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Original article

Impact of CeO_2 modified cathode and PANI modified anode on tannery wastewater fed microbial fuel cell performance

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ABSTRACT

Microbial fuel cell (MFC) technology is getting acceptance as an emphatic, sustainable and energy efficient alternative of conventional wastewater treatment strategies. MFCs utilize exoelectrogens as biocatalysts to degrade the complex organic substances present in wastewater with simultaneous power generation. The present study was aimed at investigating the impact of MFC electrode's modification with CeO_2 nanoparticles and polyaniline (PANI) on its performance characteristics. The hydrothermal approach was employed for the synthesis of CeO_2 nanoparticles followed by their deposition on carbon cloth (CC) as MFC cathode, whereas MFC's anode i.e., CF/NF was modified by in-situe deposition of PANI. The synthesized material was characterized with FTIR, XRD, SEM, EDX and BET analysis. The experiments were performed using dual chambered MFC fed with leather tannery wastewater using modified and unmodified electrodes. The highest outcomes of power density and corresponding current density were observed with PANI@NF composite anode and CeO_2@CC as cathode i.e., 279.3 mW/m^2 corresponding to the current density of 581.8 mA/m^2. The same MFC electrode configuration resulted in highest COD reduction, i.e., 80 % and coulombic efficiency of 19.86 %. On the other hand, MFC equipped with PANI@CF anode and CeO_2@CC cathode also displayed comparable results. It was ascertained that modification of NF/CF anode with PANI (conductive polymer) and CC cathode with CeO_2 nanoparticles have significantly improved the overall MFC operational performance regarding tannery wastewater treatment and bioelectricity generation.

1. Introduction

The energy crisis and environmental pollution are major issues of the current global era, and the industrial sector is one of the main contributors to this matter (Dincer, 2000). Among complex waste-producing industries, the leather industry has been considered a significant contributor of environmental pollution, particularly in developing countries. The effluent released from the leather industry comprises high concentrations of organic and inorganic pollutants, including chromium, sulfides, and other heavy metals, which are toxic to the environment and human health (Zhao and Chen, 2019; Naha et al., 2023). Moreover, untreated effluent from leather tannery industry can results in environmental degradation by degrading quality of soil groundwater, and can also be harmful to the aquatic life (Kannaujiya et al., 2019). In this context, several wastewater treatment strategies (physical, chemical, and biological) have been employed by the researchers to minimize the harmful effect of wastewater from leather tanneries on the environment (Angelucci et al., 2017).

In the recent years, microbial fuel cell (MFC) technology has been emerged as an emphatic and sustainable approach for the treatment of

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industrial effluents including tannery wastewater (Sawasdee and Pisutpaisal, 2016). MFCs exhibit dual function i.e., power generation and wastewater treatment (Kamali et al., 2023). In MFCs microorganisms serve as biocatalysts (Meylani et al., 2023) and work on the principle of redox reactions, where microbes degrade the complex organic matter present in industrial wastewater to generate protons and electrons. Afterward, these protons and electrons are transferred to the cathode and anode of the microbial fuel cells followed by the generation of bioelectricity via electron transfer through the external circuit and the proton transfer utilizing proton exchange membrane (PEM) (Subhadarshini et al., 2023). MFCs are therefore promising and sustainable alternative to the traditional wastewater treatment approaches (Li et al., 2013).

The effectiveness of the MFCs for the treatment of wastewater from tannery industry has been investigated by many researchers and reported the efficiency of MFCs towards the effective degradation of organic matter present in industrial effluents while producing bioelectricity as byproduct. Parameters that affect the functioning or performance of MFC include the anode, cathode, membrane's structure, medium's pH, temperature, ionic strength, types of substrates and electron transfer mechanism by microbes, electrode material, the distance between the electrodes, and sample of waste material being operated (Din et al., 2021; Chen et al., 2022). Since performance is correlated with electrode behavior, therefore, many researchers have recently turned their focus toward electrode materials (Mohyudin et al., 2022). The efficacy of MFC depends on the resistivity and flexibility of the electrode and the electrode material is thought to be more important in designing MFC and to make it commercially viable (Yaqoob et al., 2021). Moreover, the use of several electrode materials and polymers have been shown to enhance the efficiency of MFCs in tannery wastewater treatment. Several attempts have been made to improve the working efficiency of the MFCs technology for the biodegradation of effluents in tannery wastewater. One of these is the application of diverse electrode materials in MFCs in order to enhance the microbial enrichment over electrode surface and to improve overall working efficiency of MFCs (Aiswaria et al., 2022). To this end, modification of the MFC's electrodes (anode and cathode) for improving MFC performance is matter of great intrest.

In the present study, MFC's anode i.e., carbon felt (CF) and nickel foam (NF) were modified with polyaniline (PANI) while cathode i.e., carbon cloth (CC) was modified with CeO_2 nanoparticles and the impact of the modified electrodes on the operational performance of MFCs was investigated in terms of leather tannery wastewater treatment with simultaneous power generation

2. Materials and methodology

All the chemicals/reagents/solvents including aniline, ammonium persulfate, cerium nitrate, NaOH and H_2SO_4 etc., used in the presented work were of analytical/research grade.

2.1. In-situe preparation of PANI@CF and PANI@NF MFC's anodes

The PANI@CF and PANI@NF were prepared as anode materials by considering reported methods with few changes (Rajesh et al., 2020; Gao et al., 2021; Chen et al., 2022). The electrode material (CF/NF) was firstly sonicated in ethanol for 10 mins, washed with deionized (DI) water, and dried at 40 °C. After cleaning, the electrode material (CF/NF) was immersed in a solution mixture comprising of 1 M H_2SO_4 (40 mL) and 4 ml aniline followed by the slow addition of 1 M H_2SO_4 having (11.52 g) ammonium persulfate solution drop wise. The reaction was carried out for one hour and gently stirred in an ice bath (5 °C). When the reaction process was finished, the polyaniline-loaded CF/NF was rinsed with DI water and then dried for 6 to 8 h at 60 °C.

2.2. Preparation of CeO_2 nanoparticles

The synthesis of CeO_2 nanoparticles as a coating material for the cathode was done by considering a previously reported hydrothermal method with some modifications in the protocol (Gao et al., 2006). In 0.5 M solution of cerium nitrate, 6 M NaOH (50 mL) was added, and the formation of precipitates was observed. The solution mixture was stirred gently for 30 mins and then was shifted into a 100 mL capacity Teflon-lined autoclave and placed in an oven at a temperature of 120 °C for 24 hrs. As the reaction was completed, the autoclave was cooled down, the solution was filtered, and the washing of NPs was done twice with deionized water and ethanol. Particles were placed in the oven to dry at 60 °C for 24 hrs followed by their calcination in muffle furnace at 550 °C. This resultant product was CeO_2 nanoparticles.

2.3. Preparation of CeO_2@CC electrode

The coating of the electrodes surface by CeO_2 nanoparticles was done by immersing the carbon cloth (CC) cathode in a cerium oxide NPs solution maintained at 180 °C for 20 hrs in a Teflon-based autoclave, The CeO_2 coated cathodes were washed with deionized water after the autoclave had been cooled to room temperature (25 °C). The surface-modified electrodes were subsequently dried for 24 hrs in the oven at 60 °C. By measuring the difference in the weight of electrodes before and after the coating process, the quantity of CeO_2 that was deposited on the surface of CeO_2@CC was determined, indicating that CC had a high potential for CeO_2 coating (Miran et al., 2021).

