Utilization of biomass-derived electrodes: a journey toward the high performance of microbial fuel cells

Asim Ali Yaqoob1 · Mohamad Nasir Mohamad Ibrahim1 · Amira Suriaty Yaakop2 · Mohd Rafatullah3

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Abstract
This study aims to improve electron transfer and cobalt remediation efficiency through microbial fuel cells (MFCs) by modifying the electrode material. The fabrication and alteration of the anode can be accomplished by synthesizing biomass-derived graphene oxide (GO) and adding metal oxides (ZnO and TiO2) as modifiers. The prepared GO anode offered 0.148 mW/m2 power density while GO-ZnO delivered 8.2 times and GO-TiO2 composite anode delivered 5.3 times higher power density than GO. Similarly, the achieved current density of GO was 39.47 mA/m2 while GO-ZnO composite anode delivered 75.43 mA/m2 and GO-TiO2 composite anode offered 67.54 mA/m2. During the biological characterizations of biofilm, the Bacillus sp. and Klebsiella pneumoniae strains were majorly found as exoelectrogens and metal-reducing species. The maximum remediation efficiency of cobalt (II) was 80.10% (GO), 91% (GO-ZnO composite anode), and 88.45% (GO-TiO2 composite anode) on day 45. The remediation and SEM results of anode biofilm clearly show that the prepared anodes are highly biocompatible with the bacteria. Furthermore, the effect of pH and temperature on MFCs performance are also explained with prepared anodes. Each anode offered significant perspectives in parameter optimizations.

Keywords Microbial fuel cells · Anode modification · Graphene oxide · Metal oxide · Energy generation · Wastewater treatment

Introduction
Metal ion removal from the water supply is a big problem for the industrialized world. The increasing problem of toxic metal contamination also disturbs the green environment for human survival. Among all pollutants, the toxic metal-based pollutant is well known as the most dangerous due to its persistence, recalcitrance, and toxicity properties. Several methods were developed to remediate the heavy metal ions from wastewater. Despite all efforts, there are still major issues in techniques to remove the metal ions such as cost, non-friendly, time-consuming, production of waste as a by-product (Yaqoob et al. 2020a). Additionally, Malaysia is suffering from metal pollutants in water resources which need to be addressed on priority because 99% of Malaysians are using surface water, and only 1% use groundwater. Among many toxic metals, cobalt (Co) is one of the toxic metals found in Malaysian water resources (Ab Razak et al. 2015; Esa and Sapawe 2020; Kamaruzzaman et al. 2010). Several efforts were already reported on remediation of Co by using the different conventional methods, but still, an eco-friendly approach is not reported yet. Fu et al. (2011) carried a literature survey for different chemical and physical methods for toxic metal treatment. They concluded that there is a need to choose a natural eco-friendly method to treat the toxic metal ions from water resources. According to the literature, microorganisms are well recognized in the conversion of highly toxic forms to less toxic forms such as Cu(II) to Cu(I) (Daud et al. 2021). Therefore, a technique which works on the concept of microbial activities is most suitable for metal remediation in a safe way. A complete...
prototype of microbial fuel cells (MFCs) was developed to treat the pollutants from wastewater by using the microbial community (Logan et al. 2006; Logan and Regan 2006). MFCs is an approach in which energy was generated during the oxidation of organic substrate by the microbial community and simultaneously convert the metal ions into the insoluble form. The oxidation of organic substrates by microbial communities is carried out at the surface of the anode electrode. The anode electrode size, design, surface area, conductivity is the most important for the high performance of MFCs (Umar et al. 2021; Yaqoob et al. 2021a). Various studies showed that the MFCs is a safe and convenient approach for remediation of wastewater with energy generation but still MFCs practice at the commercial level are in question. Several efforts were carried out to commercialize this approach but there were limitations in terms of electron transportation, space for microbial activities, and poor conductivity (Kirubaharan et al. 2019). To increase the electron transportation and better microbial activities at the surface of the anode, the anode electrode needs extensive modification in terms of design, size, or material (Yaqoob et al. 2020b). The carbon-based material as an anode is the most frequently used material (Ezziat et al. 2019). The conventional carbon material failed to achieve significant results due to less conductivity, low surface area, etc. (Do et al. 2018; Mustakeem 2015). Metal-based anodes can be ideal an anode, but the corrosion issue decreases the performance of MFCs which is not preferable for the long-term operation of MFCs (Zhang et al. 2019). Several studies were focused to upgrade the anode material (Yaqoob et al. 2021a). For example, the carbon nanotubes and carbon black were found to be very high conductive and ideal materials but the cellular toxicity toward microbes decreases the performance (Thepsuparungsikul et al. 2014). The advancement in carbon-based material dragged attention toward the graphene derivatives. Graphene oxide (GO) is a conductive, high surface area, and biocompatible material to use as the anode in MFCs (Cai et al. 2020). The biomass-derived GO can be the ideal material as an anode in the sense of cost. Further, to enhance the electron transportation and biocompatibility, the composite of GO with metal oxide is a great deal to fabricate the composite-based anode. In this research, the empty fruit bunch-based lignin was used which is a common biomass material in Malaysia, to synthesize GO without spending a lot of expenditure. Similarly, composite zinc oxide (ZnO) and titanium oxide (TiO₂) were used because both materials are good conductive, biocompatible. During the literature review, it was found that several studies showed that ZnO and TiO₂ as modifiers can significantly improve the electron transportation as an anode (Ashoka et al. 2020; Shashanka et al. 2020). The experiments are carried out at the lab scale by developing three electrodes GO, GO-ZnO, GO-TiO₂ composite anode with an equal concentration of Co ions. The comparison of three electrodes in terms of Co remediation as well as energy generation is briefly discussed.

**Materials and methods**

**Chemical reagents**

Lignin material (received from Material Technology Research Group School of Chemicals Sciences USM Malaysia), Oil palm trunk sap (contribution from School of industrial Technology USM Malaysia), ethanol (approx. 97%, QRec, AR grade), potassium permanganate (R&M Chemicals), glucose (QRec D + AR grade), sodium nitrate (Sigma-Aldrich), polysulfones (PSF) (Mw ~ 35,000, Sigma-Aldrich), hydrochloric acid (37%, U-CHEMIE, AR grade), phosphate buffer (pH 7), graphite rod (GR, FUDA 2B Lead, NY, USA), sulphuric acid (95–98%, QRec, AR grade), hydrogen peroxide (30–32%, QRec, AR grade), nafion-17, dichloromethane (QRec, AR grade), deionized water. Zinc oxide (ChemPur), Titanium oxide (PubChem). Cobalt(II) nitrate hexahydrate (R&M Chemicals).

**Synthesis of lignin derived GO**

To prepare the lignin-derived GO, a modified hummer method was used in the present study. First, lignin material was placed into the furnace to get carbonized carbon. It took 4–5 h at a 10 °C/min rate with the argon gas protection to avoid impurities. The obtained carbonized carbon was further processed by following the hummer method (Zaaba et al. 2017). Around 5 g of lignin-carbonized carbon was stirred in the mixture of H₂SO₄ (200 mL) and NaNO₃ (5 g) at room temperature for 60–90 min. After that, the temperature of the mixture was maintained at 0–5 °C then added 15 g of KMnO₄ and placed on continuous stirring. The temperature 0–5 °C was maintained by using an ice bath for 180 min. After removing the ice bath, the mixture was placed at room temperature for 2 days on magnetic stirring. The colour was changed from black to violet-brown after a 2-day string then added 200 mL water and stirred again at 90 °C until brownish-black colour appeared. On achieving the brownish-black colour placed the mixture on stirring without heating until it came back to room temperature. Then further added 200 mL water with 25 mL H₂O₂ to stop the reaction. Finally, the product was washed several times by using the water and ethanol then dried in the oven at 45 °C for powder form (Yaqoob et al. 2021b).
Preparation of GO-metal oxides composite

In the present study, the ZnO and TiO$_2$ are used to prepare the composite material with biomass-derived GO. Firstly, GO (5 g) was mixed with 2.5 g of ZnO by using ethanol as solvent. The mixture was stirred for 180 min without heating to get the composite product. Later, washed the product by using the ethanol and dried at 100 °C temperature to get the final GO-ZnO composite material. A similar procedure was adapted for TiO$_2$ material. The 5 g-GO was mixed with 2.5 g-TiO$_2$ by using the ethanol solvent to prepare the GO-TiO$_2$ composite material.

