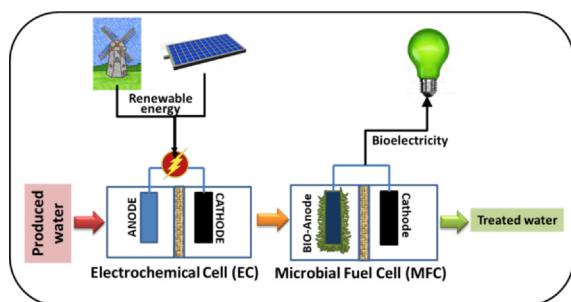


## Full Length Article

## Integrating electrochemical and bioelectrochemical systems for energetically sustainable treatment of produced water

Gunda Mohanakrishna<sup>a</sup>, Riyadh I. Al-Raoush<sup>a,\*</sup>, Ibrahim M. Abu-Reesh<sup>b</sup><sup>a</sup> Department of Civil and Architectural Engineering, College of Engineering, Qatar University, P O Box 2713 Doha, Qatar<sup>b</sup> Department of Chemical Engineering, College of Engineering, Qatar University, P O Box 2713 Doha, Qatar

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Keywords:

Bioprocess integration  
 Electrochemical oxidation  
 Produced water treatment  
 Total petroleum hydrocarbons (TPHs)  
 Energy recovery

## ABSTRACT

Pollutants present in produced water (PW) are recalcitrant in nature and difficult to treat with simple processes. Energetically sustainable and novel approach was developed by integrating electrochemical cell (EC, Primary process) and microbial fuel cell (MFC, secondary process) to treat PW. Five different current densities (26, 36, 48, 59 and 71 mA/cm<sup>2</sup>) were applied in independent EC experiments (4 h). The effluents from each EC operation was further treated by MFC (10 h), to harness bioelectricity. Operational variations were maintained only in EC phase and kept MFC phase similar. This integration revealed that the extent of bioelectricity generation depends on the electrochemical oxidation of EC process. Overall, maximum power generation of 2.74 mW was registered with EC-effluent from 48 mA/cm<sup>2</sup>. The integration also showed highest TPH removal efficiency of 89% (EC, 305 mg/L; MFC, 317 mg/L) and COD removal efficiency of 89.6% (EC, 2160 mg/L; MFC, 1960 mg/L) at 71 mA/cm<sup>2</sup>. Other pollutants of PW, such as sulfates and TDS also removed efficiently (sulfates, 42.6%; TDS, 34.3%). Cyclic voltammetric (CV) and derivative analysis of the anodic biofilm were correlated well with MFC performance during different EC-effluents as substrate, indicating NADH involvement in bioanodic electron transfer. The balance between energy utilization in EC and bioelectricity generation by MFC was depicted that the integration of EC and MFC results in net positive energy. Maximum net power generation of 565 mWh (350 mL of anode volume) was resulted by integration. This integration depicts its potential to generate 1615 Whm<sup>-3</sup> from the treatment of 1KL PW.

\* Corresponding author.

E-mail address: [riyadh@qu.edu.qa](mailto:riyadh@qu.edu.qa) (R.I. Al-Raoush).<https://doi.org/10.1016/j.fuel.2020.119104>

Received 7 May 2020; Received in revised form 26 July 2020; Accepted 24 August 2020

Available online 03 September 2020

0016-2361/ © 2020 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Produced water (PW) is the wastewater generated during the exploration and production of crude oil and gas. PW brought to the surface, contains a complex mixture of pollutants such as dissolved and dispersed organics, inorganic compounds. PW contains heavy metals such as Cd, Zn, Ni, V, Cu, Pb, etc., and production solids [1,2]. Polycyclic aromatic hydrocarbons (PAH) and BTEX (benzene, toluene, ethylbenzene, and xylene) compounds are commonly available organic contaminants in PW. The type of pollutants present in PW and their concentrations are largely impacted by geographical location, type of petroleum resource, and age of the well [3,4]. These pollutants are creating serious operational problems such as corrosion, scale formation, therefore, environmental regulations are imposed to control the disposal of PW [5,6]. The nature of the PW also varies depending on the origin and the age of the wells. PW can be categorized based on the source and type of fossil fuels [7]. Conventional oil, gas, and unconventional petroleum resources are broad categories for PW sources. Shale oil and gas, tight sands and coal bed methane can be categorized into unconventional petroleum sources [8]. According to Arowshola et al., [9], PW to oil ratio is approximately 3:1, which is increasing rapidly and estimated to reach 12:1 (v/v) by 2025, due to ageing of wells. PW is a waste by-product of the oil and gas industry, treating this wastewater appropriately will provide beneficial application and reuse. The appropriate type and degree of treatment applied to PW determine the quality of treated water for reuse applications [8–10]. Based on the quality of the treated PW, it can be used for crop irrigation, gardening, livestock, municipal and industrial usage, etc., [11].

The regulatory framework for discharge and reuse of PW is varying globally. The management practices to use PW beyond oil and gas industries are not well developed [12,13]. However, U.S. Environmental Protection Agency (USEPA) and the Department of the Interior's Bureau of Land Management (BLM) are working for federal regulatory guidelines in USA. Moreover, PW management is regulated by more than one agency in each state in USA. Majority of the agencies established total saturated hydrocarbons in the range of 17–30 mg/L, along with total oil and grease content of 2–560 mg/L [10]. In the case of COD, US Geological Survey (USGS-National Produced Waters Geochemical Database) [14] that imposed limit of 125 mg COD/L, which is slightly lower than china (150 mg COD/L) [15]. Environmental impacts caused due to the unsafe disposal of PW have been reported since the first oil and gas wells were drilled and operated. Unsafe disposal of PW resulted in environmental deterioration with respect to soils, groundwater, surface water, and ecosystems [16]. The trace elements present in PW were also found phytotoxic [17]. High concentration of sulfates present in PW was found to show adverse effects on ecology. Sulfates in PW also encourage the growth of sulfate-reducing bacteria. Sulfate ions in the presence of calcium, magnesium, forms calcium carbonate, calcium sulfate, and magnesium hydroxide scales. If the treated PW is considered for reinjection purpose, along with the presence of sulfate ions, calcium and magnesium ions forms calcium carbonate, calcium sulfate and magnesium hydroxide scales. The scaling exerts further adverse effects such as temperature and pressure variations inside the petroleum wells [4–6]. In this direction, integration of MFC is considered as a secondary process to further remove sulfates from PW.