2.4. Characterization of CeO_2 nanoparticles and MFC electrodes

The synthesized nanoparticles were characterized using FTIR Spectroscopy, XRD, SEM, EDX and BET analysis. The functional group attributes of the synthesized nanoparticles were examined using Cary 630 Agilent FT-IR spectrometer. The samples were scanned within range from 4,000 to 500 cm^{-1}. XRD analysis was performed utilizing XRD model (d8 discover Bruker Germany) while SEM microscopy (SEM model: S2380N (Hitachi)) was used to explore the surface morphology of the synthesized CeO_2 nanoparticles, PANI coated CF/NF and CeO_2 coated carbon cloth cathode. The surface area and porosity of cerium oxide and polyaniline was determined using the BET (V-Sorb 2800P, Beijing, China) surface area and porosimetry analyzer. Degassing of cerium oxide was performed at 350 °C for 3 hrs while for polyaniline degassing conditions time and temperature was 120 °C for 6 hrs. The combination of N_2 and He gas was used for area analysis. N_2 adsorption isotherms were obtained at − 196 °C. The multi-point BET method was used to calculate the surface area on the basis of adsorbed N_2 gas adsorbed on the surface of cerium oxide and polyaniline with relative pressure range of 0.00 to 0.35 (Masood et al., 2022). The isotherms were classified according to the International Union of Pure and Applied Chemistry (IUPAC).

2.5. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)

The electrochemical studies were performed based on CV and EIS. Electrochemical analyses were performed using potentiostat (Gamray 3000) with three electrode system in which platinum wire was employed as counter electrode, MFC electrode served as working electrode, while Ag/AgCl was used as reference electrode. CV of the working electrode was executed by sweeping applied voltage ranging from − 0.9 V to + 0.7 V with different voltage scanning rates.

The EIS method is one of the low cost and convenient diagnostic techniques to understand the underlying electrochemical impedance. EIS measurements were performed using Gamray 3000 within frequency range from 1.00 mHz to 100 kHz at an AC signal amplitude of 10 mV. Impedance spectra were recorded for an electrode considering that

electrode as working electrode i.e., for getting impedance spectra of anode, anode was selected as working electrode. In addition, Ag/AgCl electrode was used as reference electrode (Manohar et al., 2008). In this work, EIS spectroscopy was performed, and equivalent Randle circuits have been calculated using commercial software EC-Lab®. The Randle circuit model for EIS is usually composed of circuit elements such as Resistor, Inductor and Capacitor in various configurations and present the equivalent model for the whole "electrochemical cell system". Therefore, selecting the suitable circuit and right components for designing the Randle circuit is of vital importance in EIS. It is worth mentioning that the technique used for obtaining these values in EC-lab® is "Randomize + Simplex method".

2.6. Collection of leather tannery wastewater and microbial inoculum/ sludge for MFC reactor

Tannery wastewater was obtained from Leather Tannery industries, Sialkot, Pakistan using the standard analytical sampling procedure to ensure its representative nature. The samples were stored at 4 °C, subjected to physio-chemical characterization using APHA analytical methods, and were used in the MFC as the anolyte. The initial microbial inoculum was collected as sludge from sampling points nearby. This sludge underwent pretreatment by passing through a 300 mesh screen, removing larger foreign particles. Subsequently, the sludge was stirred to achieve a homogeneous and uniform mixture, ensuring consistent microbial distribution before its addition to the MFC system. The physio-chemical parameters of the leather tannery wastewater were EC (7.47 ± 1.2 dS/L), pH (5.4 ± 0.2), COD (3650 ± 30.5 mg/L), BOD (1480 ± 50.2 mg/L), TDS (4500 ± 10.5 mg/L), TSS (185 ± 10.5 mg/L), bicarbonates (465.25 ± 16.5 mg/L), chloride (1597.5 ± 18.2 mg/L), sulfates (4992 ± 30.2 mg/L), sulphide (S^{2-}) (2.8 ± 0.28 mg/L), oil and gease (14.7 ± 1.3), phenolics as phenol (24.5 ± 1.25), sodium (1610 ± 5.5 mg/L), potassium (38 ± 1.5 mg/L), calcium (340 ± 6.5 mg/L), magnesium (24 ± 1.1 mg/L), chromium (3.4 ± 10.5 mg/L), zinc (0.95 ± 0.004 mg/L), arsenic (0.02 ± 0.001 mg/L), lead (0.2 ± 0.001 mg/L).

The feed water COD was adjusted to ~ 500 mg/L by dilution. The MFC medium was sparged with nitrogen gas and an anaerobic environment was maintained in the anodic chamber with continuous stirring. The phosphate buffer (0.1 M) having a pH of 7.0 was introduced to the cathodic chamber as a catholyte, and oxygen from the ambient air was provided using an air pump equipped with a control mechanism. Each chamber was equipped with openings for input, sample extraction, and removal of the ultimately treated medium. In the first three cycles, 50 % medium was decanted and exchanged with the fresh medium to maintain the advanced growth of the biofilm on the anode, however, only the anolyte was introduced for additional cycles after the third one (Miran and Mumtaz, 2023).

2.7. Assembly and operation of the MFC

In the present research work, double-chamber MFC systems were used. The operational volumetric capacity of each anodic and cathodic chamber was 200 mL (Fig. 1). The functioning of MFCs equipped with varied electrode compositions i.e., **(MFC I)** CF anode & CeO_2@CC cathode, **(MFC II)** PANI@CF anode & CeO_2@CC cathode, **(MFC III)** NF anode & CeO_2@CC cathode and **(MFC IV)** PANI@NF composite foam anode & CeO_2@CC cathode were investigated in terms of wastewater treatment and bioelectricity generation using tannery wastewater as the substrate. The cathode in the experiment was made of carbon cloth modified with cerium oxide nanoparticles (5-cm x 5-cm); whereas the anode was 5-cm x 5-cm CF/NF with *in situ* polyaniline coating.

A PEM (Nafion® 117, Dupont Co., United States) was employed to decrease the internal resistance (R_{int}), while also maintaining a minimal gap between the electrodes. To optimize MFC performance, the proton exchange membrane underwent treatments with H_2O_2, sulfuric acid, and deionized water. The electrodes were linked to an external resistor with a resistance (R_{ext}) of 500 Ω. Using a water bath, the MFC setup temperature was maintained at 30 °C.

The anolyte of tannery effluent was diluted to COD levels of 500 mg/L.Nutrients of specific compositions were also added, which included trace mineral solution, $NaHCO_3$, $MgSO_4{\cdot}7H_2O$, $MnSO_4{\cdot}H_2O$ and $(NH_4)_2SO_4$ (Miran and Mumtaz, 2023). For the MFC setup, a mixture of 80 % anolyte and 20 % sludge was utilized to improve the biofilm's growth on the anodic electrode. For the first three cycles, half of the medium was drained, replaced with fresh sludge and medium in the same ratio (1:4), and from the fourth cycle onwards, only the anolyte was added.

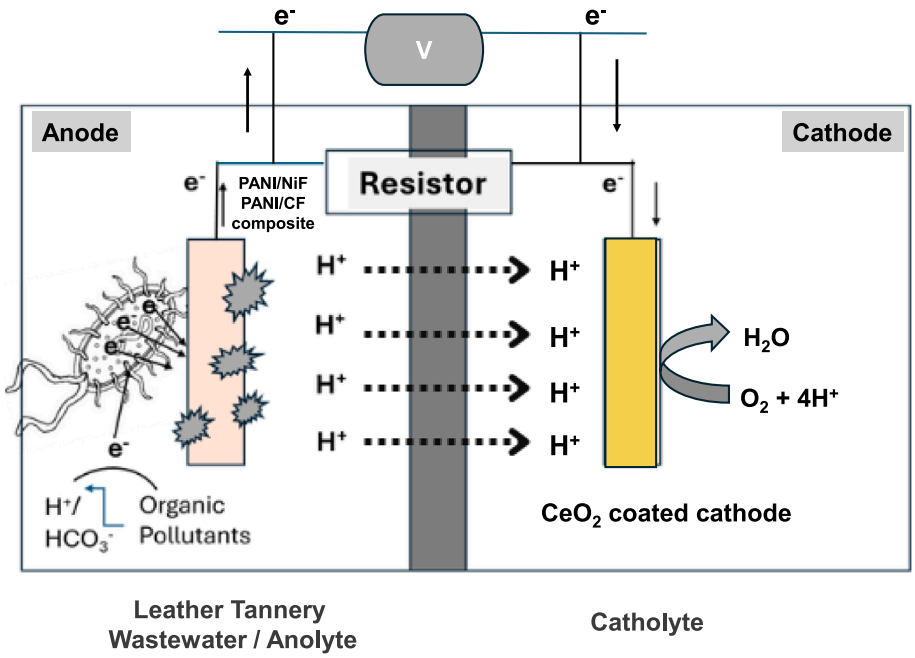

Fig. 1. The design and operation of the microbial fuel cell (MFC).