Characterization of prepared material

The prepared material such as GO, GO-ZnO, GO-TiO$_2$ composite was characterized by using different techniques. To study the physical, optical, thermal, structural properties, the Fourier transform infrared (FT-IR; Perkin Elmer model System 2000), X-ray powder diffraction (XRD; Philips PW 1710 X-ray diffractometer), UV−Vis spectroscopy (UV-2600i Shimadzu UV−Vis Spectroscopy), Brunauer−Emmett−Teller (BET; ASAP-Micromeritic 2020 Surface area analyzer, USA), thermal gravimetric analysis (TGA- Perkin Elmer Thermal Analyser, model TGA/SDTA 851), Raman spectroscopy (RA-82; Renishaw inVia Raman microscope) were used. Similarly, to investigate the morphological activities the scanning electron microscope (SEM-Zeiss, model DSM-960, Germany), atomic force microscopy (AFM-SII Sciko Instrument INC SPI 3800 N Probe station), transmission electron microscope (TEM; Model Zeiss Libra 120. the USA), X-ray photoelectron spectra (XPS; Axis Ultra DLD XPS, Kratos) and energy dispersive X-ray (EDX-Zeiss, model DSM-960, Germany) were used.

Preparation of anodes and inoculation source for MFCs

Three types of anodes were fabricated in this study, GO, GO-ZnO, GO-TiO$_2$ composite anode. During the fabrication process, a commercial graphite rod was used as supportive and current collector material. In fabrication, it took 60% GO powder with a 40% mixture of PSF (PSF mixture was prepared by using dichloromethane). The obtained paste of GO-PSF was successfully coated around the graphite rod then dried at 45 °C for 3 days for mechanical strength. Similarly, 60% of GO-ZnO and GO-TiO$_2$ composite was mixed with a 40% mixture of PSF to get the paste-like substrate which further coated the individual on the graphite rod. Later, place it into the oven for 3 days. The prepared electrodes were ready to be used as anode for further operation. The size of both fabricated anodes was 8 cm × 1.3 cm with 76 cm$^2$ surface area. A simple graphite rod was used in each operation. The preparation of inoculation was carried out at the Material Research Group Laboratory at Universiti Sains Malaysia. The wastewater was collected from the local pond of Pulau Pinang Malaysia. The physicochemical properties of collected pond wastewater were studied by using different parameters as shown in Table 1. Next, the wastewater was further treated with 100 ppm of cobalt(II) nitrate hexahydrate. The cobalt(II) nitrate hexahydrate was completely soluble in wastewater. The supplement of Co(II) changed the physicochemical properties of the wastewater which was also studied and mentioned in Table 1. The thermometer (GH, ZEAL LTD, China), electrical meter (ECM) (Alpha-800 conductivity meter), pH meter (EUTECH instrument-700 USA), was used to study the physicochemical properties.

MFCs setup and start up

The reactor configuration used in this study is a double chamber which was separated by using the proton exchange membrane (PEM). Anode and cathode chambers are present in the setup. The double chamber MFCs was fabricated by using the glass material and the size of the anode chamber was 10 cm × 9.5 cm and the cathode chamber was 10 cm × 9 cm. The anode chamber has an anode electrode (self-fabricated anode electrode), and the cathode chamber contains a cathode electrode. The distance between anode and cathode electrodes was 7 cm. The anode and cathode electrodes were connected by using the outer circuit (a copper wire) which helped to transfer the produced electrons from anode to cathode. The 1000 Ω external resistance was coupled with the outer circuit to stabilize the electron movement. Therefore, a digital multimeter was used to measure the potential. Further, an aeration pump was connected to the cathode chamber to supply the external oxygen to complete the reaction. In operational mode, the anode chamber was filled with cobalt supplemented wastewater (350 mL) and the cathode was filled with pond wastewater and 0.1 M phosphate buffer (pH 7) solution as electrolytes. Cobalt supplemented wastewater is also named synthetic wastewater in each operation.

| Table 1  | Summary of physicochemical analysis of inoculation source |
|----------|----------------------------------------------------------|
| Physicochemical properties | Pond wastewater | Cobalt supplemented wastewater |
| Colour | Light yellowish | Dark yellowish |
| Electrical conductivity | 65 µS/cm | 70 µS/cm |
| Temperature | 25 °C | 25 °C |
| Odor | Bad smell | Bad smell |
| pH | 6.89 | 6.65 |
| Co (II) | 0 ppm | 100 ppm |
the present study. According to the schedule, it was used to supply the 3 mL organic substrate (oil palm trunk sap) every day in an anode chamber for microbial growth and respiration process. A series of experiments were carried out by using three self-fabricated electrodes as anode separately versus graphite rod as a cathode. All experiments were operated at room temperature for 90 days. The reactor setup is shown in Fig. S1.

**MFCs tests**

Different MFCs tests were carried out to investigate the performance of anodes in terms of remediation efficiency as well as energy generation. During the experiment, it was recorded the voltage daily at 24 h intervals by using the digital multimeter (UNI-T, Model UT120A, China) which was further calculated by using the Ohm law to find the current value. Similarly, during operation, the polarization behaviour by changing the external resistance from 150 Ω to 10 kΩ to evaluate the polarization behaviour of the cell is also considered. The power density (PD), current density (CD), and internal resistance were determined by using the following Equations:

\[
V = IR
\]

(1)

\[
PD = \frac{V^2}{RA}
\]

(2)

\[
CD = \frac{1}{A}
\]

(3)

\[
r = \frac{E - V}{V}R
\]

(4)

where, \( R = \) external resistance; \( r = \) internal resistance; \( V = \) voltage; \( A = \) cross-sectional area; \( I = \) current; \( E = \) Electromotive force (Emf). Emf can be determined through open-circuit voltage (OCV). Next, cyclic voltammogram (CV; Model BAS Epsilon Version 1.4, Germany), and electrochemical impedance spectroscopy (EIS-Gamry Instrument group Metrohm, PGGSTAT12, Autolab, Echochemistry) was used for electrochemical measurements to study the redox potential and resistance effect of electrodes. The CV experiment was carried out with a +1.0 to −1.0 V window potential range and the scan rate was 10 mV/s. In the CV three-electrodes system was applied in our system, AgCl/Cl was used as a reference electrode, glassy carbon as a working electrode, and Pt wire as a counter electrode. Moreover, EIS operated on the completion of the reaction to study the charge resistance effect during electron transportation. The measurement was carried within the frequency range from 100 kHz to 100 mHz at 1.0 mV AC amplitude. The selection of frequency range is based on biofilm impartiality to prevent biofilm disturbance.

Further in MFCs, to study the remediation efficiency rate, the atomic absorption spectrometer AAS (PerkinElmer AAnalyst 400) was used. Equation 5 was used to calculate the value from AAS results. During the operation different readings were taken, every 10 days around 1 mL was taken from the anode chamber for AAS analysis.

\[
RE = \frac{T_{\text{initial}} - T_{\text{final}}}{T_{\text{initial}}} \times 100
\]

(5)

where, \( RE = \) remediation efficiency, \( T_{\text{initial}} = \) initial toxic metal concentration, \( T_{\text{final}} = \) final toxic concentration of metal.

During the MFCs biological tests, the SEM and EDX of the anode electrode on the completion of reaction to study the self-fabricated anode biocompatibility and interaction toward the microbial growth was carried out. The SEM images were directly taken by using the anode electrode biofilm. Biofilm is a collection of bacteria on the surface of the anode. The EDX of electrodes was also taken to explain the cobalt fate toward the biofilm growth. The biofilm performance can also be calculated by using the CV peaks by following the specific capacitance (\( C_s \)) Eq. 6.

\[
C_s = \frac{A}{2mk(V^2 - V)}
\]

(6)

whereas \( A = \) CV curve area, \( m = \) loaded quantity, \( k = \) scan rate (mV/s), \( \Delta V = \) is CV potential range.

Finally, it was carried out the bacterial identification process to know the bacterial species which are responsible for energy generation as well as remediation efficiency. On the completion of the operation, the anodes were washed with distilled water. It was scratched the biofilm from the surface of anodes by using the sterilized blades to carry out the serial dilution. The scratched biofilm was placed into the 10 mL distilled water in a falcon tube and \( 10^{-1} \) to \( 10^{-8} \) serial dilutions were performed. Next, 1.0 mL of each dilution was spread on the nutrient agar plates for mix culture growth.

On the growth of mixed culture, the selection of the pure culture was carried out based on their morphology. The selected pure culture bacterial species was further assessed by colony polymerase chain reaction (PCR) to amplify the 16 s rRNA sequence of the isolated bacteria DNA. A 27F forward primer and 1492R reverse primer were used for the amplification. The 16S rRNA sequences obtained were deposited in the GenBank (Umar et al. 2021).

**Different parameter optimizations**

Different parameters were considered in this study to optimize the performance of self-fabricated anode in presence
of 100 ppm Co(II) solution. First, pH was considered at different ranges such as 2, 3, 4, 5, 6, 7, 8, 9, 10 by using individual three fabricated anodes to measure the energy as well as remediation efficiency. The first 10 days reading (voltage generation and remediation efficiency) of each pH range was considered to formulate the hypothesis. Second, the temperature ranges from 20 to 35 °C was analyzed and reading was taken in 10 days of operation. The three electrodes were separately analyzed by each parameter range with Co(II) ions.