PW treatment is being carried out through several processes such as physical treatment (adsorption, cyclones/centrifugal acceleration, flotation) [8], membrane based treatment (reverse osmosis, nanofiltration, ultrafiltration/microfiltration, etc.) [18], biological treatment [19] and thermal treatment (multi effect distillation, evaporation) etc. [620]. On the other hand, chemical processes such as electrochemical, chemical precipitation and advanced oxidation processes shown to exhibit PW treatment [21]. Among all the above listed processes, electrochemical oxidation is found to exhibit advantages for treatment efficiency [22]. However, electrochemical processes are energy intensive. Microbial fuel cells (MFCs) that use bacteria as biocatalyst are known to treat

produced water effectively with no energy input [23–26]. Moreover, MFCs found to generate bioelectricity from the treatment of PW. In the recent decade, extensive research has been developed using MFCs which are known for sustainable and energy efficient treatment processes [27–29]. MFCs are hybrid processes, in which electrochemically active bacterial catalyst triggers oxidation and reduction (redox) reactions.

MFCs also evidenced treatment of petroleum hydrocarbons, BTEX compounds, desalination and removal of sulfates [30,31]. However, limitations were noted with respect to treatment efficiency. Physico-chemical nature of PW such as high saline conditions and complex pollutants of PW were shown to inhibit the anodic bacteria [32]. In our previous study using PW, MFC alone proved to remove 65 mg/L of total petroleum hydrocarbons (TPH), 354 mg/L of sulfates and 1746 mg/L of TDS in dual chamber configuration [33]. The treatment of PW in MFC also resulted in energy generation of 1027 mW/m<sup>2</sup>. The effluent from the MFC has shown significant residual TPH concentration (> 60 mg/L TPH). Other studies with petroleum-based wastewater such as PW and petroleum refinery wastewater (PRW) also exhibited incomplete treatment which leaves considerable amounts of TPH, sulfates and other pollutants in the effluents [34,35]. The complexity of the TPH that present in PW is one of the major limitations for the residual TPH. MFCs were also used as secondary processes for several treatment processes to improve the treatment efficiency and to tap the energy present in pollutants [36]. In this direction, integrating energy intensive electrochemical process as primary treatment and energy generating MFC as secondary treatment process can be studied for energetically sustainable treatment of PW.

The present study is designed to improve the treatment efficiency of PW and to generate bioenergy by integrating EC as primary process to MFC. Bioelectrochemical system are known to exhibit improved performance through integration with other processes [37,38]. In this direction, electrochemical cell (EC) was considered as primary treatment process where external energy was used for the degradation of complex petroleum hydrocarbons to relatively simple hydrocarbons. The effluents from the primary process were used in the secondary process (MFC) for efficient and enhanced treatment of petroleum hydrocarbons. The process was designed using simple and cost-effective carbon electrodes for both electrochemical and bioelectrochemical systems. In the electrochemical reactor, selected carbon-based electrodes exhibit stability at higher current densities and minimizes possible interferences such as electrocoagulation. Integration of electrochemical process as primary stage prior to bioelectrochemical treatment of PW minimizes the treatment time and helps to improve the efficiency.

## 2. Materials and Methods

### 2.1. Produced water composition

PW is found to have high amount of total dissolved solids (TDS) along with considerable concentration of total petroleum hydrocarbons. Based on the concentrations reported from various studies, synthetic PW was prepared in the laboratory and used as substrate for the present study [4,10]. The following salts concentration (in g/L, NH<sub>4</sub>Cl, 0.25; FeSO<sub>4</sub>, 0.25; CaCl<sub>2</sub>·2H<sub>2</sub>O, 15.0; KCl, 2.0; MgCl<sub>2</sub>, 15.0; NaCl, 55.0; Na<sub>2</sub>SO<sub>4</sub>, 2.0; NaHCO<sub>3</sub>, 1.0; H<sub>3</sub>BO<sub>3</sub>, 0.25) adapted along with the addition of commercial gear box oil was used to mimic the petroleum hydrocarbons present in PW. The prepared synthetic PW was exhibited pH as 8.75. As bioelectrochemical system planned as secondary treatment process, which do not perform under high TDS conditions [28], synthetic produced water was diluted to bring the TDS to 17500 ± 200 mg/L. After dilution, 500 μL of commercial gear box oil was added to one liter of diluted PW, it was continuously stirred using magnetic at an rpm of 120 for 2 days (minimum) in amber glass bottle. The resultant PW was used immediately for the study.

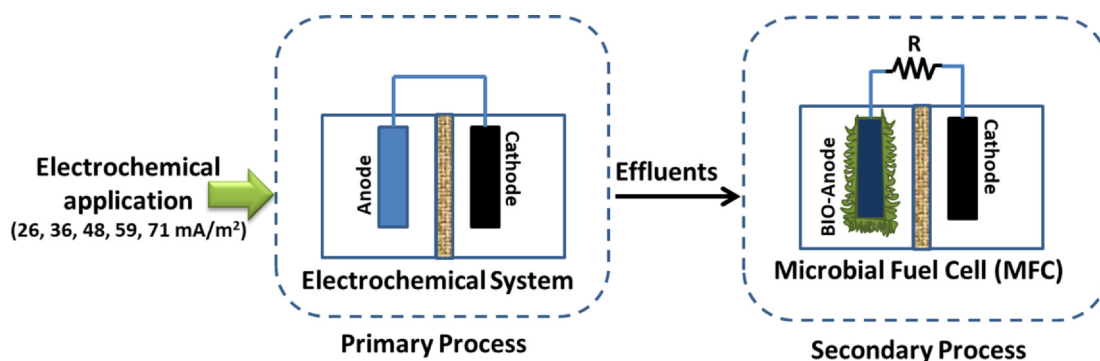


Fig. 1. Schematic representation of the experiments conducted to treat produced water using integrated approach of electrochemical cell (EC) and microbial fuel cell (MFC). Produced water primarily treated in EC and the effluent of EC was fed to MFC for bioelectricity generation and PW treatment simultaneously.