2.8. Investigation of electrochemical performance

Anodic and cathodic electrodes were connected to a multimeter, which was used to measure the voltage, and voltage data was tracked periodically. Ohm's law ($I = V/R$) was applied by considering the recorded voltage (V) and resistance to get the actual value of current (I). The power density (P), normalized to the anode surface area exposed to the anodic compartment, was calculated with the equation $P = V^2/(R_{ext}A)$. In this equation, 'A' (m^2) stands for the anode's surface area, R_{ext} represents the resistance of the external circuit, and 'V' (voltage) denotes the potential of the MFC. The polarization curves were obtained by adjusting R_{ext} systematically from 10 KΩ to 10 Ω. Every resistor was kept in place for 30 mins or until the steady voltage. Chemical oxygen demand (COD) was determined by APHA technique. The following relation was used to calculate the percentage reduction of COD:

$$\%\ \text{of COD removal} = \frac{(COD_0 - COD_f)}{COD_0}$$

Where, COD_0 and COD_f stand for the COD values recorded at time zero (0) and final time (f), respectively.

The relation presented as follows was used to estimate the MFC's Coulombic Efficiency (CE):

$$CE\,\% = \frac{8 \times I \times \Delta t}{\Delta COD \times Van \times 96,485 \times 100} \times 100$$

Here, Van (L) represents the volume of wastewater treated in the anodic chamber, I (Amp) denote the average current produced, and 't' represents the duration of the experiment. The ΔCOD indicates the change in Chemical Oxygen Demand from the initial to the final value. The number 8 in the equation stands for the constant related to the molecular weight of the oxygen molecule (32 g/mol), considering that four electrons are transferred for each oxygen molecule that is reduced.

2.9. Statistical analysis

Selecting the suitable circuit and right components for designing the Randle circuit holds a vital importance in EIS. This was done by software EC-lab® using "Randomize + Simplex method". Further statistical analysis was carried out as per requirement and the details are presented in the results and discussions.

3. Results

3.1. Characterization of coating materials

The synthesized CeO_2 NPs were characterized by FTIR, XRD, and SEM analysis. Scanning Electron Microscopy (SEM) was used to elucidate the surface characterization of synthesized nanoparticles (CeO_2). As per SEM image (Fig. 2 **A**), the CeO_2 nanoparticles exhibit homogeneous spherical morphology with agglomeration.

X-ray diffraction (XRD) is a popular and reliable method for the characterization of nanoparticles, especially for determining crystalline structures, sizes, and phase angles. Each type of crystalline structure creates a unique pattern of diffracted X-rays, known as a diffraction pattern. The XRD pattern or diffractogram is collected over a range of angles (2θ). Each peak in the XRD pattern corresponds to a specific crystallographic plane in the nanoparticle's crystal lattice.

The variations in structures are accepted in many structure parameters such as grain or crystallite sizes and dislocation line densities are important variables. The grain sizes (D) can be determined using the Scherrer formula.

$$\boldsymbol{D = \frac{K\lambda}{\beta \cos\theta}}$$

where Constant K is Shape factor 0.94, λ = 1.5406 \AA is the wavelength of the X-rays, β is the full width at half maximum (FWHM) in radians and

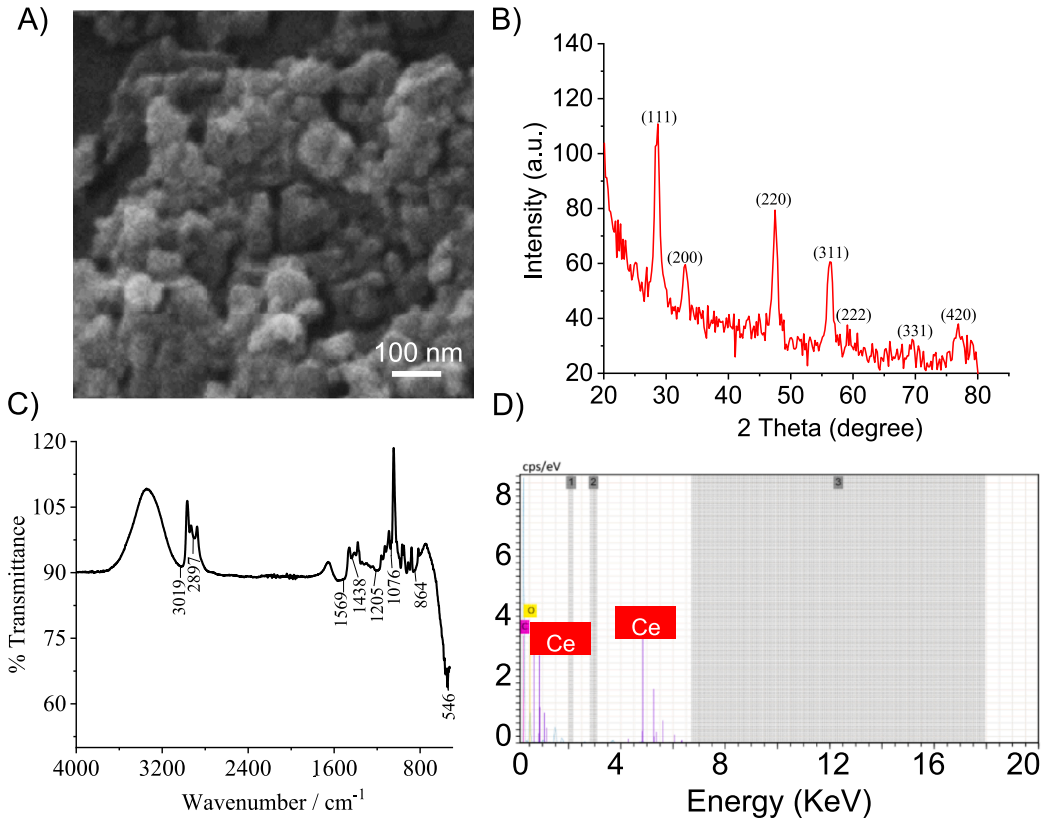

Fig. 2. (A) SEM image of CeO_2 nanoparticles (B) XRD spectrum of CeO_2 nanoparticles (C) FTIR spectrum of polyaniline (D) EDX of CeO_2 nanoparticles.

the peak position is in θ (degree). microstrain (ε) are calculated using the relations

$$\varepsilon = \frac{\beta \cos\theta}{4}$$

These formulae are valuable in dissecting the basic changes.

The X-ray diffraction (XRD) technique was utilized to evaluate the crystallinity and phase angle of the CeO_2 nanoparticles, as referenced by the JCPDS Card No. 34–0394. The obtained 2θ values align with the hkl indices (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (3 3 1) and (4 2 0) in the given order (Fig. 2B) and crystal structure is face-centered cubic. The results of this XRD analysis are found to comply with the prior studies conducted by other investigators (Vashistha and Rohilla, 2020). Peak sharpness is attributed to better crystallinity and no appearance of any additional peak shows the purity of the synthesized nanoparticles. According to Table 1 of XRD studies, peak at $2\theta = 59.24^{\circ}$ found to be broader as compared to the other peaks in the sample. This shows the poor crystal growth of (2 2 2) plan. Calculations of lattice constant a is also in accordance with the literature values (Gao et al., 2006; Jayakumar et al., 2017). Peak sharpness is attributed to better crystallinity and no appearance of any additional peak shows the purity of the synthesized nanoparticles.