Results and discussion

Material characterizations of prepared anodes

To ensure the excellence of the physicochemical properties of the prepared materials, several characterizations were performed. Figure 1a showed the FTIR spectra of the GO, GO-ZnO, and GO-TiO2 composite. The GO spectrum depicted some peaks which clearly indicated that there are oxygen functional groups in the sample. For example, peak at 3450 cm⁻¹ referred to the presence of OH group, 1710 cm⁻¹, 1540 cm⁻¹, 1150 cm⁻¹, 1030 cm⁻¹ correspond to the presence of the C=O, sp²-hybridized C=C, C–OH stretching, and C–O vibrational stretching. These all-functional groups are oxygen-based, meaning there is a presence of oxygen between the graphitic layers of the GO. These peaks are attributed to carboxyl, carbonyl, and epoxy (Alamdari et al. 2019). The peak intensity of the OH group and epoxy groups seem to be decreased in the case of the GO-ZnO composite, it could happen due to the interaction of the GO sheet with ZnO particles. The GO sheets showed restacking during the composite formation which are certifying the excellency of the composite formation. The reduction in peak intensity indicated that the ZnO particles are successfully anchored on GO. The bands appearing between ~1000 cm⁻¹ to 1600 cm⁻¹ is corresponding to the presence of carboxyl and carbonyl groups in the GO-ZnO composite. Particularly, the peak at 1120 cm⁻¹ is associated with the Zn-C stretching bonding (Yaqoob et al. 2020c). It was found that there are some peaks below 500 cm⁻¹ which represent the ZnO bond. The variation or shifting of the peaks are showing the successful formation of the GO-ZnO composite. A similar effect in GO-TiO2 composite material was observed, there is also clear variation in peaks as compared to the plain GO. The peaks from 500 to 1000 cm⁻¹ are correspond to Ti–O–Ti bond. The peak at 1570 cm⁻¹ indicated the interaction of Ti–O–C in the composite. All FTIR peaks evidence corresponds to the successful synthesis of GO, GO-ZnO, and GO-TiO2 composite from biomass waste.

Figure 1b showed the XRD spectra of the prepared GO, GO-ZnO, and GO-TiO2 composite. In GO XRD spectra, the peak at (002) corresponds to the 2θ = 25°. The peak at 2θ = 25° is the primary stage of the carbon oxidation into graphite oxide. This peak confirmed that the carbonized carbon could be graphite-natured material successfully. On the completion of the hummer methods, the peak at (001) referred to the oxidation of the graphite oxide (Peng 2013). The (001) showed a 9.8° theta value which confirmed the presence of GO nature. Similarly, in the GO-ZnO composite, it was observed that several bands appeared such as (001), (002), (100), (101), (102), (110), and (112). The band except (001) corresponds to the presence of ZnO particles on the surface of the GO. According to the Yaqoob et al. (2020c), the peaks at 28.5°, 30.2°, 31.5°, 34.5°, 48.4°, 58.6°, and 68.9° are presenting the ZnO particles in the sample. Further, the peak at 2θ = 25° and 2θ = 27.5° are confirming the presence of TiO2 particles. These peaks are attributed to the presence of rutile and anatase tetragonal phase (Krishna et al. 2012). These peak appearances in the GO-TiO2 composite showed that the TiO2 is of a biphasic nature. During the formation of the composite, the reduction or variation of peaks were carried out e.g., the GO-TiO2 composite did not show the peak at 2θ = 9.8°. It means that the
composite format completely reduces the GO and converts it into graphene.

Raman analysis was carried out to study the defect disorders and bonding relation of the functional groups. Figure 1c showed the Raman studies of the GO, GO-ZnO, and GO-TiO2 composite. Generally, the Raman spectroscopy showed two bands G and D in the spectrum. The bands represent the C–C bond stretching. In GO, a band at 1575 cm\(^{-1}\) appeared due to the E\(_{2g}\) phonon of sp\(^2\) carbon atoms scattering at the Brillouin zone (Krishna et al. 2012). The band at 1350 cm\(^{-1}\) corresponds to the D band in GO which showed the presence of the oxygen functional group. Further, a bit of variation was found in the GO-ZnO composite due to π–π restacking of the GO during the formation of GO-ZnO composite. While peaks near ~ 440 cm\(^{-1}\) correspond to the ZnO particles in the sample. Moreover, the peaks at 395 cm\(^{-1}\), 480 cm\(^{-1}\), 1350 cm\(^{-1}\), and 1575 cm\(^{-1}\) are openly related to ZnO vibrational E\(_2\) state and defective carbon state. In GO-TiO2 composite spectra also showed peaks at 150 cm\(^{-1}\), 470 cm\(^{-1}\), 500 cm\(^{-1}\), and 650 cm\(^{-1}\). The TiO\(_2\) particle introduction showed variation in spectra and newly appeared peaks are assigned as E\(_g\), B1\(_g\), and A1\(_g\) + B1\(_g\). The newly appeared peaks showed the rutile and anatase phasic nature of the material.

UV-absorbance spectroscopy was performed to study the optical behaviour of the prepared material as shown in Fig. 2a. In GO spectra the peak at 240 nm is attributed to the sp\(^2\) carbon due to the π─π* transition state. This peak confirmed the presence of an oxygen functional group between the graphite layers. Similarly, during the formation of the GO-ZnO composite, it found an extra peak at 365 nm which clearly showed the presence of ZnO particles. This might have appeared due to the fundamental absorption band gap of the ZnO. In GO-ZnO the peak of sp\(^2\) carbon showed bit variation and appeared at 237 nm. Similarly, the GO-TiO2 composite showed peaks at 234 nm and 350 nm which also verified the successful attachment of TiO\(_2\) particles. According to the UV curves, both composites showed a bit of shifting of the band which clearly shows the excellent formation of composite material (Alamdari et al. 2019). Further, in the present study, the most important is the conductivity of the material. The less band gap exhibited more conductivity. The band gap was calculated by Eq. 7.

\[
E_g = \frac{hc}{\lambda}
\]

where, \(h\) = Planck’s constant i.e. \(6.626 \times 10^{-34}\) Js; \(\lambda\) = wavelength; \(c\) = velocity of light (\(3 \times 10^8\) ms\(^{-1}\)); and 1 eV = \(1.6 \times 10^{-19}\) Joules. The measured bandgap of the GO, GO-ZnO, GO-TiO\(_2\) composite was 5.1 eV, 3.40 eV, 3.54 eV. The results showed that the metal oxide introduction improved the conductivity of biomass-derived GO.

TGA analysis of GO, GO-ZnO, and GO-TiO\(_2\) composite were carried out. Thermal conductivity is also an important aspect as a material for anode application. The biomass-derived material and its modification with metal oxides delivered an excellent performance as shown in Fig. 2b. In a broad sense, three materials depicted excellent thermal stability below 100 °C. The GO sample showed the first reduction after 100 °C which is due to the reduction of oxygen molecules. The initial weight loss at 200 °C was less than 20% in GO. The GO showed 57% thermal stability at a very high temperature (600 °C). As compared to plain GO, the modified GO-ZnO composite showed excellent stability, the first weight loss was less than 10% at 200 °C while it showed more than 80% stability at 600 °C. The GO-TiO\(_2\) composite also showed more than 70% stability at 600 °C and the first weight loss was less than 15% above 200 °C. TGA spectra of GO, GO-ZnO, and GO-TiO\(_2\) composite showed that the metal oxide introduction improved the thermal stability of

Fig. 2  a UV-absorbance and b TGA spectra of GO, GO-ZnO and GO-TiO\(_2\) composite
the GO material (Umar et al. 2019). Hence, the biomass-derived material can be used as anode in a high temperature environment without losing its stability.