## 2.2. Design and operation of reactors

The study of enhanced treatment of PW was carried out using two different types of reactor. Initially, electrochemical cell (EC) was employed for electrochemical oxidation, which helps for partial oxidation of organics present in PW. Effluent from the EC was fed to MFC in the second stage to generate bioelectricity from the treatment of residual organics of PW. All the experiments were operated at ambient room temperature (Fig. 1).

## 2.3. Electrochemical cell (EC)

Electrochemical oxidation was considered as the primary treatment process for PW. EC constructed with Perspex glass, was employed to execute the present study. The EC employed non-catalyzed carbon brush as anode and carbon cloth as cathode electrode. Prior to use, carbon cloth and carbon brush were heat-treated in distilled water at 100 °C. Cation exchange membrane (CMI- 7000, Membranes International, Inc., USA) was fixed between anode and cathode chambers of dual chambered system. The EC system consists of 350 mL working volume along with 50 mL head space. The quality of PW was kept constant in all the five different current density variations studied. Adjustable DC (direct current) power pack was used to supply the required current in the system. From DC power supplier, anode and cathode lead were extended to respective electrodes of EC system. Electrochemical evaluation was done by supplying a constant current for 4 h. Each variation of current density was operated continuously for six cycles, which were considered as replicates. Due to variation in operating time for EC and MFC, samples from each cycle of EC were collected and stored to feed MFC system for the secondary process. Mean values from all the cycles (from each variation) were presented in the figures. Further, collected effluents from EC were used as substrate for the four consecutive cycles of MFC operation in the secondary stage.

## 2.4. Microbial fuel cell (MFC)

The effluent generated from the EC was considered as feed to the MFC. Configuration and design of MFC were similar to EC. Instead of plain carbon brush in the anode, well-adapted electrochemically active biofilm on the carbon brush was used. This biofilm was used for treatment of PW for more than 6 months and generated bioelectricity. The effluent collected from EC in each voltage variation was stored at 4 °C and used as a feed to the anode chamber of MFC without adjusting the pH and concentration. Cathode chamber of dual chamber MFC was filled with 50 mM phosphate buffer with continuous aeration to perform cathodic reduction reaction. Retention time of 10 days for the anolyte was maintained constant for all the effluents collected from EC system at different current supply conditions. Wastewater samples from the anolyte were collected at the beginning and the end of the operating

cycle to evaluate parameters such as TPH, COD, pH and TDS. Collected samples were immediately stored at 4 °C refrigerator.

## 2.5. Data acquisition and analysis

Current recorded from the DC power supplier was considered for power consumption calculations in the electrochemical studies. Closed circuit voltage generated from the bioelectrochemical systems was recorded by connecting a resistor of 100 Ω between anode and cathode in series. Average voltage generated from MFC during the 10 days of operation was considered for the average data of all the electrochemical parameters. Power was calculated using Ohms Law. Current density and power density were calculated by normalizing the current and power with the surface area of cathode electrode (40 cm<sup>2</sup>). Electrochemical response of EC and MFC systems over a range of potentials was evaluated by cyclic voltammetry (CV) technique using Bio-Logic potentiostat (Model no. SP-150) system (Biologic, France). Scan range (from -1.0 to +1.0 V) and scan rate (20 mV/s) were maintained similar for both EC and MFC. Here, anode was connected as working electrode and cathode as counter electrode. The final cycle of each experimental variation was considered for CV analysis. Samples collected from EC and MFC operations in all the experimental variations were analyzed for the pH (Hach, USA, Model No. HQ11D Portable pH Meter), TDS, chemical oxygen demand (COD), sulfates and TPHs (Horiba OCMA-350 oil content/TPH analyzer, Japan) by adapting the methodologies described in the Standard Methods of Analysis [39]. COD was measured by LANGE COD testing kit, UK and digester was from Hach, USA (Model No. DRB 200 reactors). Prior to analysis, all the samples were brought to room temperature.

## 2.6. Energy balance

Energy consumption and energy production from EC and MFC, respectively were calculated based on the respective operating conditions. Total power consumption (TPC, mWh) was calculated by multiplying time of operation (4 h) with maximum power recorded in EC. An expression of TPC in Wh can be obtained. Further, volumetric power consumption (VPC, Wh/L) was calculated by dividing TPC (Wh) with volume of anode chamber of EC (0.35 L). VPC can be converted to m<sup>3</sup> volumes to visualize the practical applicability. Similar to power consumption in EC, power production was calculated in MFC. Total power production (mWh) was derived as a product of average power (mW) from 10 days of operation (mW × 10 days × 24 h). TPP can be converted from mWh to Wh by dividing with 1000. Further, volumetric power production (VPP, Wh/L) was derived by normalizing the TPP (Wh) with volume of the anode chamber. Wh/L units of TPP were converted to Wh/m<sup>3</sup>. The derived VPC and VPP values were used to calculate the net energy/power production from the integration of EC and MFC during treatment of PW.