The Fourier Transform Infrared (FT-IR) spectrum of polyaniline is described in Fig. 2 **C**, the characteristics peak observed at 1438 cm^{-1} is credited to C = C of the benzene ring while 1569 cm^{-1} is due to the presence of benzenoid ring. FTIR peak at 1205 cm^{-1} is associated with the presence of C-N, whereas, the characteristic peak at 3020 cm^{-1} is attributed to the stretching vibration of C–H bond. The results of the current study are comparable with previous research (Gholami et al., 2017). The chemical composition of prepared CeO_2 particles was analyzed by energy-dispersive X-ray spectroscopy (EDX), as shown in Fig. 2D. EDX analysis confirmed that there was no other element in the prepared sample of CeO_2. The only elements present were cerium and oxygen with mass percentages of 69.89 % and 27.79 %, respectively. The presence of cerium and oxygen within the sample was demonstrated, while the detected carbon peak arose because of the carbon tape used to mount the sample for analysis (Arul and Mangalaraj, 2015; Jayachandran et al., 2022).

Scanning Electron Microscopy (SEM) was also utilized to examine the surface structure of the modified electrodes (Fig. 3 **A — F**). It is clear from the SEM images that the surfaces of the bare CF and NF anodes were comparatively smooth which after having modification with PANI become rough with increased surface area. The rough electrode surface supports the microbial adhesion leading toward a stable and enriched microbial biofilm development over the anode surface which is a key requirement of an efficiently working MFC. Furthermore, the deposition of PANI over CF/NF anode enhances electrode's conductivity.

Similarly, the deposition of CeO_2 nanoparticles is also obvious from the SEM images. CeO_2 nanoparticles possess a high oxygen storage capacity and excellent electron transport properties, which can facilitate more efficient and rapid ORR (oxygen reduction reactions). Moreover, CeO_2 nanoparticles exhibit remarkable chemical stability and strong resistance to poisoning/corrosion, which is important for their utilization in long-term operations (Escudero et al., 2021). Hence, CeO_2 holds great promise to be employed as catalysts for the modification of MFC electrodes especially cathode.

Table 1
XRD parameters for CeO_2 sample.

Peak Position 2θ	FWHM (rad)	Crystallite size (nm)	hkl	Microstrain	Average Lattice constant a (Å)
28.56	1.09858	7.48	111	0.26	5.4073
33.04	1.35507	6.13	200	0.32	
47.52	1.18458	7.34	220	0.27	
56.44	1.21723	7.42	311	0.29	
59.24	3.49283	2.62	222	0.75	
76.96	1.94272	5.23	331	0.38	
79.08	1.85457	5.56	420	0.35	

3.2. BET analysis

In the case of cerium oxide we get a type IV adsorption isotherm with lower adsorption value at low relative pressures (0.01–0.7) with a sudden increase in the adsorption rate at values (>0.85). This could be due to multi-layer adsorption of adsorbate at higher pressures or due to macropores filling by adsorbate molecules. The latter is more convincing as the adsorption volume reached nearly 330 cm^3/g which is only possible due to meso and macroporous adsorption (Masood et al., 2022). At lower relative pressures the adsorbate is adsorbed at more energetically favorable sites. The specific surface area of the powder was calculated and had a value 75.85 m^2/g owing to porous nature of the sample. Similar isotherm was observed by Manjushree and coworkers who used nano sized CeO_2 in their work (SG et al., 2022). The desorption isotherm also showed a type III hysteresis which was due to existence of macropores in the sample's surface texture that could be necked and shaped in a manner to enhance pore blocking during desorption. This type of hysteresis occured mostly for plat-like layered pore structures. In similar study, desorption isotherm and existence of H3 & H2 hysteresis for smaller sized CeSD5, CeSD15, CeSD25 particles synthesized through Phyto-functionalization were reported (Navada et al., 2023). Pore size distribution of this CeO_2 showed a mesoporous surface with a cumulative pore volume of 0.515 (ml/g) and average pore size of 60–160 nm.

Polyaniline displays a type III isotherm. Lower adsorption occurred at lower relative pressures in range (0.0–0.4) which was due to lower attraction of adsorbate with the adsorbent material. At higher relative pressures the isotherm showed increase in adsorbed quantity of adsorbate through monolayer adsorption and adsorption at macropores. The specific surface area of the sample was calculated to be around 12.274 m^2/g which is lower than sample CeO_2. The desorption isotherm showed an unclosed hysteresis suggesting pore blocking in the sample due to uneven macropore structures. This type of hysteresis was inconclusive in nature. Additionally, the adsorption of N_2 could be due to presence of polymeric porous structure which was irregular in texture causing difficulty during desorption. The BJH model analysis reveals to us an average pore size of 70 nm to 130 nm with cumulative pore volume of 0.054 (mL/g) (Budi et al., 2018). Similar results were obtained by Anjana et al in fabrication of High-performance electrochemical supercapacitors based on polyoxometalate integrated into polyaniline and activated carbon nanohybrid where BET of PANI correlated to its surface area was crucial for adsorption of ions. The isotherms are shown in Fig. 4.

3.3. Bioelectricity generation for MFC reactor equipped with CeO_2@CC cathode and operated on leather tannery wastewater

The voltage generation was monitored for MFCs using different electrode material compositions, i.e., **(MFC I)** carbon felt (CF) anode & CeO_2 coated carbon cloth (CeO_2@CC) cathode, **(MFC II)** polyaniline coated CF (PANI@CF) & CeO_2 coated carbon cloth (CeO_2@CC) cathode, **(MFC III)** nickel foam (NF) anode & CeO_2 coated carbon cloth (CeO_2@CC) cathode and **(MFC IV)** polyaniline coated NF (PANI@NF) & CeO_2 coated carbon cloth (CeO_2@CC) cathode. MFCs (MFC I, II, III and IV) operated on tannery wastewater (COD; ~500 mg/L) as electron donor were first stabilized to achieve reproducible voltage. The stable voltage during MFC operation carried out using bare CF anode and CeO_2@CC cathode (MFC I) was depicted to be 0.247 ± 0.02 V, however when MFC studies were carried out using PANI coated CF anode (PANI@CF) and CeO_2@CC cathode (MFC II) the observed stable voltage was 0.46 ± 0.03 V. An increase in stable voltage was observed after having modification of CF with PANI (Fig. 5 & 6).