Moreover, the XPS spectra of GO, GO-ZnO, and GO-TiO$_2$ composite are shown in Fig. 3 to study the chemical states of the elements. Particularly, the interaction of ZnO and TiO$_2$ particles with the GO sheet during solvothermal was assessed by XPS. First, the GO deconvoluted carbon 1 s (C 1 s) spectrum showed three major peaks at 285.0 eV, 287.1 eV, and 289.3 eV. These correspond to the presence of C–C, C–O, and C=C in the sample (Al-Gaashani et al. 2019). Similarly, the GO-ZnO composite C 1 s spectrum indicated the presence of C=O, C–O, and C=C but with little variation in binding energy. The intensity of C=O, C–O, and C=C peaks are reduced in the composite while the deconvoluted peaks intensity are changed. It might be due to the strong interaction developed between the GO and ZnO during the solvothermal method. The same effect was also observed in the GO-TiO$_2$ composite. The peak at 284.1 eV, 285.7 eV, and 288.5 eV also indicated the presence of C=O, C–O, C=C, C(O)OH groups. The intensity of peaks also decreased in GO-TiO$_2$ due to the interaction of GO and TiO$_2$ particles. Later, after the deconvolution, the oxygen 1 s (O 1 s) spectrum of the prepared material is also illustrated in Fig. 3. The GO showed the four functional groups in the spectra such as C–O–C, C=O, O–C=O, and C–OH. These groups are indicated by the peak at 533.1 eV, 531.0 eV, 530.9 eV, and 532.5 eV. While in the GO-ZnO composite, the peaks appeared at 530 eV, 531 eV, 533 eV which correspond to the presence of ZnO with oxygen interaction. Due to the strong interaction, the shifting of the peaks was observed in the GO-ZnO composite O1s spectrum (Li et al. 2015). Similarly, the GO-TiO$_2$ composite showed the Ti-2p spectra which clearly showed the variation in the peaks intensity which verifies the relation of TiO$_2$ particles with GO. The peak 463.08 eV showed the Ti–O–Ti interaction, the composite which was successfully developed during the solvothermal method.

SEM studies were carried out for prepared materials to evaluate the morphological characteristics of the material. Figure 4a–c are the SEM images of the GO, GO-ZnO, and GO-TiO$_2$ composite which depict the surface morphology image. SEM images of GO showing that the particles are not uniform, and they are scattered on the surface. Usually, the non-uniform scattered particles exhibited less than 100 nm as stated by Umar et al. (2015). While GO-ZnO composite showed a smooth surface with uniform distribution of ZnO particles on the surface. During the formation of the GO-ZnO composite, it might be possible that ZnO size was reduced to nanometres. A similar effect was observed in the GO-TiO$_2$ composite that the distribution of the TiO$_2$ particles is very uniform and regular. Hence, according to SEM images, the average size of the GO-ZnO composite is between 20 and 50 nm and the GO-TiO$_2$ composite showed
20–40 nm. Therefore, the composite can carry more electrochemical performance in energy transportation applications.

Additionally, the SEM coupled EDX technique was also performed to study the elemental composition of the material as shown in Fig. S2. EDX spectra of GO showed a 26.67% oxygen-based functional group while 66.71% is carbon-natured. The XRD peak (001) already confirmed that the carbon-nature material belongs to the GO derivatives. The presence of an oxygen functional group proved the excellency of the prepared GO. In EDX spectra of the GO-ZnO composite showed the reduction of the oxygen functional group. It might have occurred due to the strong interaction of ZnO and GO sheets. The GO-ZnO composite showed 44.67% carbon nature, 40.96% ZnO, and 14.37% oxygenated group. Similarly, GO-TiO2 composite showed 14.90% oxygen-based, 30.98% carbon natured, and 54.11% Ti. During the formation of composite, we noticed there is a minor variation in composite compositions. It might be an indication of the successful formation of composite materials.

To study the surface heterogeneity and particle size of the prepared material, TEM was performed. Figure 4d–f shows the TEM images of GO, GO-ZnO, and GO-TiO2 composite. In the GO TEM image, a transparent sheet was observed with accumulated carbon particles on the surface of the GO sheet. The folded edges and elastic corrugation demonstrate the intensity of GO. While in the case of the GO-ZnO composite irregular ZnO particles are found on the surface of transparent sheets. GO-ZnO composite TEM images showed an irregular distribution of ZnO particles. A similar effect was observed in the case of the GO-TiO2 composite. The bit variation in the surface of GO-TiO2 composite was observed. It means that the formation of composite brings some variations on the surface morphology. It is a good indication that metal oxide anchored is very excellent with GO. Additionally, AFM studies were carried out to study surface roughness. According to observation, the AFM images of the prepared materials are very smooth and have fine roughness. The prepared material can offer good compatibility with the bacterial species. AFM images of GO, GO-ZnO, and GO-TiO2 composite are shown in Fig. S3.

**Electrochemical characterizations of prepared anodes**

The electrochemical behaviour of the prepared anodes was assessed briefly in the present study. The operation was operated for 45 days with prepared anodes. The voltage trend was recorded with the presence of the fixed external resistance (1000 Ω) as shown in Fig. 5a. The GO anode showed the maximum voltage (155 mV) on day 16 while GO-ZnO composite offered 320 mV on day 21 and GO-TiO2 composite anode offered 271 mV on day 22. The GO-ZnO composite delivered the highest voltage generation trend as compared to the others. On day 16 the GO-ZnO composite offered 220 mV which is still higher than GO. To ensure the maximum voltage trend, each anode was operated for a minimum of three cycles with continued operation and supply of organic substrate. The GO anode showed maximum voltage (155 mV) on day 16 while GO-ZnO composite offered 320 mV on day 21 and GO-TiO2 composite anode offered 271 mV on day 22. The GO-ZnO composite delivered the highest voltage generation trend as compared to the others. On day 16 the GO-ZnO composite offered 220 mV which is still higher than GO. To ensure the maximum voltage trend, each anode was operated for a minimum of three cycles with continued operation and supply of organic substrate. The GO anode offered maximum voltage on day 16 in the first cycle then it gradually reduced. During the 2nd and 3rd cycles, the GO did not offer more voltage efficiency than the first cycle. In the end, the continued reduction in the voltage might be an indication of reaction completion. The bacterial species might be starting the death phase. During each cycle when gradual reduction starts it means it is a turning point of the Co(II)
ion into Co$_{3+}$. A similar effect was observed in GO-ZnO and GO-TiO$_2$ composite anode. The GO-ZnO composite and GO-TiO$_2$ composite anode also operated for three cycles, but they offered maximum on the first cycle rather than 2$^{nd}$ and 3$^{rd}$. Additionally, the delivered maximum PD and CD of GO anode in the closed circuit was 0.002356 mW/m$^2$ and 20.39474 mA/m$^2$. While GO-ZnO composite offered 2.2 times higher PD and CD than plain GO. Moreover, the GO-TiO$_2$ composite anode also delivered 1.5 times higher PD and CD efficiency than plain GO. Among all, the GO-ZnO composite showed maximum efficiency in electron transportation. It might be due to the introduction of ZnO particles which improved the GO properties more efficiently than the TiO$_2$ introduction. So far, the GO-TiO$_2$ composite anode is also better than the plain GO anode. The introduction of metal oxide in GO indicated the difference in voltage trend.

The polarization behaviour of each operation was studied to evaluate the current-resistance relationship. Each anode (GO, GO-ZnO, GO-TiO$_2$ composite) was assessed through variation of external resistance from 10 kΩ to 150 Ω. Generally, the higher external resistance offered more potential stability than low external resistance. While at high external resistance the current generation was low due to the high external electronic resistance as compared to inside the cell. Similarly, the low external resistance increased the voltage generation, but the stability was very low which could not offer a precise value. Furthermore, the voltage destabilization was relatively faster than high external resistances. Some previous studies described a similar power trend (Mateo et al. 2018; Sarma and Mohanty 2018). During the operation when voltage gradually started reduction, the polarization behaviour was observed by varying the different external resistances. The measurement started from 10 kΩ to 150 kΩ. A decreasing trend of voltage was observed from higher to lower resistance. The GO anode showed the decreasing voltage trend such as 10 kΩ (370 mV), 9 kΩ (355 mV), 8 kΩ (340 mV), 7 kΩ (320 mV), 6 kΩ (300 mV), 5 kΩ (280 mV), 4 kΩ (260 mV), 3 kΩ (230 mV), 2 kΩ (190 mV), 1.5 kΩ (168 mV), 1 kΩ (140 mV), 750 Ω (120 mV), 560 Ω (102 mV), 450 Ω (90 mV), 300 Ω (70 mV), 250 Ω (50 mV), 200 Ω (30 mV), 100 Ω (10 mV), 50 Ω (5 mV), 10 Ω (1 mV).
and 150 Ω (45 mV). During the voltage generation trend, we observed maximum PD (0.148 mW/m²) at external 1 kΩ resistance while the internal resistance was 2210 Ω. The GO-ZnO composite delivered voltage was at 660 mV (10 kΩ), 634 mV (9 kΩ), 625 mV (8 kΩ), 620 mV (7 kΩ), 610 mV (6 kΩ), 600 mV (5 kΩ), 587 mV (4 kΩ), 535 mV (3 kΩ), 463 mV (2 kΩ), 435 mV (1.5 kΩ), 390 mV (1 kΩ), 330 mV (750 Ω), 265 mV (560 Ω), 230 mV (450 Ω), 165 mV (300 Ω) and 86 mV (150 Ω). Among all resistance, the highest PD was 1.15 mW/m² at 1 kΩ external resistance while the measured internal resistance was 840 Ω. While GO-TiO₂ composite anode showed 599 mV (10 kΩ), 590 mV (9 kΩ), 580 mV (8 kΩ), 569 mV (7 kΩ), 560 mV (6 kΩ), 554 mV (5 kΩ), 529 mV (4 kΩ), 480 mV (3 kΩ), 410 mV (2 kΩ), 368 mV (1.5 kΩ), 310 mV (1 kΩ), 273 mV (750 Ω), 220 mV (560 Ω), 185 mV (450 Ω), 137 mV (300 Ω) and 77 mV (150 Ω). The observed maximum PD was 0.75 mW/m² at external resistance 750 Ω while internal resistance was 1035 Ω. Among the three electrodes, the GO-ZnO composite anode showed more voltage stabilization and a better electron transfer rate than others due to the high conductivity of ZnO. The GO offered a maximum of 39.47 mA/m² CD, the GO-ZnO composite anode offered a maximum of 75.43 mA/m² CD, while the GO-TiO₂ composite anode showed a maximum of 67.54 mA/m² CD.