### 3. Results and discussion

#### 3.1. Electrochemical oxidation of produced water in EC

To achieve efficient and cost-effective treatment of produced water, several factors should be considered. Electrochemical oxidation of PW was previously studied using different metal-based catalysts, synthetic catalyst doped electrode materials, etc., in which wide range of current densities (5 mA/cm<sup>2</sup> to 320 mA/cm<sup>2</sup>) were evaluated [40,41]. These processes were found to exhibit 80% of treatment efficiency. The time of electrochemical process was found to vary with each study. PW with high TPH was employed for 20 h to achieve 92% efficiency [42]. Since the present EC process was aimed for partial oxidation of TPH and to operate with non-catalyzed carbon-based electrodes, five different current densities (26, 36, 48, 59 and 71 mA/cm<sup>2</sup>) were employed for 4 h. A 4 h of operating time was chosen from the preliminary evaluation of PW with various operating time in the range of 2–10 h. Petroleum hydrocarbons are the most contributing organic pollutants in PW, which is also represented as TPH. It was observed that the current density used for EC is directly proportional to the oxidation of TPH in anode. Among the five current densities studied, a maximum TPH degradation of 305 mg/L was registered with 71 mA/cm<sup>2</sup> operation, which contributing for 43.6% removal efficiency (Fig. 2a, Table 1). The minimum TPH degradation was registered with 26 mA/cm<sup>2</sup> (139 mg/L, 19.9%). In the case the intermediate current densities studied, TPH degradation was also registered in the intermediate range (36 mA/cm<sup>2</sup>–176 mg/L and 25.1%; 48 mA/cm<sup>2</sup>–227 mg/L and 32.4%; 59 mA/cm<sup>2</sup>–260 mg/L and 37.1%). Electrochemical oxidation of PW using the five different current densities for 4 h of operation resulted in marginally higher than 50% organics in the effluents. Some of the residual TPH content present in the EC effluents are products of the process. Part of these TPHs might be simpler than the original TPH molecules [43]. Relatively simpler molecules are more feasible for biological or bioelectrochemical degradation. In this direction, bioelectrochemical oxidation by MFC was integrated as secondary process. The effluents from each variation of EC were collected and forwarded to MFC without any change in the concentration and pH. After operation for more than 20 cycles with all the variations, no visible difference in the electrode was identified. Salinity and sulfates present in PW are corrosive for many types of electrodes [44,45]. However, carbon-based electrodes used in the present study were found to be stable under harsh environmental conditions.

Along with TPH, the system was also evaluated for COD removal. The trend of COD removal was found to correlate with TPH removal in the respective experiments (Table 2, Fig. 2b). Inlet COD of all EC experiments was kept constant at 4600 mg/L. Maximum COD removal of 2160 mg/L (47%) was observed with 71 mA/cm<sup>2</sup>, followed by 59 mA/cm<sup>2</sup> (1820 mg/L, 39.6%) and 48 mA/cm<sup>2</sup> (1660 mg/L, 36.1%). The drop in COD degradation efficiency was decreased while lowering the applied potential in EC system. Further, the lowest COD degradation efficiency was registered with the lowest applied potential of 26 mA/cm<sup>2</sup> (1200 mg/L, 26.1%). Many types of metal-based anode electrodes used for the electrochemical oxidation of PW. The output of the present study using carbon electrode was compared in Table 3. The coulombic efficiency (CE%) between electricity consumed to degrade COD was evaluated for all the five experimental variations using the formula suggested elsewhere [46]. The EC system showed a maximum CE of 17.3% with 26 mA/cm<sup>2</sup> operation, followed by 36 mA/cm<sup>2</sup> (14.5%) and 48 mA/cm<sup>2</sup> (12.8%). A gradual drop in coulombic efficiency was observed with increase in applied potential. In the case of 59 and 71 mA/cm<sup>2</sup>, CE was registered as 10.6% and 9.2%, respectively. Coulombic efficiency was decreased gradually from the lowest applied to the highest applied potential. From the coulombic efficiency analysis, it was observed that the electrochemical losses were increasing at high potentials.

#### 3.2. Integration with MFC

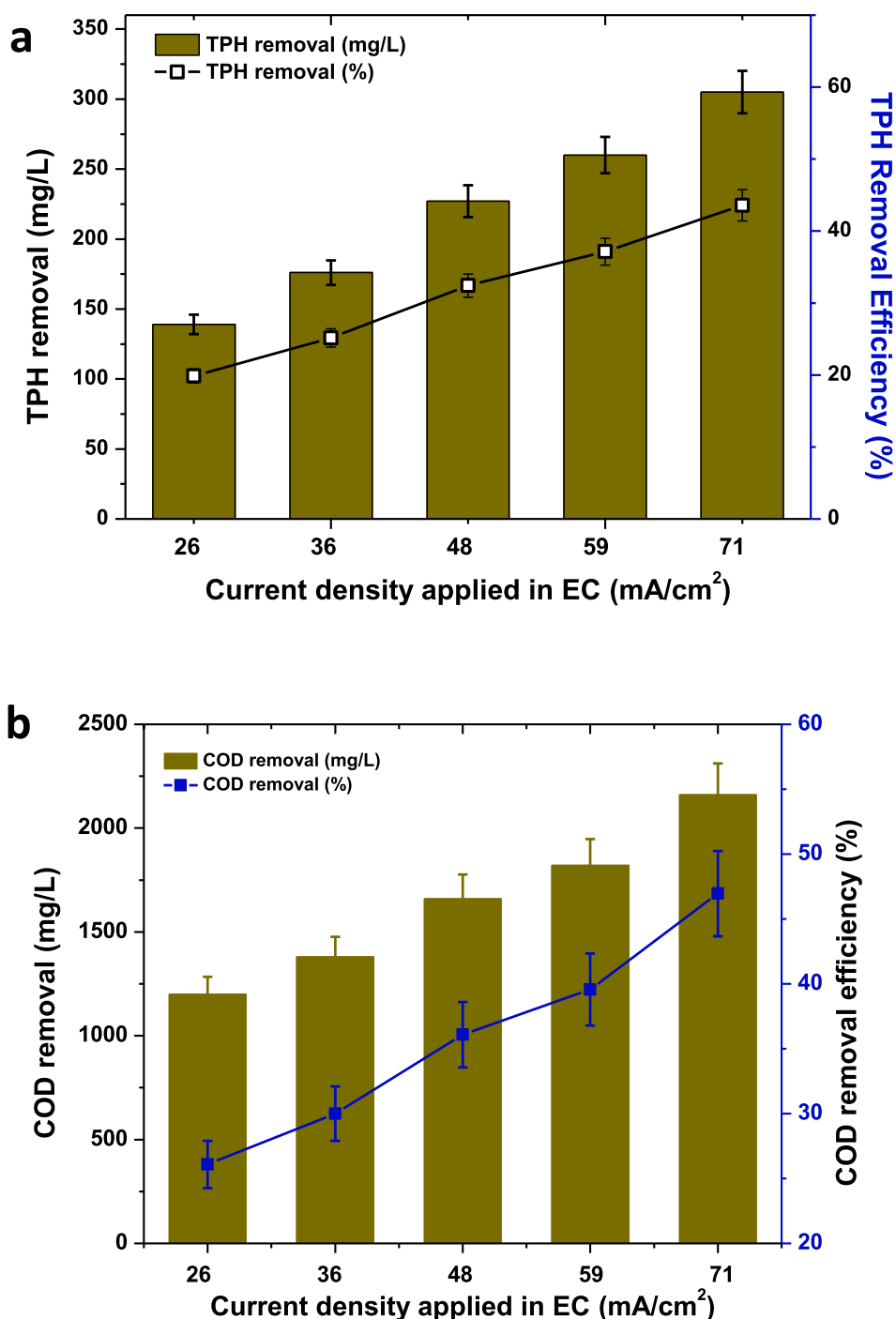
Primary treatment process is energy intensive, which do not warrant the economics and sustainability of the whole process. Complete degradation of petroleum hydrocarbons demands much more energy. In this direction, MFCs was integrated as the secondary treatment process, which harvest the energy from the treatment of organic matters. The residual TPHs were further treated for bioelectricity generation. The effluents of different current densities of EC individually fed to MFC and evaluated for power generation and concomitant treatment.