Comparatively, when MFC experiments were conducted using MFC

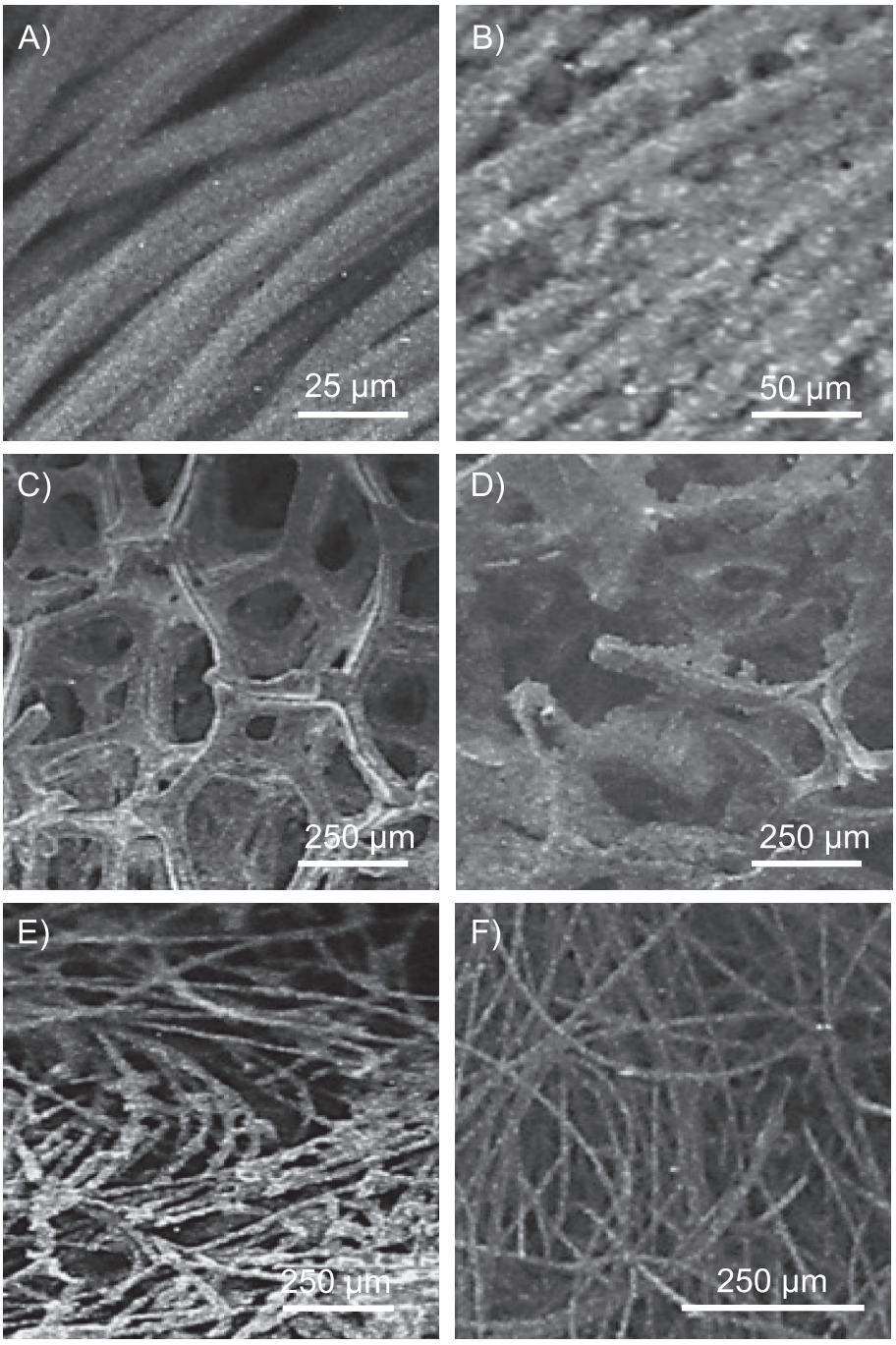

Fig. 3. SEM images of (A) carbon cloth (CC), (B) CeO_2 coated carbon cloth (CeO_2@CC), (C) nickel foam (NF), (D) polyaniline coated nickel foam (PANI@NF), (E) polyaniline coated carbon felt (PANI@CF) & (F) carbon felt (CF).

equipped with NF anode and CeO_2@CC cathode (MFC III) the stable voltage noted was 0.40 ± 0.022 V. The stable voltage was increased to 0.562 ± 0.026 V when NF anode was coated with PANI and cathode was CeO_2@CC cathode (MFC IV).

3.4. Power and current densities

Power and corresponding current densities were also estimated for different MFCs electrode compositions (EMC I, II, III & IV). MFC I displayed power density (105.8 mW/m^2) and corresponding current density (460.12 mA/m^2) (Fig. 7 **A**).

Power densities for MFC II (equipped with PANI coated CF (PANI@CF) anode and CeO_2 coated CC (CeO_2@CC) cathode) was 267 mW/m^2, while its corresponding current density was 569.0 mA/m^2 as indicated in Fig. 7 **B**. On the other hand for MFC III (equipped with NF anode and CeO_2 coated CC (CeO_2@CC) cathode) and MFC IV (equipped with PANI coated NF (PANI@NF) anode and CeO_2 coated CC (CeO_2@CC) cathode) the recorded power densities were 143.0 mW/m^2 and 279.3 mW/m^2 with corresponding current densities 416.3 mA/m^2 and 581.8 mA/m^2, respectively as shown in polarization and power curves (Fig. 7 **C & D**). These results clearly indicate that anode modification coupled with cathode modification resulted in improved power density. The best results were obtained with PANI coated NF (PANI@NF) while comparable results were displayed by PANI coated CF (PANI@CF) anode and CeO_2 coated CC (CeO_2@CC) cathode. Increased surface area increased microbial attachments, and higher conductivity of modified

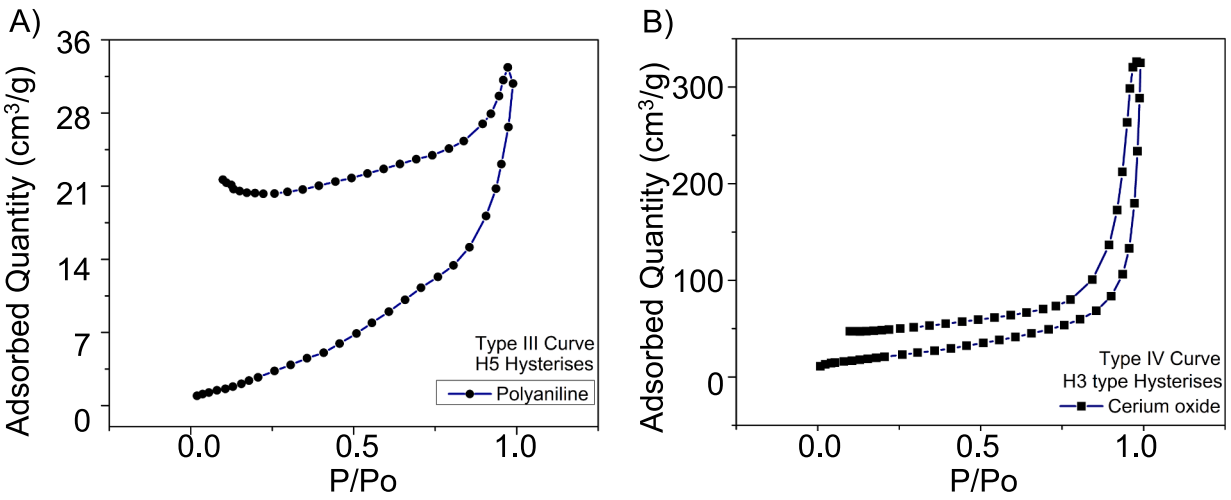

Fig. 4. The isotherms (A) polyaniline (B) CeO_2 nanoparticles.

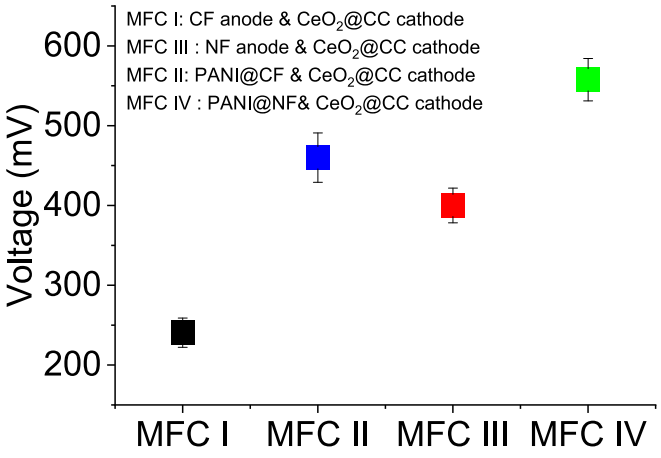

Fig. 5. Average stable voltage values for MFC I, II, III and IV fed with leather tannery wastewater.

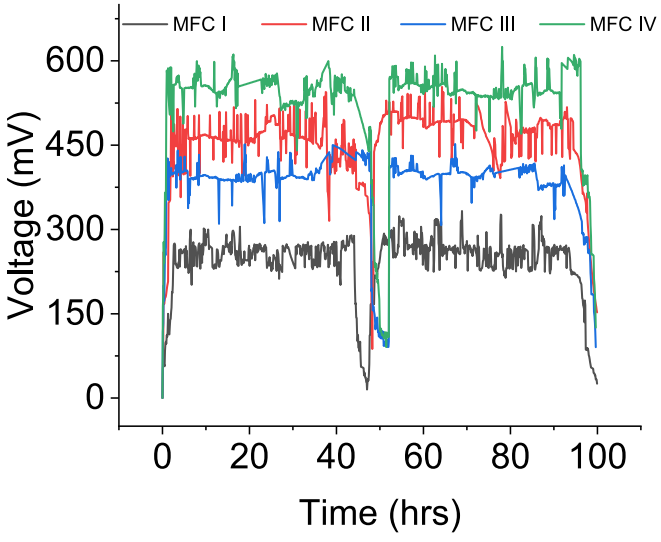

Fig. 6. A typical voltage curve with respect to time for MFCs operated on leather tannery wastewater.

anode supports higher electron transfer rate whereas improved oxygen reduction with CeO_2 further helps in achieving higher power density.