Additionally, the present study was well supported by carrying out the CV and EIS analyses of the prepared anode. The CV was measured at different time intervals during each operation of the prepared anode (GO, GO-ZnO, GO-TiO₂ composite anode). In CV analysis Pt wire was used as a counter electrode while Ag/AgCl was as a reference electrode. Figure 6a showed the CV curves with reverse scan (RS) and forward scan (FS). The FS rate at different time interval was 2.0 × 10⁻⁶ µA (day 10), 3.8 × 10⁻⁶ µA (day 20), 6.0 × 10⁻⁶ µA (day 30), 1.0 × 10⁻⁵ µA (day 45) and RS was – 1.9 × 10⁻⁶ µA (day 10), – 2.8 × 10⁻⁶ µA (day 20), – 3.1 × 10⁻⁶ µA (day 30), – 6.0 × 10⁻⁶ µA (day 45). Similarly, in GO-ZnO the FS rate was 0.4 × 10⁻⁵ µA (day 10), 0.8 × 10⁻⁵ µA (day 20), 2.0 × 10⁻⁵ µA (day 30), 3.9 × 10⁻⁵ µA (day 45) and RS was – 0.1 × 10⁻⁵ µA (day 10), – 0.2 × 10⁻⁵ µA (day 20), – 0.6 × 10⁻⁵ µA (day 30), – 1.0 × 10⁻⁵ µA (day 45) as shown in Fig. 6b. While the Fig. 6c showed the GO-TiO₂ composite anode FS rate = 5.0 × 10⁻⁶ µA (day 10), 1.0 × 10⁻⁵ µA (day 20), 1.7 × 10⁻⁵ µA (day 30), 3.9 × 10⁻⁵ µA (day 45) and RS was – 0.1 × 10⁻⁵ µA (day 10), – 0.2 × 10⁻⁵ µA (day 20), – 0.6 × 10⁻⁵ µA (day 30), – 2.1 × 10⁻⁵ µA (day

![Fig. 6](image-url) CV curves of a GO anode b GO-ZnO composite anode c GO-TiO₂ composite anode d Nyquist plots (EIS) of prepared anodes

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According to the observation, the GO offered a high FS rate on day 45 and RS was maximum on day 45. While the GO-ZnO composite delivered a high FS and RS rate on day 45. The GO-TiO₂ composite also showed a high FS and RS rate on day 10. The FS and RS rate indicated the speed of the reduction and oxidation during the operation, and it was found that in the beginning, the rate of oxidation/reduction was high. With the passage of time, it starts reducing the efficiency due to the completion of metal reduction or bacterial life cycle. To analyze the GO oxidation = E oxidation and reduction, E oxidation and E reduction peak of CV, it was recorded as the day 10 (0.60 V - E oxidation and - 0.59 V - E reduction), day 20 (0.64 V - E oxidation and - 0.61 V - E reduction), day 30 (0.81 V - E oxidation and - 0.62 V - E reduction), day 45 (0.85 V - E oxidation and - 0.8 V - E reduction). Similar, the GO-ZnO showed on day 10 (0.78 V - E oxidation and - 0.79 V - E reduction), day 20 (0.85 V - E oxidation and - 0.80 V - E reduction), day 30 (0.78 V - E oxidation and - 0.81 V - E reduction), day 45 (0.83 V - E oxidation and - 0.82 V - E reduction). The GO-TiO₂ composite anode showed on day 10 (0.79 V - E oxidation and - 0.79 V - E reduction), day 20 (0.79 V - E oxidation and - 0.80 V - E reduction), day 30 (0.82 V - E oxidation and - 0.81 V - E reduction), day 45 (0.84 V - E oxidation and - 0.81 V - E reduction). It was found that the electrodes showed the excellent performance to support the oxidation/reduction reaction during the operation. The higher oxidation rate might be due to the highly efficient (oil palm trunk sap) organic substrate. As oxidation reaction rate increases the reduction was also improved and achieved the metal maximum reduction limit. Among all electrodes, the GO-ZnO showed better efficiency which might be due to the high conductivity of anode material. Previously several studies followed this trend (Xu et al. 2017; Yaqoob et al. 2021c). For example, Yaqoob et al. (2021b) studied the biomass-derived waste GO anodes to remediate the Pb²⁺ ions from wastewater, and they explained the oxidation and reduction via these channels. The Cₗ values were calculated by using the CV curves, this study was done to analyze the efficiency of biofilm or formation rate of biofilm during different time intervals as presented in Table 2. The Cₗ results showed an increasing trend in the beginning but after a certain point, it showed a lower Cₗ value. The increasing trend corresponds to the formation and stability of the biofilm and the decreasing trend corresponds toward the mortality of the bacterial species. The present study showed the excellent growth and stability of biofilm within 30 days. Several studies have also followed a similar trend to justify the strength of biofilm (Hong et al. 2011).

EIS- Nyquist plots were plotted in Fig. 6d to analyze the charge transfer resistance of the prepared anodes by employing the fuel cell circuit. The GO curve shows the semi-bent curve at a higher frequency which shows the moderate rate of electron transportation while GO-ZnO and GO-TiO₂ showing bent lines at low frequency which are indicating the higher electron transfer efficiency than GO due to stable capacitive behaviour (Hung et al. 2019). The Nyquist curves showed that the composite-based anodes delivered more electronic mobility with poor charge resistance toward the electrolytes. The reason for the poor electronic mobility of GO was the presence of high internal resistance (2210 Ω) than other composite anodes. The GO-ZnO even showed more activity than the GO-TiO₂ anode due to less internal resistance. The low charge resistance was found at low internal resistance which led to high electron mobility in operation. The introduction of metal oxide significantly reduces the internal resistance toward electrolytes by providing a high conductivity medium for electron transportation.

### Comparative profile of prepared electrode durability with previous studies

The durability studies of the prepared anodes were briefly discussed in the present work to prove that the material can work for the long term at an industrial scale. The durability performance was analyzed by operating each reaction for 45 days with continuous operating three cycles. Figure 5a showed the voltage trend of each prepared anode until 45 days and three cycles were operated at fixed external load (1000 Ω). The GO anodes delivered 0.155 mA while the GO-ZnO composite anode offered 0.322 mA and the GO-TiO₂ composite delivered 0.271 mA on the completion of the first cycle. Similarly, the 2nd and 3rd cycles of GO, GO-ZnO composite, and GO-TiO₂ composite anode offered lower current efficiency than the first cycle. It might be due to (i) the utilization of fresh incubation sources in the beginning (ii) the biofilm was more active in the beginning but with the passage of time, it decreases the efficiency due to mortality of bacteria species (Min and Logan 2004). According to the recorded voltage trends for 45 days it was noticed that the prepared anodes showed electron transportation efficiency in the 2nd and 3rd cycles. For example, GO offered 0.118 mA (2nd cycle), 0.111 mA (3rd cycle), GO-ZnO composite delivered 0.300 mA (2nd cycle), 0.199 mA (3rd cycle) and GO-TiO₂ composite anode delivered 0.340 mA (2nd cycle), 0.143 mA (3rd cycle). It means that the prepared anodes still

| Measurement time interval (days) | Capacitance (F/g) |
|----------------------------------|------------------|
|                                 | GO anode         | GO-ZnO composite anode | GO-TiO₂ composite anode |
| 10                               | 0.00004          | 0.00001                 | 0.00014                 |
| 20                               | 0.00013          | 0.00004                 | 0.00024                 |
| 30                               | 0.00017          | 0.00038                 | 0.00005                 |
| 45                               | 0.00003          | 0.00007                 | 0.00004                 |
perform active until 45 days to transport the electrons. In a broad sense, it found that the GO-ZnO composite anode offered more efficiency than others which might be due to the material conductivity. However, in terms of durability, the prepared anodes offer high durability and stability for a minimum of 45 days. On the completion of the operation, the visualization test was also carried out to analyze the stability and it was found still active and powerful. In Fig. 5b–d the polarization behaviour of each anode was studied. The variation in external resistance from 10 kΩ to 150 Ω may be led to disturbing the biofilm morphology but the electrode stability and durability resist this effect to save the biofilm stability. During analysis, the maximum CD offered by GO was 39.47 mA/m² (CD), GO-ZnO composite anode (75.43 mA/m²), and GO-TiO2 composite anode (67.54 mA/m²). Several studies such as CV, SEM images of bacterial species, and remediation efficiency demonstrate that the prepared material offers excellent durability and stability. In the later section, different parameter optimization was also carried out in the present study to analyze the performance of prepared anodes in different environmental conditions. A similar trend to justify the electrode stability and durability is already reported by several researchers (Kirubaharan et al. 2019; Senthilkumar et al. 2019). For example, recently Senthil et al. (2020) studied the waste-derived three-dimensional carbon aerogel/ ceria-nitrogen doped reduced graphene oxide anode. They reported 360 h durability with fixed external resistance and followed a similar trend as was explained above. Additionally, a comparative summary of our electrode durability with few earlier reported electrodes in MFCs is shown in Table 3.