##### 3.2.1. Power generation

Five different effluents generated from EC process were evaluated in MFC, which depicted that the bioelectrogenesis potential of each effluent is different. MFC performance was influenced by the concentration and nature of pollutants present in the feed. As bioelectrochemical processes show considerable fluctuations during the operation cycle, average values of power generated from the total operation period were considered for MFC evaluation. Effluents of EC with 71 mA/cm<sup>2</sup>, depicted voltage generation of 443 mV (average) and current density of 1108 mA/m<sup>2</sup> from 10 days of operation (Fig. 3a). When effluent of 59 mA/cm<sup>2</sup> was evaluated, it registered current density of 1200 mA/m<sup>2</sup> (480 mV). Among the five effluents, the effluent that generated from 48 mA/cm<sup>2</sup> was depicted maximum current density of 1308 mA/m<sup>2</sup> (523 mV). In the case of 36 and 26 mA/cm<sup>2</sup>, current densities were registered as 1215 mA/m<sup>2</sup> and 1203 mA/m<sup>2</sup>, respectively. Bioelectrogenic potential of effluents generated from 26, 26 and 59 mA/cm<sup>2</sup> were found similar, in a narrow range of 1200 to 1215 mA/m<sup>2</sup>, which is in contrary to the substrate concentration of effluents generated from the primary process. Based on the average voltage and current density recorded using 5 different EC effluents, 48 mA/cm<sup>2</sup> effluent showed the highest performance that suggest this substrate as more suitable than the other four effluents studied in MFC. Hourly data recorded from each operating variation of MFC also depicting similar behavior (Fig. 3b). Electrochemical oxidation process might be degraded petroleum hydrocarbon molecules to smaller or simpler molecules, which further helps bacteria to effectively degrade these molecules in MFC for bioelectricity generation [43]. The subsequent Sections 3.3 and 3.4 are focused on the overall efficiencies of integration study with respect to treatment, energy consumption and energy recovery.

##### 3.2.2. TPH degradation

Without MFC integration, TPH removals attained was in the range of 19.9 to 43.6% using current densities of 26 to 71 mA/cm<sup>2</sup>. Average TPH degradation using all the variations in EC was registered as 31.6% during 4 h and using carbon-based electrodes, suggesting that electrochemical oxidation with carbon brush could highly contribute to TPH degradation. Upon feeding to MFCs, these effluents resulted in bioelectrogenesis and TPH degradation. TPH degradation was found to depend on the initial concentration, which largely influenced the overall TPH degradation in MFC operation. Among the five effluents evaluated in MFC, effluent generated from 26 mA/cm<sup>2</sup> has the highest TPH concentration of 561 mg/L that showed substrate degradation of 375 mg/L (Fig. 4a, Table 1). In the case of effluents from 36 mA/cm<sup>2</sup> (524 mg/L), TPH degradation registered as 377 mg/L. This is the highest TPH degradation recorded. In the case of 48 mA/cm<sup>2</sup> effluents, TPH concentration of 473 mg/L was degraded to 108 mg/L, depicting 365 mg/L TPH degradation. Among all the PW effluents treated in MFCs, the effluents from 26, 36, 48 and 59 mA/cm<sup>2</sup> were showed substrate degradation in the range of 377 to 358 mg/L, depicting a comparable metabolic activity of electroactive bacteria in the system. In the case of effluents from 71 mA/cm<sup>2</sup>, relatively lower TPH degradation (317 mg/L) was documented. The minimum degradation registered might be due to the lower substrate concentration available in the feed. When TPH degradation efficiency was compared, the maximum value was noted with 59 mA/cm<sup>2</sup> effluent (81.4%), followed by 71 mA/cm<sup>2</sup>



**Fig. 2.** Degradation of total petroleum hydrocarbons (TPHs) (a) and chemical oxygen demand (COD) in electrochemical cell (EC) (b) under five different current densities in 4 h of operation.

**Table 1**

Total petroleum hydrocarbons (TPH) removal from PW through integration of electrochemical cell and microbial fuel cell system and overall efficiency.

Current density used in EC (mA/cm <sup>2</sup> )	Voltage maintained in EC (V)	TPH inlet EC (mg/L)	TPH degradation in electrochemical cells (EC)		TPH inlet MFC (outlet of EC) (mg/L)	TPH degradation in microbial fuel cell (MFC)		Overall TPH degradation through integration	
			mg/L	%		mg/L	%	mg/L	%
26	8	700	139	19.9	561	375	66.8	514	73.4
36	10	700	176	25.1	524	377	71.9	553	79.0
48	12	700	227	32.4	473	365	77.2	592	84.6
59	16	700	260	37.1	440	358	81.4	618	88.3
71	20	700	305	43.6	395	317	80.3	622	89.0

**Table 2**

Chemical oxygen demand (COD) removal from PW through the integration of electrochemical cell and microbial fuel cell system and overall efficiency.