3.4.1. *Electrochemical behavior of MFC electrodes*

3.4.1.1. Cyclic voltammetry (CV) of MFC electrodes. The results obtained from CV analysis of different MFC anode materials i.e., CF, PANI@CF, NF and PANI@NF and cathode material i.e., CC and CeO_2@CC used in these experiments are shown in (Figs. 8 & 9).

It was observed that the cyclic voltammogram of the PANI@CF /PANI@NF anode and CeO_2@CC cathode of MFCs showed a large peak area and significant peak current for oxidation and reduction as compared to bare CF, NF and CC MFC electrodes. This means that modification of MFC anode with PANI and of cathode with CeO_2 displayed better electrical activity and improved electrochemical behavior as compared to bare MFC electrodes. The results are comparable to the previous studies (Zhong et al., 2018).

3.4.1.2. Electrochemical impedance spectroscopy (EIS). Impedance spectroscopy was performed to assess the performance of MFC anodes and cathode used in presented work based on the measurement of ohmic resistance as solution resistance (Rs) and charge transfer resistance (Rct). The MFC studies were carried out using different type of anode materials i.e., bare carbon felt as anode (CF), CF modified with PANI (PANI@CF), nickel foam (NF) and NF modified with PANI (PANI@NF). In the case of CF anode, the solution and charge transfer resistances were depicted to be 2.42 Ω, and 39.0 Ω, respectively, while when the CF has been modified with PANI a decrease in Rs (1.71 Ω) and Rct (26.0 Ω) was observed. One the other hand, when NF was used as anode in MFC, the solution and charge transfer resistances were depicted to be 5.01 Ω, and 16.5 Ω, respectively whereas, in case of PANI@NF anode material the observed solution and charge transfer resistances were 3.65 Ω, and 12.5 Ω, respectively (Fig. 10). It was revealed that modification of both CF and NF anodes with PANI has considerably lowered the internal resistance.

Similarly, Rs and Rct for MFC cathode was also investigated when MFC was operated using carbon cloth (CC) and carbon cloth modified with CeO_2 (CeO_2@CC). The Rs and Rct for CC cathode were depicted to be 4.69 Ω and 32.0 Ω, respectively. On the other hand, when MFC was equipped with CeO_2@CC cathode, the Rs and Rct were found to be to 2.42 and 22.0 Ω. A significant decrease in both the Rs and Rct were observed when CeO2@CC cathode was employed comparative to CC based cathode (Fig. 11).

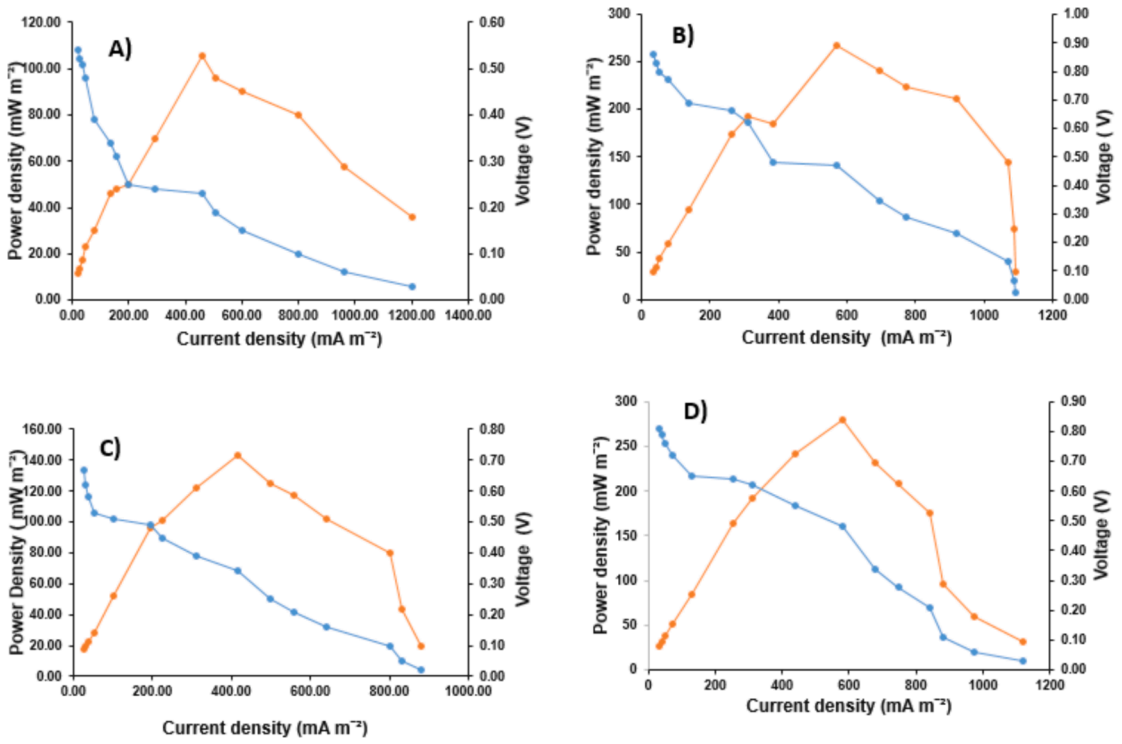

Fig. 7. Polarization/Power curves for (A) MFC I (equipped with CF anode and CeO_2 coated cathode) (B) MFC II (equipped with PANI@CF anode and CeO_2 coated cathode) (C) MFC III (equipped with NF anode and CeO_2 coated cathode) (D) MFC IV (equipped with PANI@NF anode and CeO_2 coated cathode).

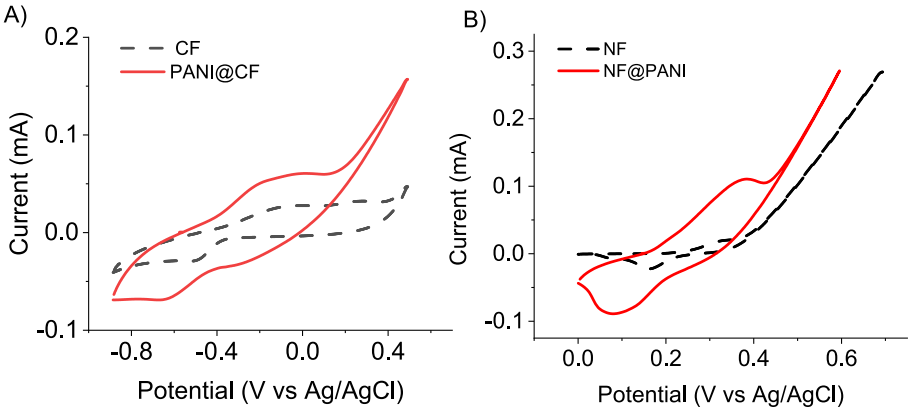

Fig. 8. Comparative voltammogram of (A) CF and CF@PANI anodes (B) NF and PANI@NF anodes.

3.4.2. Tannery wastewater treatment efficiency

3.4.2.1. COD reduction (%) & coulombic efficiency (%). For MFC configuration consisted of CF anode and CeO_2@CC cathode (MFC I), a 55 % COD reduction was achieved, whereas MFC II with PANI@CF anode and CeO_2@CC cathode resulted in 73 % COD reduction (%). In comparison, MFC III that was equipped with NF anode and CeO_2@CC cathode displayed 64 % COD reduction. The highest % COD reduction i. e., 80 % was observed for MFC IV with PANI modified NF was employed as anode while CeO_2@CC was the cathode (Fig. 12 **A**).