### Biological characterizations

#### Remediation efficiency

Several studies showed that the MFCs is one of the most suitable technique to remediate the heavy metals without any energy consumption or expense (Yaqoob et al. 2020b). The present study was carried out to remediate the Co(II) by using the prepared anode separately. The performance of Co(II) remediation efficiency is stated in Table 4. In the case of the GO, the remediation efficiency increases gradually. During the operation, the MFCs was operated for three cycles to achieve maximum remediation as well as energy efficiency. On day 10, the remediation efficiency was 23.50% but with the passage of time, the rate is going to be high. It might be due to the formation of active biofilm around the surface of the anode. At the 3rd cycle, it was noticed that the voltage trend decreased gradually, and a similar effect was also observed in remediation efficiency. After 40 days the remediation efficiency rate was low. This is an indication

### Table 3 Comparative summary of electrode durability and efficiency

| Anode electrode                     | Size of electrode | Surface area of anode | Inoculation source | Dura-    | Current density (mA/ m²) | References                  |
|-------------------------------------|-------------------|-----------------------|-------------------|---------|-------------------------|-----------------------------|
| Fe₃O₄/AC₁/SSM²                      | 4 cm × 3 cm       | –                     | Pre-acclimated effluent | 5       | 1.9                     | Peng et al. (2013)           |
| NGNS³                              | 1 cm × 1.5 cm     | –                     | Escherichia coli  | 4.1     | 6300                    | Kirubaharan et al. (2015)    |
| CP⁵/HAPNW⁵                         | 3.14 cm × 2.5 cm  | 88.5 cm²              | Shewanella Loihica | 2.2     | 2.9                     | Zhao et al. (2011)           |
| AC₁/PANI⁹/D-CSA⁷/GF₈               | Length:100–200 nm, Diameter: 80 nm | –                     | Domestic wastewater | 6.2     | 110                     | Scott et al. (2007)          |
| CNT⁹/KCC¹⁰                        | 6 cm × 3.5 cm     | 208.81 cm²             | Wastewater         | 8–9     | 65                      | Tsai et al. (2009)           |
| Graphene/PEDOT¹¹/CP¹⁴              | 2 cm × 2.5 cm     | 10 cm²                | Escherichia coli | 24      | 3.59                    | Wang et al. (2013)           |
| PEI¹²/GF⁸                         | –                 | 7 cm²                 | Saccharomyces cerevisiae | 5       | -                       | Christwardana et al. (2018)  |
| Fe₃O₄/CP⁴                        | 2.5 cm × 4.5 cm   | 22.5 cm²              | Domestic wastewater | 16.5    | -                       | Kim et al. (2005)            |
| GO¹³                              | 7.5 cm × 1.2 cm   | 71.0 cm²              | Synthetic wastewater | 40    | 24.56                   | Yaqoob et al. (2021c)        |
| GO-PANI¹⁴                         | 7.5 cm × 1.2 cm   | 71.0 cm²              | Synthetic wastewater | 40    | 87.71                   | Yaqoob et al. (2021c)        |
| Lignin-derived GO                  | 8.0 cm × 1.3 cm   | 76.0 cm²              | Synthetic wastewater | 45    | 39.47                   | Present work                 |
| Lignin-derived GO-ZnO composite   | 8.0 cm × 1.3 cm   | 76.0 cm²              | Synthetic wastewater | 45    | 75.43                   | Present work                 |
| Lignin-derived GO-TiO₂ composite  | 8.0 cm × 1.3 cm   | 76.0 cm²              | Synthetic wastewater | 45    | 67.54                   | Present work                 |

¹Activated carbon; ²Stainless steel meshes; ³N doped graphene nanosheets; ⁴Carbon paper; ⁵Hydroxylated and aminated polyaniline nanowire; ⁶Polyaniline; ⁷D-camforsulfonic Acid; ⁸Graphite felt; ⁹Carbon nanotubes; ¹⁰Carbon cloth; ¹¹Poly(3,4-ethylenedioxythiophene); ¹²Polyethyleneamine; ¹³Graphene oxide; ¹⁴Polyaniline
of maximum remediation of Co(II) ions. In the GO-ZnO composite, the remediation efficiency was higher than GO. It might be due to the introduction of metal oxide (ZnO) which showed more biocompatibility toward the bacterial species. On day 10 the rate was 26% which increased gradually and reached 91% on day 45. The GO-TiO$_2$ composite anode offered 88.45% which is higher than GO but it was a bit lower than the GO-ZnO composite. It might be due to the higher physicochemical properties of ZnO than TiO$_2$. Further, to scale the MFCs at an industrial scale for remediation of heavy metals is preferable with some advancement in environmental factors (Zhang et al. 2016). According to the literature, there is no report on the remediation of Co (II) from synthetic wastewater via MFCs, but several studies also reported on remediation of other metals such as chromium, nickel, lead, cadmium, etc. (Kumar et al. 2021; Wu et al. 2018; Yaqoob et al. 2021c).

### Bacterial identification

In biological characterization, the bacterial identification from biofilm of each anode was carried out on the completion of the operation. Isolation and identification of the bacteria obtained from prepared anodes as shown in Table 5. In each GO anode, it was found almost the same bacteria species. The major bacteria found was determined as *Klebsiella pneumoniae* sp. and *Enterobacter* sp. Both this bacteria strain could be responsible for electron transfer as well as reduction of Co(II) to Co$_{(s)}$. Previous studies have proved that these two species are exoelectrogens and capable of reducing the metal ions (Kumar et al. 2021; Wang et al. 2020; Yaqoob et al. 2020b). Zhang et al. (2008) found the *Klebsiella pneumoniae* sp. strain on the surface of the anode and reported 151.11 mW/m$^2$ power density. They are mentioned that the species is active exoelectrogens and transfer the electrons via conductive pili. Uddin et al. (2020) broadly reviewed the reduction mechanism of the metals through different bacterial species. They stated that *Enterobacter* sp. and *Klebsiella pneumoniae* sp. is the most effective bacterial species to degrade the heavy metals from a high toxic state to a less toxic state. For the GO-ZnO composite anode, *Bacillus* sp. and *Lysinibacillus* sp. were the dominant strain found on the surface of the GO-ZnO anode. These strains are also considered exoelectrogens which can degrade the metal ions from wastewater. Treesubsuntorn et al., (2019) found the *Bacillus* species strains during their 120 days operation. They recorded the 20–35 mW/m$^2$ power density. They stated that the *Bacillus* species strains are responsible for energy generation and metal degradation. Nandy et al. (2013) also found the *Lysinibacillus* sp. on the surface of the anode and they recorded 85 mW/m$^2$ power density. Further Mathivanan et al. (2016) found *Lysinibacillus* sp. for reduction of copper and cadmium from wastewater. GO-TiO$_2$ composite anode also shows the presence of *Bacillus* sp. on the surface. It means that the incubation