Current density used in EC (mA/cm <sup>2</sup> )	COD inlet EC (mg/L)	COD degradation in electrochemical cells (EC)		COD inlet MFC (outlet of EC) (mg/L)	COD degradation in microbial fuel cell (MFC)		Overall COD degradation through integration	
		mg/L	%		mg/L	%	mg/L	%
26	4600	1200	26.09	3400	2510	73.82	3710	80.65
36	4600	1380	30.00	3220	2460	76.40	3840	83.48
48	4600	1660	36.09	2940	2310	78.57	3970	86.30
59	4600	1820	39.57	2780	2300	82.73	4120	89.57
71	4600	2160	46.96	2440	1960	80.33	4120	89.57

effluent (80.3%), 48 mA/cm<sup>2</sup> (77.2%), 36 mA/cm<sup>2</sup> (72.0%). The minimum value of 66.8% was registered with 26 mA/cm<sup>2</sup> effluents. Significant variation in the TPH degradation efficiency might be due to the higher variation in the effluent generated from the EC. Bioelectrochemical systems are capable of degrading in various environments. Soil based MFC was effectively treated TPHs at three different loading conditions and resulted in bioelectrogenesis. Among the three loading conditions, 840 mg TPH/L showed 49.38% TPH removal efficiency [47].

### 3.2.3. COD degradation

In EC treatment alone the COD degradation was ranged between 26.1 and 47.0% efficiency. When the MFC was submitted with the EC effluents, further treatment was observed (Fig. 4b). Inlet and outlet COD values of EC and MFC were reported in Table 2. Over 10 days of MFC operation, the maximum amount of COD was degraded with effluent from 26 mA/cm<sup>2</sup> (2510 mg/L), followed by 36 mA/cm<sup>2</sup> (2460 mg/L) and 36 mA/cm<sup>2</sup> (2310 mg/L). The minimum COD degradation was recorded with effluent from 71 mA/cm<sup>2</sup> (1960 mg/L). The effluent collected from EC system with lower potential showed high COD. The same effluents showed higher amount COD degradation (Table 2). When the COD degradation efficiency was evaluated, the maximum was registered with effluent from 59 mA/cm<sup>2</sup> (82.7%) and the minimum was registered with 26 mA/cm<sup>2</sup> (73.8%). The overall COD degradation efficiency (integrating EC and MFC) was recorded in the range of 80.7 and 89.6%.

**Table 3**

Comparison of different electrode materials used for the electrochemical oxidation treatment of produced water.

S.No.	Electrode material used	Substrate concentration	Time of operation	Current density	Removal efficiency	Reference
1	Modified Ti/Sb-SnO <sub>2</sub> anode by graphene oxide	3386 mg COD/L	2 h	10 mA/cm <sup>2</sup>	46.6%	[67]
			2 h	15 mA/cm <sup>2</sup>	56.8%	
			2 h	20 mA/cm <sup>2</sup>	67.2%	
2	titanium electrode coated with titanium oxide and ruthenium oxide	192 mg/L Phenol	6 h	20 mA/cm <sup>2</sup>	94.5%	[68]
			6 h	20 mA/cm <sup>2</sup>	70.1%	
3	dimensionally stable anode (DSA*)	4980 mg/L COD	70 h	100 mA/cm <sup>2</sup>	57%	[69]
4	porous graphite electrode	2845 mg/L COD	10 h	1.41 mA/cm <sup>2</sup>	66.5%	[70]
5	Lead dioxide and boron-doped diamond electrodes	19842 mg/L COD	7 h	100 mA/cm <sup>2</sup>	85%	[40]
			11 h		96%	
6	Pt/Ir	3080 mg/L COD	4 h	12.8 mA/cm <sup>2</sup>	85–100%	[71]
7	Si/BDD	3471 mg/L COD	2 h	320 mA/cm <sup>2</sup>	98%	[72]
8	Carbon brush	700 mg/L TPH	4 h	26 mA/cm <sup>2</sup>	19.9	Present study
				36 mA/cm <sup>2</sup>	25.1	
				48 mA/cm <sup>2</sup>	32.4	
				59 mA/cm <sup>2</sup>	37.1	
				71 mA/cm <sup>2</sup>	43.6	
9	Carbon brush	4600 mg/L COD	4 h	26 mA/cm <sup>2</sup>	26.0%	Present study
				36 mA/cm <sup>2</sup>	30.0%	
				48 mA/cm <sup>2</sup>	36.1%	
				59 mA/cm <sup>2</sup>	39.6%	
				71 mA/cm <sup>2</sup>	47.0%	

### 3.3. Sulfates removal

Along with degradation of TPH, both electrochemical and bioelectrochemical systems were evaluated for the removal of other pollutants such as total dissolved solids and sulfates. In the case of EC, PW initial concentration of 1125 mg SO<sub>4</sub><sup>2-</sup>/L was reduced to different values through application of different current densities. The difference in removal of sulfates was found to depend on the current densities used in EC. The highest removal of sulfates (120 mg SO<sub>4</sub><sup>2-</sup>/L) was registered with 71 mA/cm<sup>2</sup>, constituting 10.7% sulfate removal efficiency (Fig. 5a). In the case of 59 mA/cm<sup>2</sup>, sulfate removal was registered as 105 mg/L (9.3%), followed by 48 mA/cm<sup>2</sup> (93 mg SO<sub>4</sub><sup>2-</sup>/L, 8.3%), 36 mA/cm<sup>2</sup> (85 mg SO<sub>4</sub><sup>2-</sup>/L, 7.6%). The minimum sulfate degradation of 71 mg SO<sub>4</sub><sup>2-</sup>/L (6.3%) was registered with 26 mA/cm<sup>2</sup>. From these results, it was clearly evidenced that the sulfate removal is directly proportional to the electrical current densities. Sulfate removal at the highest current density evaluated also depicted only 10.7%, which is not encouraging target for the effluents.

