (12.87%) was higher than those with other two electrodes, which were 1.18 and 2.8 times higher than the MFC EFs with PANI/CF (10.87%) and with CF (4.6%), respectively, indicating more effective energy recovery in the MFC EFs with PANI-Mn/CF. MnO₂ can speed up redox reactions, as demonstrated in earlier research [76], and PANI owns excellent electrical conductivity owing to its conjugated electronic structure with high quinone ring content. Compared to PANI-H, PANI-Mn has a greater level of electron delocalization, guaranteeing high conductivity of the electrode and ensuring a smooth transfer of electrons [77].

The molecular structure of the cross-linked porous loading layer created by PANI and MnO₂ is more stable than the lack of MnO₂. An improved energy recovery rate eventually resulted from forming more appropriate and accessible routes for electrons to pass through, which caused electrons to move fast to the electrode surface with rapid generation.

### 3.4. Evaluation of the MFC EFs with PANI-Mn/CF Anode and Outlook

Electricity consumption is commonly an important indicator for evaluating environmental sustainability of a technology. Electrical energy per order \( E_{EO} \) can be used to compare energy consumption of various technologies to remove pollutants (Eq. 6).

\[
E_{EO} = \frac{P}{t \times V \times C_f}
\]

where \( P \) is power input (kW), \( t \) is reaction time (h), \( V \) is wastewater volume (m³), \( C_i \) and \( C_f \) are initial and final concentrations of the target pollutant (mg/L), respectively.

Based on the above equation, the \( E_{EO} \) of MFC EFs treating tetracycline wastewater was calculated and compared with other advanced oxidation technologies used for treating antibiotic wastewater (Table 1). In comparison to the conventional MFC EFs [11.16 kWh/(m³-order)], the \( E_{EO} \) of the MFC EFs with PANI-Mn/CF anode [6.25 kWh/(m³-order)] was much lower, indicating its more efficiency due to a better supply of electrons and thus a shorter treatment time.

As MFC EFs does not require an external voltage, energy consumption is only limited to a low aeration supply, resulting in an efficient degradation with reduced energy consumption and a lower \( E_{EO} \) compared to alternative methods. The waste sludge (a by-product of wastewater treatment plant) for MFC EFs is rich in organic matter and is an eco-friendly green energy source. The MFC EFs can also provide an additional environmental benefit of simultaneously treating sewage.

<table>
<thead>
<tr>
<th>Processes</th>
<th>Contaminant</th>
<th>( E_{EO} ) (kWh/(m³-order))</th>
<th>Reference</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC EFs with PANI-Mn/CF</td>
<td>Tetracycline hydrochloride (TC)</td>
<td>6.25</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>MFC EFs with CF</td>
<td>Tetracycline hydrochloride (TC)</td>
<td>11.16</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>UV/CaO₂</td>
<td>Thiamphenicol (TAP)</td>
<td>72.1</td>
<td>[78]</td>
<td></td>
</tr>
<tr>
<td>Visible-light /ZnS-SnS₂</td>
<td>Tetracycline hydrochloride (TC)</td>
<td>21.6</td>
<td>[79]</td>
<td>Tap water</td>
</tr>
<tr>
<td>UV/H₂O₂</td>
<td>Tetracycline hydrochloride (TC)</td>
<td>66.27</td>
<td>[80]</td>
<td>Biological effluent</td>
</tr>
<tr>
<td>O₃</td>
<td>Sulfamethoxazole (SMX)</td>
<td>27.53</td>
<td>[81]</td>
<td></td>
</tr>
<tr>
<td>Hybrid persulfate-photo-bioelectrochemical (PPBEC)</td>
<td>Carbamazepine (CBZ)</td>
<td>88.1</td>
<td>[28]</td>
<td>Secondary effluent</td>
</tr>
</tbody>
</table>
sludge while degrading refractory organics, considerably facilitating their reduction and eventual disposal in comparison to other advanced oxidation technologies.

However, there are still a number of issues that demand targeted attention in order to hasten the process of large-scale adoption of MFC EFs. To reduce the constraints imposed by construction costs, new membrane materials, such as nanoporous ceramic membranes, need to be investigated. The determination of optimal conditions and the improvement of system adaptability by the optimization of system configuration and catalyst composition are also urgent.

In conclusion, the MFC EFs with PANI-Mn/CF anode holds significant potential as an environmentally sustainable technology with low energy consumption and high eco-efficiency for efficient energy conversion and utilization.

4. Conclusion

The PANI-Mn/CF composite anode introduced into MFC EFs innovatively was demonstrated as an essential component of electron generating sites to improve the system performance successfully. The PANI-Mn/CF composite anode facilitated more electrical energy generation via efficient degradation of anodic sewage sludge while accomplishing cathodic TC wastewater treatment through in-situ utilization of the generated electricity. The formation of N-Mn bonds in polyaniline and MnO₂ led to a lower electron transfer resistance and faster electron transfer rate, resulting in a higher power density (1.98 times that of PANI/CF and 5.49 times of CF) and lower ohmic resistance (7.17 Ω). Within 10 h of operation of the MFC EFs with PANI-Mn/CF, a sludge TCOD removal of 37.14% and lower in the anodic chamber (11.43% and 37.35% higher than those of PANI/CF and CF) and the most effective TC removal of 93.02% in the cathodic chamber could be achieved simultaneously. The relative abundance of Bacteroidetes and Chloroflexi increased to 15.93% and 11.08% on PANI-Mn/CF anode surface, which was vital in degrading organic matters to generate electricity. The MFC EFs with PANI-Mn/CF anode owned a lower E_{EO} [6.25 kWh (m²·order)], allowing them to achieve lower energy consumption and higher eco-efficiency. These results indicated that it was feasible to implement waste and wastewater treatment from wastewater treatment plants (WWTPs) utilizing resource recovery methods as an innovative way to save energy and reduce consumption. Future research is suggested to concentrate on continuous-flow and multi-pollutant wastewater treatment based on relevant advancements in Coulomb efficiency and optimization of operational parameters due to the complexity and volatility of actual wastewater.

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Declarations 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.

Author Contributions

L.J.Q. (Postgraduate student) conducted all the experiments and wrote the original manuscript. W.W.Y. (PhD student) processed data, wrote and revised the manuscript. Z.Q.L. (Professor) clarified the direction, supervised and revised the manuscript. W.K. (Professor) wrote and revised the manuscript.

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