### Table 4 Trend of remediation efficiency of Co(II) in present study

| Prepared anodes      | Size of anodes | Surface area (cm$^2$) | Incubation source | Initial concentration (ppm) | Target pollutant | Operational time (days) | Remediation efficiency (%) of Co(II) |
|----------------------|----------------|------------------------|-------------------|------------------------------|-----------------|------------------------|-------------------------------------|
| GO                   | 8 cm × 1.3 cm  | 76                     | Synthetic wastewater | 100                         | Co(II)          | 0                      | 0.00                               |
|                      |                |                        |                    |                              |                 | 10                     | 23.50                             |
|                      |                |                        |                    |                              |                 | 20                     | 44.30                             |
|                      |                |                        |                    |                              |                 | 30                     | 60.20                             |
|                      |                |                        |                    |                              |                 | 40                     | 78.10                             |
|                      |                |                        |                    |                              |                 | 45                     | 80.10                             |
| GO-ZnO composite     | 8 cm × 1.3 cm  | 76                     | Synthetic wastewater | 100                         | Co(II)          | 0                      | 0.00                               |
|                      |                |                        |                    |                              |                 | 10                     | 26.00                             |
|                      |                |                        |                    |                              |                 | 20                     | 54.35                             |
|                      |                |                        |                    |                              |                 | 30                     | 72.00                             |
|                      |                |                        |                    |                              |                 | 40                     | 85.00                             |
|                      |                |                        |                    |                              |                 | 45                     | 91.00                             |
| GO-TiO$_2$ composite | 8 cm × 1.3 cm  | 76                     | Synthetic wastewater | 100                         | Co(II)          | 0                      | 0.00                               |
|                      |                |                        |                    |                              |                 | 10                     | 25.00                             |
|                      |                |                        |                    |                              |                 | 20                     | 45.50                             |
|                      |                |                        |                    |                              |                 | 30                     | 65.10                             |
|                      |                |                        |                    |                              |                 | 40                     | 81.90                             |
|                      |                |                        |                    |                              |                 | 45                     | 88.45                             |
source carries a direct effect on the growth of bacteria. Almost all anodes have similar species because the incubation source was similar. According to previous literature, it is possible to create a hypothesis that the found bacterial species are responsible for the reduction of Co(II) to Co and energy generation. The energy efficiency was different in the three electrodes which might be due to other factors such as conductivity, biocompatibility, etc. Further, the

Table 5 Summery of identified bacterial species from anode biofilm

| Accession number1(6S rRNA Gene) | Bacterial species                          | Identity (%) | Query cover (%) |
|---------------------------------|--------------------------------------------|--------------|-----------------|
| GO anodic bacterial species     |                                            |              |                 |
| NR_117683.1                     | Klebsiella pneumoniae strain DSM 30,104    | 98.47        | 98              |
| NR_113072.1                     | Klebsiella pneumoniae strain NBRC 14,940  | 98.22        | 98              |
| NR_113240.1                     | Klebsiella pneumoniae strain JCM 1662     | 98.22        | 98              |
| NR_119278.1                     | Klebsiella pneumoniae strain ATCC 13,883  | 98.22        | 98              |
| NR_117686.1                     | Klebsiella pneumoniae strain DSM 30,104    | 98.22       | 98              |
| NR_044978.1                     | Enterobacter cloacae subsp. dissolvens strain LMG 2683 | 97.36 | 98 |
| NR_118011.1                     | Enterobacter cloacae subsp. dissolvens strain ATCC 23,373 16 | 97.20 | 98 |
| NR_117547.1                     | Enterobacter soli ATCC BAA-2102 strain LF7 | 97.11       | 98              |
| NR_118106.1                     | Citrobacter amalonaticus strain LMG 7873  | 96.94        | 98              |
| NR_104823.1                     | Citrobacter amalonaticus strain CECT 863  | 96.94        | 98              |
| NR_114108.1                     | Klyuyera cryocrescens strain NBRC 102,467 | 96.86        | 98              |
| NR_104940.1                     | Atlantibacter hermannii strain CIP 103,176 | 96.85       | 98              |
| NR_119278.1                     | Klebsiella pneumoniae strain ATCC 13,883  | 98.22        | 98              |
| NR_116275.1                     | Enterobacter bugandensis strain 247BMC    | 96.77        | 98              |
| NR_159317.1                     | Kosakonia radicincitans DSM 16,656        | 96.34        | 98              |
| GO-ZnO composite anodic bacterial species |                              |              |                 |
| NR_157736.1                     | Bacillus tropicus strain MCCC 1A01406     | 97.06        | 99              |
| NR_157732.1                     | Bacillus nitratireducens strain MCCC 1A00732 | 97.08 | 99 |
| NR_157730.1                     | Bacillus luti strain MCCC 1A00359         | 97.08        | 99              |
| NR_157729.1                     | Bacillus albus strain MCCC 1A02146        | 97.08        | 99              |
| NR_157734.1                     | Bacillus paramycoideis strain MCCC 1A04098 | 96.99      | 99              |
| NR_074540.1                     | Bacillus cereus strain LF7                | 96.26        | 98              |
| NR_113266.1                     | Bacillus cereus strain JCM 2152           | 96.99        | 99              |
| NR_152692.1                     | Bacillus wiedmannii strain FSL W8-0169    | 96.90        | 99              |
| NR_157728.1                     | Bacillus paranthracis strain MCCC 1A00395 | 96.72        | 99              |
| NR_041378.1                     | Bacillus ginsengihumi strain Gsoil 114    | 91.71        | 99              |
| NR_024697.1                     | Bacillus mycoides strain DSM 11,821       | 96.46        | 99              |
| NR_114581.1                     | Bacillus thuringiensis strain ATCC 10,792 | 96.63        | 99              |
| NR_115848.1                     | Virgibacillus xinjiangensis strain SL6-1  | 82.84        | 91              |
| NR_042072.1                     | Lysinibacillus fusiformis strain DSM 2989 | 82.334       | 95              |
| NR_112628.1                     | Lysinibacillus fusiformis strain NBRC 15,717 | 82.334      | 95              |
| GO-TiO2 composite anodic bacterial species |                              |              |                 |
| NR_157735.1                     | Bacillus proteolyticus strain MCCC 1A00365 | 99.39     | 99              |
| NR_157731.1                     | Bacillus mobilis strain MCCC 1A05942      | 99.39        | 99              |
| NR_157728.1                     | Bacillus paranthracis strain MCCC 1A00395 | 99.39        | 99              |
| NR_152692.1                     | Bacillus wiedmannii strain FSL W8-0169    | 99.39        | 99              |
| NR_115526.1                     | Bacillus cereus strain IAM 12,605         | 99.39        | 99              |
| NR_043403.1                     | Bacillus thuringiensis strain IAM 12,077  | 99.39        | 99              |
| NR_101761.1                     | Bacillus toyonensis strain BCT-7112       | 99.39        | 99              |
| NR_114581.1                     | Bacillus thuringiensis strain ATCC 10,792 | 99.39        | 99              |
| NR_157732.1                     | Bacillus nitratireducens strain MCCC 1A00732 | 99.30   | 99 |
| NR_157729.1                     | Bacillus albus strain MCCC 1A02146        | 99.30        | 99              |
| NR_157734.1                     | Bacillus paramycoideis strain MCCC 1A04098 | 99.22     | 99              |
limited number of bacterial species is a good indication for effective remediation of metal-based pollutants from wastewater.

**Scanning electron microscope studies of electrode surface**

Additionally, the SEM analyses were performed for GO, GO-ZnO, and GO-TiO₂ composite anodes and used graphite cathodes to evaluate the bacterial morphology on the surface of anodes. According to Fig. 7a–c, the SEM images of GO, GO-ZnO, and GO-TiO₂ composite anode showed quite similar morphology on the surface anode. In-depth, the SEM image of GO-ZnO and GO-TiO₂ composite anode is almost similar in morphology. This is an indication that there are almost similar species strains present. This similar morphology already proved in our bacterial identification process that it was found almost similar bacterial species strain as shown in Table 5. Figure 7d–f showed the SEM image of the cathode electrodes which are used with prepared anodes. They also showed some bacterial species colonies on the surface while the anode showed very dense clusters of bacteria. All anodes SEM images showed a tube or rod-shaped morphology which is most dominant in the images. It is an indication that present bacterial species have conductive pili. Conductive pili are filamentous structures/ a rod shape wires, bacteria use these pili to transfer the electrons from cell to anode electrode (Serrà et al. 2021). This is a strong and direct interaction between the bacteria cell and the anode surface. Many studies are present which showed that the conductive pili can transfer the electrons efficiently from bacterial cells to anode surface (Guang et al. 2020; Lovley 2017; Reimers et al. 2017). Additionally, by referring to this study it can assume that the dense growth of biofilm is an indication of good biocompatibility of the prepared anodes toward living organisms. Recently, according to Fadzli et al. (2021) the dense growth of bacterial species on the surface of electrodes indicated that the electrode material was not toxic to the bacterial population. The SEM images of prepared anodes showed very good biofilm and dense bacterial species which is proving that prepared anodes do not have toxicity effects against the bacterial activities. Hence, the prepared anodes are highly biocompatible for long-term studies.