Treating the EC effluents in MFC (secondary process) has shown promising results for removal of sulfates. The effluent generated from 26 mA/cm<sup>2</sup> having 1054 mg SO<sub>4</sub><sup>2-</sup>/L was reduced to 722 mg SO<sub>4</sub><sup>2-</sup>/L evidencing removal of 332 mg SO<sub>4</sub><sup>2-</sup>/L (31.5% efficiency) (Fig. 5b). Similarly, effluents generated from other electrochemical processes also depicted removal efficiency in the narrow range of 32.2 (removal, 335 mg SO<sub>4</sub><sup>2-</sup>/L) to 35.8% (removal, 360 mg SO<sub>4</sub><sup>2-</sup>/L), which is leaving the residual sulfates concentration in the range of 645 to 705 mg SO<sub>4</sub><sup>2-</sup>/L. This integration was resulted in significant amount of sulfates removal. Overall, collective efficiencies of both electrochemical and bioelectrochemical systems was depicted in the range of 35.8 to 42.6% sulfate removal (Fig. 7a). However, the final concentration of sulfates in the treated PW is still high and may need further suitable treatment. Even though the bioelectrochemical processes were known for efficient removal of sulfates [44,48], due to the high sulfate concentration present in PW, it could remove only about 40%.

### 3.4. Removal of dissolved salts

Dissolved solids are one of the major concerns in PW treatment. Based on geological location and age of wells, TDS concentrations can be different. However, most of the PW samples were found to have TDS concentration higher than 30 g/L. High concentrations of TDS is a major obstacle for the selection of a suitable treatment process. Wide

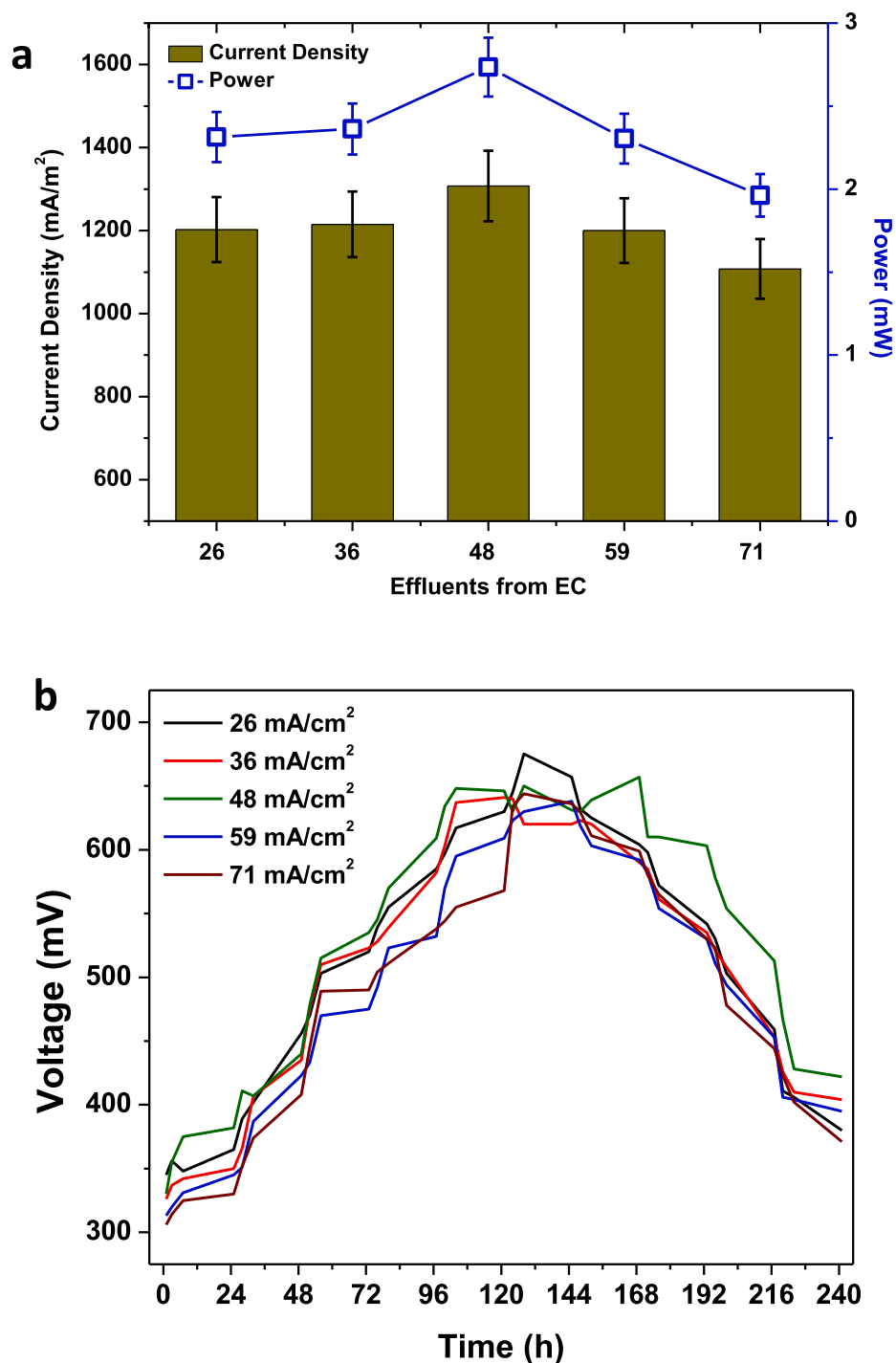


Fig. 3. (a) Bioelectricity generation (current density and power) patterns recorded in microbial fuel cells (MFCs) treating effluents generated from the electrochemical cell (EC) and (b) hourly voltage data for one MFC cycle of each experimental variation.

range of treatment processes such as membrane based, electrochemical based, bioelectrochemical based, deionization based processes face hindering effects due to the high TDS concentrations in PW [49]. However, integration of different processes will shed a light on the removal of TDS from PW. Based on the TDS of treated PW, the application can be chosen, such as for irrigation, industrial use, re-injection into the wells, livestock maintenance etc.[6]. In the present study, the EC evidenced a TDS removal in the range of 9.0 to 13.1%. The highest TDS removal of 2330 mg TDS/L (13.1%) was recorded for 71 mA/cm<sup>2</sup> and 59 mA/cm<sup>2</sup> current density variations, followed by 48 mA/cm<sup>2</sup> (2090 mg TDS/L, 11.8%), 36 mA/cm<sup>2</sup> (1890 mg TDS/L, 10.7%)

(Fig. 6a). The lowest TDS removal of 9% (1600 mg TDS/L) was evidenced with the lowest current density used in EC (26 mA/cm<sup>2</sup>). Drop in salts concentration is due to the movement of ions due to external power supply through the system. Electrode and membrane surface area are two possible fates for ions. Here, an attempt was made to quantify the salts deposited on the anode surface area. A correlation was made between TDS removed over 6 cycles of operation in single experimental variation and salts recovered from the anode surface. It showed that salts recovery was ranged between 39.3 and 47.0% (Table 4). The rest of the salts or ions might be deposited on the membrane or deposited to the bottom of the reactor.