Coulombic efficiency is one of the most important parameters to evaluate the overall operational performance of MFCs. The coulombic efficiency of different MFCs is presented in Fig. 12 **(B)**.

For MFC I and MFC II, the coulombic efficiencies were found to be 12.21 % and 17.38 %, respectively. While for MFC III and MFC IV, the columbic efficiencies were 18.29 % and 19.86 %, respectively. It has been revealed that modification of MFC electrodes imparted significant impact on the operational characteristics of MFCs in context with their coulombic efficiencies.

4. Discussion

Taking in to account the rising energy demand and environmental concerns due to wastewater pollution, MFC an emphatic technology is being considered as a sustainable strategy for the generation of bioelectricity along with the treatment of wastewater. However, to make it commercially viable and to get the optimal performance different operational parameters are being optimized. It has been ascertained that modification of MFC electrodes with nano/conductive materials impart significant impact in this regard, probably due to the large surface area and high conductivity associated with these materials. Higher surface area and greater roughness of the modified MFC anode with nano/conductive materials results in increased microbial biofilm attachment over the electrode surface that serve as biocatalyst for the degradation of

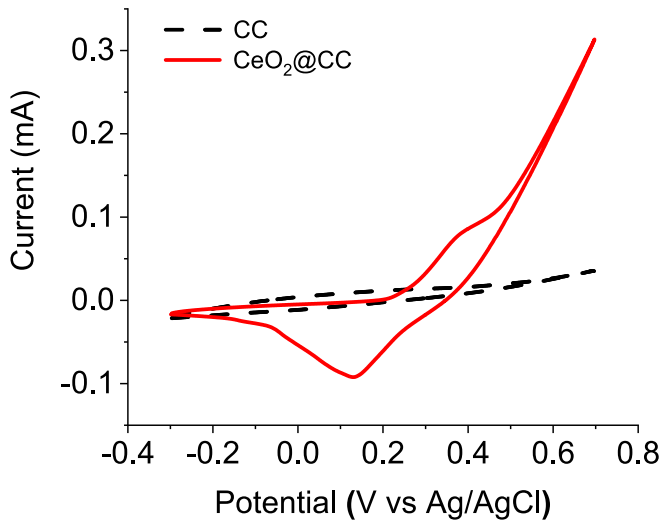

Fig. 9. Cyclic voltammogram of carbon cloth (CC) electrode and CeO_2 coated carbon cloth CeO_2@CC electrode in MFCs.

complex waste hence converting chemical energy associated with the waste to the electrical energy. Modification of MFC anode plays pivotal role toward the electroactive biofilm enrichment, while modified MFC cathode might be helpful to facilitate the oxygen reduction reaction. Usually, Pt coated cathode is being used for this purpose, but the high cost of the Pt and its corrosion render its usage at the large scale. Pt coated carbon cloth based MFCs have been used by the researchers in many studies, although Pt is effective catalyst however, platinum is a relatively scarce element in the Earth's crust, further contributing to its high cost and raising concerns about the long-term viability of Pt-based MFCs. The Pt catalyst can be susceptible to poisoning by various compounds and this occurs when certain molecules or ions attach to the surface of the catalyst, blocking its active sites and thereby reducing its catalytic activity (Ficca et al., 2020). Under operating conditions, Pt can corrode, and the catalyst layer can degrade over time, reducing the performance of the MFC (Zhao et al., 2021). On the other hand, cerium oxide coated carbon cloth (CeO_2@CC) holds promise to be used in MFCs because of the prospective benefits associated with CeO_2. Cerium oxide, due to its relative abundance, is less expensive than platinum. This cost-effectiveness could make MFCs more economically viable for widespread use (Aigbe and Osibote, 2022). Cerium oxide exhibits interesting catalytic properties and displays strong thermal stability and resistance to catalyst poisoning, and hence outperforming platinum in this regard too (Liu et al., 2011; Gholami and Luo, 2018). Moreover, CeO_2 nanoparticles have the ability to function as both oxidizing and reducing agents (Aneggi et al., 2020). An enhanced fuel cell's performance can result from improved oxygen storage and release kinetics, which can be facilitated by the cerium oxide coating on electrodes. In the present study, anode and cathode of the MFC fed with leather tannery wastewater were modified with a conductive polymer polyaniline (PANI) and CeO_2 nanoparticle, respectively, to evaluate its performance. PANI modified anode with CeO_2 modified cathode resulted in significant improvement in overall operational performance of MFC regarding COD reduction of leather tannery wastewater and generation of higher voltage, power and current densities. The improved voltage in the case of MFC operations using modified electrodes is likely due to high conductivity and large surface area of the modifiers i.e., PANI and CeO_2 (Zhao et al., 2021). Previously, CeO_2-NPs modified anode and cathode of MFC fed with benthic sediment and seawater, respectively, also exhibited power density of 43 and 60 mW/m3, respectively. Results revealed that the CeO_2-NPs modified cathode displayed better results comparative to when were used for the modification of anode (Pushkar et al., 2019). Comparatively in our study, the highest outcome of power density was observed with PANI@NF composite MFC anode and CeO_2@CC as cathode, i.e., 279.3 mW/m^2. In another previous study, The MFC reactor with a platinum-coated cathode and cerium-coated anode resulted in a power density of 63.81 mW/m^2. The improvement in extracellular electron transfers due to the cerium coating at the anode and the increased rate of oxygen reduction reaction due to the platinum coating at the cathode work in coherence to improve performance

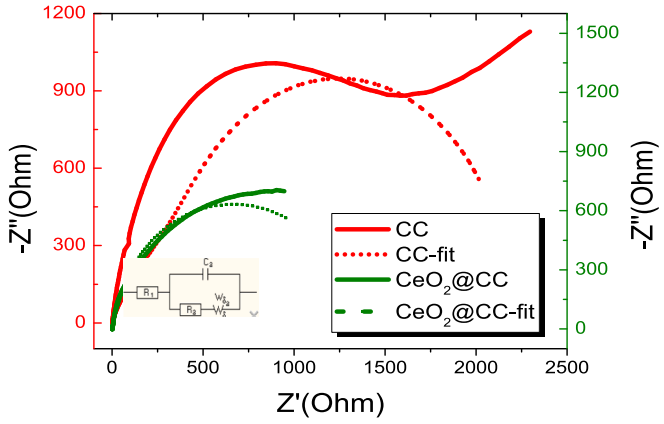

Fig. 11. Impedance spectroscopy (EIS) of CC & CeO_2@CC MFC cathode.

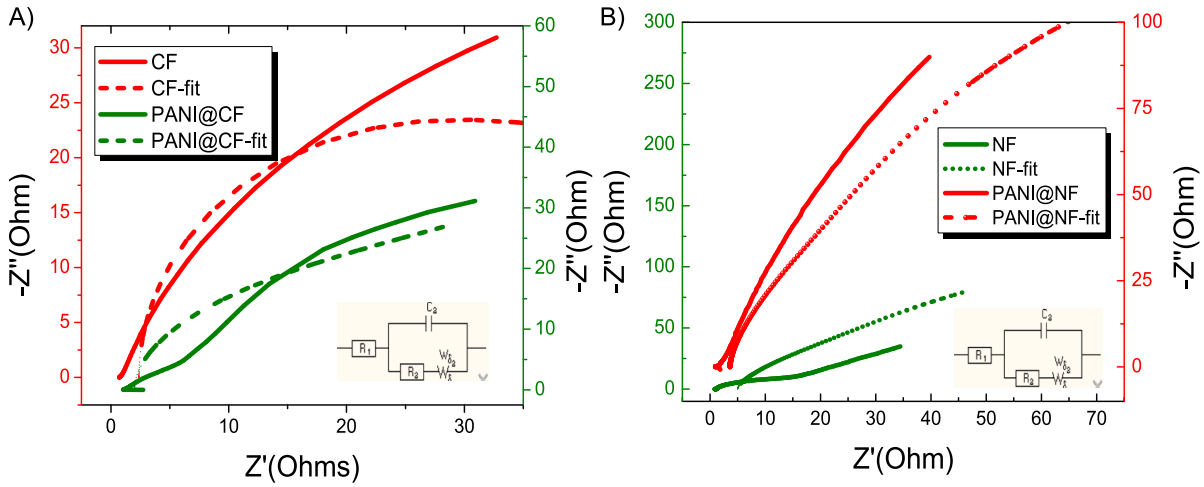

Fig. 10. Impedance spectroscopic (EIS) outputs of (A) CF & PANI@CF MFC anode, (B) NF & PANI@NF MFC anode materials.