**Mechanism of electron generation/transfer and reduction of Co(II) in present study**

To understand the reduction mechanism of metal, we need to study the energy generation principle. In MFCs, the organic substrate is oxidized by bacterial species which serve as biocatalysts in operation. Several bacterial groups can generate the electrons and protons during their respiration activities. The most-reported species are *Rhodofexax ferrireducens*, *E. coli*, *Geobacter* spp. *Clostridium*

![Fig. 7 SEM images of (a, d) GO-anode Vs graphite-cathode (b, e) GO-ZnO anode Vs graphite cathode (c, f) GO-TiO₂ anode Vs graphite cathode](image)
butyricum, Bacillus, Klebsiella pneumoniae, Aeromonas hydrophila and Shewanella sp. (Asim et al. 2021; Yaqoob et al. 2020d). These all are considered the most efficient exoelectrogens in MFCs. During the operation, the bacterial species started to be gathered at an anode surface which produces a biofilm that helps to generate and transfer the electrons. However, the oxidation of organic substrate occurred at the anode while the reduction was done at the cathode electrode. During the oxidation process, first, the used oil palm trunk sap breaks down into simple sugar which is further oxidized to produce the electrons and protons during the bacterial respiration (Krebs cycle process). The biochemical reaction can be written as:

\[
\begin{align*}
\text{Anode: } & C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \\
\text{Cathode: } & 24H^+ + 24e^- + 6O_2 \rightarrow 12H_2O \\
\text{Overall reaction: } & C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{Electricity} + \text{Biomass}
\end{align*}
\]

During the oxidation, these produced electrons are used to transfer toward the cathode via the outer circuit, and the proton moves directly through PEM (Yaqoob et al. 2020e). There are two main mechanisms to transfer the electrons from a bacterial cell to an anode electrode as shown in Fig. S4. Usually, it is called direct electron transfer and indirect electron transfer.

- The direct electron transfer is further consisting of two paths: electron transfer via conductive pili and electron transfer through redox-active proteins. Some bacteria showed the conductive pili such as Acinetobacter radiore sistens strains, Bacillus, Klebsiella pneumoniae, Aeromonas hydrophila etc. Similarly, some bacteria such as Geobacter sulfurreducens used redox-active proteins to transfer the electrons. Many redox-active proteins like OmcZ, OmcB, OmcS, OmcT, and OmcE used by exoelectrogens.

- The indirect electron transfer mechanism is depending on the soluble electron’s shuttles. The Desulfuromonadaceae and Geobacteraceae mostly used this mechanism to transfer the electrons.

However, Table 5 and SEM images (biofilm-based anodes) indicating the direct electron transfer mechanism for the present study. The analyzed bacterial species have conductive pili which are shown in SEM images like a tube or rod-shaped. Next, the electrons are transferred from bacteria to the anode, further transfer to the cathode via the outer circuit to initiate the reduction mechanism. As a reduction result, Co\(^{2+}\) to Co would be highly favourable than Co\(^{3+}\) to CoO and more CoO could be further reduced to Co. The reduction of Co (II) to Co can be written as:

\[
\begin{align*}
\text{Co}^{2+} + 2e^- & \rightarrow \text{Co}(s) \\
2\text{Co}^{2+} + 2H_2O & \rightarrow 2\text{CoO} + 4H^+ \\
\text{CoO} + 2e^- + 2H^+ & \rightarrow \text{Co}(s) + H_2O
\end{align*}
\]

Multiple parameter optimization

Effect of pH

The self-prepared anodes with different ranges of pH of anodic solution for 10 days operation were carried out to formulate a hypothesis for suitable environmental conditions. The GO, GO-ZnO, and GO-TiO\(_2\) composite anodes are individually treated and carried out a series of experimental trials to optimize the performance. Figure S5a demonstrating the voltage generation trend of the prepared anodes. The GO-ZnO composite delivered maximum voltage (139 mV) while the GO-TiO\(_2\) composite anode offered 123 mV. Both composite anodes showed higher voltage generation efficiency than GO anode (78 mV). According to the observation, it was found the maximum voltage at pH 7 in three cases while at highly acidic pH 2 showed 11 mV (GO), 17 mV (GO-ZnO composite anode), and 14 mV (GO-TiO\(_2\) composite anode). The highly alkaline condition pH 10 offered 23 mV (GO), 35 mV (GO-ZnO composite anode), and 31 mV (GO-TiO\(_2\) composite anode). During measurement it was observed that at a highly acidic condition, the voltage was low but as gradually it increased the pH the voltage received significant improvement until pH 7. Further Fig. S5b showed the remediation efficiency of three anodes in different pH ranges. Like voltage generation, it was found the high remediation efficiency of Co(II) at pH 7. It showed 23% (GO anode), 26% (GO-ZnO), and 25% (GO-TiO\(_2\)) remediation efficiency on 10-day operation of Co(II). During observation very low remediation efficacy at pH 2 such as 1% (GO anode), 3% (GO-ZnO), and 1.5% (GO-TiO\(_2\)) and even at pH 10 it was zero in three cases was recorded. A highly alkaline condition might convert the Co(II) simultaneously into CoO. It is not a highly preferable state instead of Co\((s)\). The highly acidic and basic conditions disturb the biofilm activities which led to poor performance.

Effect of temperature

The temperature is the important environmental factor for high performance MFCs. The trend of voltage generation
and remediation performance of anodes (GO, GO-ZnO, and GO-TiO₂ composite) is shown in Fig. S5 (c-d). The present study was limited to 20, 25, 30, and 35 °C. The GO anode delivered 56 mV (20 °C), 76 mV (25 °C), 70 mV (30 °C) and 65 mV (35 °C) while GO-ZnO delivered 89 mV (20 °C), 138 mV (25 °C), 129 mV (30 °C) and 110 mV (35 °C). The GO-TiO₂ composite offered 78 mV (20 °C), 122 mV (25 °C), 119 mV (30 °C) and 99 mV (35 °C). According to our observations, the prepared anodes were the most preferable to use as a remediation application. According to our observations, the prepared anodes are the most preferable condition for bacterial growth and respiration to generate the electrons. Similar, the GO delivered 15% (20 °C), 23% (25 °C), 22.5% (30 °C) and 20% (35 °C) while GO-ZnO offered 18% (20 °C), 26% (25 °C), 25.7% (30 °C) and 22% (35 °C). The GO-TiO₂ composite offered 16.5% (20 °C), 25% (25 °C), 24.7% (30 °C) and 21% (35 °C). According to our observations, the prepared anodes are the most preferable to use as a remediation application because it does not show any toxicity against the bacterial community. The remediation efficiency was high at room temperature, but it was still good at 30 °C.

**Conclusion and future perfective**

The lignin-derived GO and further modified with a metal oxide such as ZnO and TiO₂ were examined as an anode in MFCs. The synthesis of GO and its modification was carried out through simple carbonization and solvothermal methods. Several physicochemical characterizations were performed to evaluate the excellency of the synthesized material. Later, as anode different electrochemical and biological characterizations were extensively performed to highlight the performance of biomass-derived anodes electrodes in MFCs. According to the electrochemical results, it was demonstrated that the GO-ZnO anode showed higher electron transportation than GO anode. GO-TiO₂ composite also showed higher performance than the GO, but it was lower than the GO-ZnO composite. It might be due to the excellent physicochemical properties of ZnO. The prepared biomass-derived modified anodes offered more than 45 days of durability in the continued operation of MFCs. Further, in the present study, the Co(II) supplemented wastewater was used as an incubation source, and it was found good remediation efficiency of Co(II) in three anodes. The prepared anodes offered excellent biocompatibility towards the bacterial community as was well explained in the present study. The bacterial identification process was carried out and found that there are limited exoelectrogens on the surface of the prepared anodes. The limited number of bacterial species or similar morphology species is a good indication for effective remediation of metal ions from wastewater. According to the present results, the Co(II) was successfully reduced to its maximum limits within 45 day even though the operation of each anode was operated for three cycles. Also, the energy generation was found higher at the first cycle than 2nd and 3rd in three cases. Once the reduction reached its maximum limits and voltage generation failed to achieve the highest value again it corresponds to the mortality of bacteria species. It is an indication that the MFCs operation achieved its destination. Additionally, the involved mechanism of electron transfer from bacteria to the anode and even oxidation/reduction reaction of the present study are also considered. Despite all this, some challenges are still in question: how and why mortality of bacterial species is involved in operation even at the constant supply of organic substrate. The bacterial instability needs careful study to minimize this issue to scale the MFCs operation at a pilot scale. As concerns the anode electrode, the present anodes are the most preferable, and the introduction of metal oxide as an anode modifier to expand the MFCs applications should be on priority.

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**Data availability** The authors confirm that all data underlying the findings are fully available without restriction. Data can be obtained after submitting a request to the corresponding/first author.

**Declarations**

**Conflict of 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. Furthermore, Prof. Dr. Rokiah Hashim’s research group had no role in the design of the study; experiment, in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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