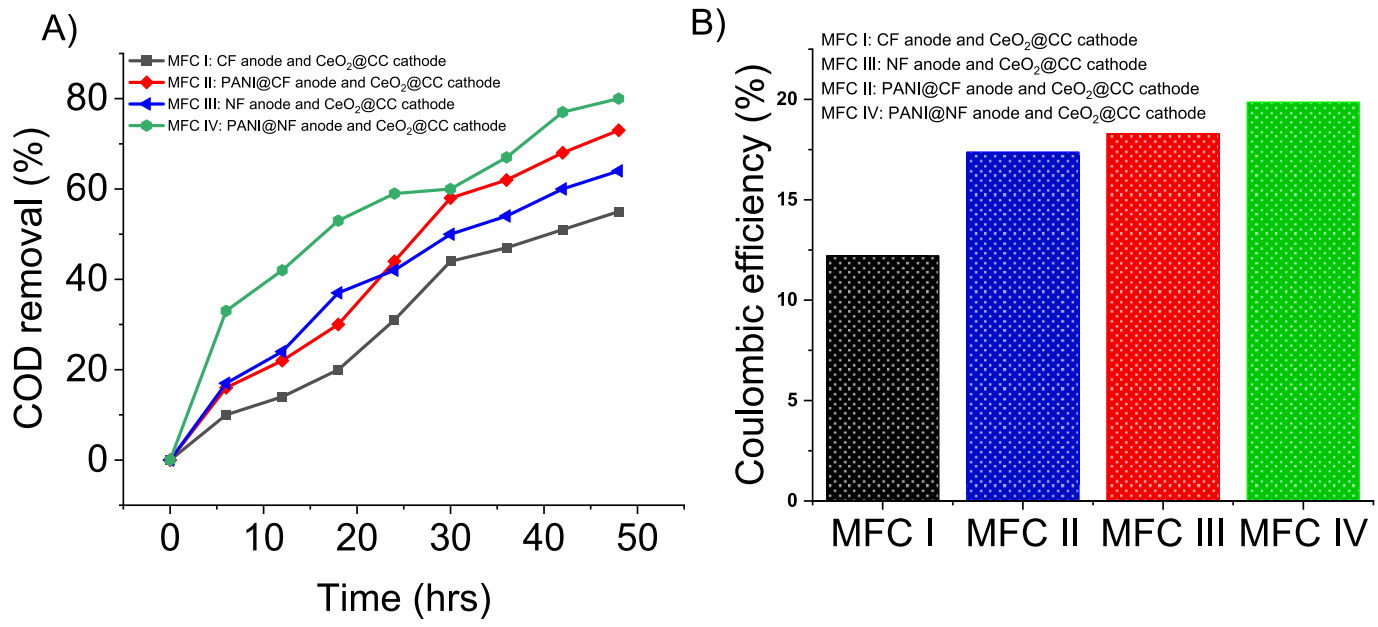

Fig. 12. (A) COD reduction (%) (B) Coulombic efficiency (%) for MFCs operated on tannery wastewater using different MFC electrode materials.

(Imran et al., 2019). Conclusively, modification of MFC cathode with CeO_2 can be an emphatic, low cost and sustainable option to be employed for the treatment of leather tannery wastewater with simultaneous power generation.

The electrochemical studies i.e., CV and EIS also supports over findings. As per CV outputs, higher peak currents and longitudinal extensions associated with the PANI modified MFC anodes and CeO_2 modified MFC cathode might be attributed to the higher electron transfer efficiency, decreased electron transfer resistance and increased surface area of these modified electrodes probably because of the inherent characteristics of PANI and CeO2 comparative to those which were unmodified (Zhang, 2011; Xiao et al., 2012). These attributes associated with the PANI modified MFC anodes and CeO_2 modified MFC cathode revealed that conductivity of these electrodes is significantly enhanced. Increase in electrode's specific surface area results in an increase of the electrochemical active sites on MFC electrode surface, hence enhanced MFC performance. Likewise, as per EIS results, MFC equipped with PANI@CF or PANI@NF anode and CeO_2@CC cathode, resulted in significant decrease in both the Rs and Rct comparative to bare CF, NF anode and CC cathode. On the other hand, a significant increase in % COD reduction and % coulombic efficiency was recorded when CF/NF anodes were coated with PANI in combination with CeO_2@CC cathode. The order of % COD reduction and % coulombic efficiency for different MFCs was MFC IV > MFC II > MFC III > MFC I. The improved leather tannery wastewater treatment ability of MFC with the modified electrodes might be attributed to the higher surface area provided by the modifiers to the microbes leading to the establishment of a dense biofilm at the surface of electrode, while then efficiently degraded the complex waste present in leather tannery wastewater.

Our studies suggested that modification of MFC cathode with CeO_2 nanoparticle may be considered as an economic, imperative and efficient alternative to the Pt for the generation of power treating leather tannery wastewater. MFCs processes allow simultaneous pollutant removal and energy recovery, in most cases MFCs show a better decontamination performance, especially for removal of aqueous recalcitrant contaminants including many persistent contaminants (Huang et al., 2011). MFC operation could prove energy-saving in contrast with multiple other treatment systems (Fan et al., 2012). MFCs have a low carbon footprint due to low energy consumption and CO_2 sequestration. They produce low sludge, reduce secondary pollution risks, and are energy-saving, potentially generating extra economic revenue. The recovery of value-added products from wastewater may further strengthens their economic justification (Li et al., 2014).

Scaling up the production of CeO_2-coated electrodes needs a detailed approach, which balances efficiency with ensuring high quality. This involves optimizing the production process of CeO_2 for consistent results by obtaining reliable raw materials and executing precise quality control measures. In addition, thorough cost analysis, environmental impact assessment, and observance of regulations are necessary for ensuring sustainable and affordable process that have compliant with all necessary standards. Hence, MFC technology hold promise to be used on commercial scale in future as a sustainable alterative to the traditional waste water treatment strategies with additional benefits of simultaneous bioelectricity generation.

5. Conclusion

The DC-MFC system was used for leather tannery wastewater treatment and to produce bioenergy. It was found that employing PANI/CF or/and PANI/NF anode, and cerium oxide coated CC cathode improved the performance of the MFC reactor. When the MFC anodes (CF/NF) were treated with polyaniline, better electrochemical properties, and COD removal efficiencies were observed. An effective and successful tannery wastewater treatment helps to resolve local social problems and environmental problems. Even though power output increased significantly with the modified electrode, however, the rate at which tannery wastewater is biodegraded could potentially be enhanced by identifying the particular microbial population in it and subsequently modifying their proportions. Conclusively, it is possible to improve MFC performance by altering the influencing factors in the anodic and cathodic chamber, which can aid in resolving issues with MFC commercialization. Further adjustments and improvement of MFC designs and operations are necessary for commercial use.

CRediT authorship contribution statement

Muhammad Waseem Mumtaz: Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – review & editing. **Hamid Mukhtar:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **Waheed Miran:** Formal analysis, Methodology, Resources, Software, Validation, Writing – review & editing.

Abdulrahman H. Alessa: Funding acquisition, Validation, Writing – review & editing. **Aashir Waleed:** Formal analysis, Validation, Visualization, Writing – original draft. **Zoha Sarwar:** Data curation, Investigation, Methodology, Writing – original draft. **Haseeb Ashraf:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft.

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.

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