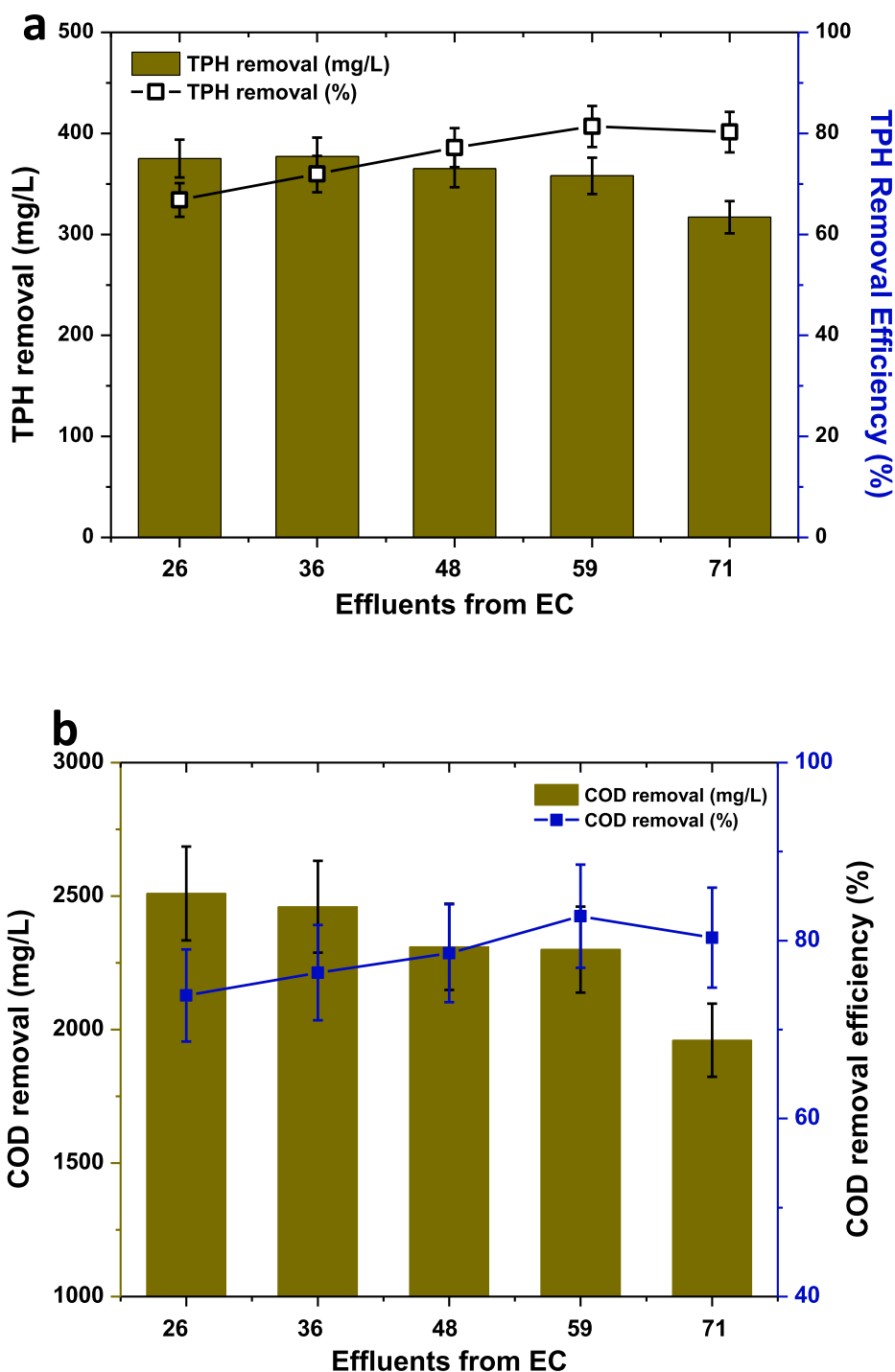


Fig. 4. Degradation of total petroleum hydrocarbons (TPHs) (a) and chemical oxygen demand (COD) in microbial fuel cell (MFC) (b) under five different current densities in 10 days of operation.

Further treatment through MFCs also evidenced significant TDS removal. Among all the five EC effluents evaluated for bioelectrogenesis along with TDS removal, the highest efficiency (24.4%, 3760 mg TDS/L) was registered with effluent from 71 mA/cm<sup>2</sup> of current density (Fig. 6b). In the case of effluents generated from 36, 48 and 59 mA/cm<sup>2</sup>, TDS removal was registered in a very narrow range of 3440 to 3460 mg TDS/L, comprising efficiencies of 21.7 to 22.5% through operation by MFC. The effluent of 26 mA/cm<sup>2</sup>, depicted minimum TDS removal (3140 mg TDS/L, 19.5%) among all the variations studied. Combining both electrochemical and bioelectrochemical processes, TDS removal was found very significant. In bioelectrochemical systems, removal of

ions is driven by several processes such as bioelectrodeposition, biosorption and bioelectrochemical reduction/oxidation [28,35,50,51]. In the present integration, complex conditions prevail in both EC and MFC helps for TDS removal. From the consolidation of all the TDS removal through integration, a maximum of 6090 mg TDS/L (34.3%) was registered with 71 mA/cm<sup>2</sup>. The minimum TDS removal of 4740 mg TDS/L (26.7%) was registered at 26 mA/cm<sup>2</sup> condition (Fig. 7a). In the case of 59 mA/cm<sup>2</sup> (5790 mg TDS/L, 32.7%), 48 mA/cm<sup>2</sup> (5530 mg TDS/L, 31.2%) and 36 mA/cm<sup>2</sup> (5330 mg TDS/L, 30%), intermediary TDS removal efficiency was registered. For the removal of TDS from PW, various physico-chemical processes such as electro dialysis, reverse



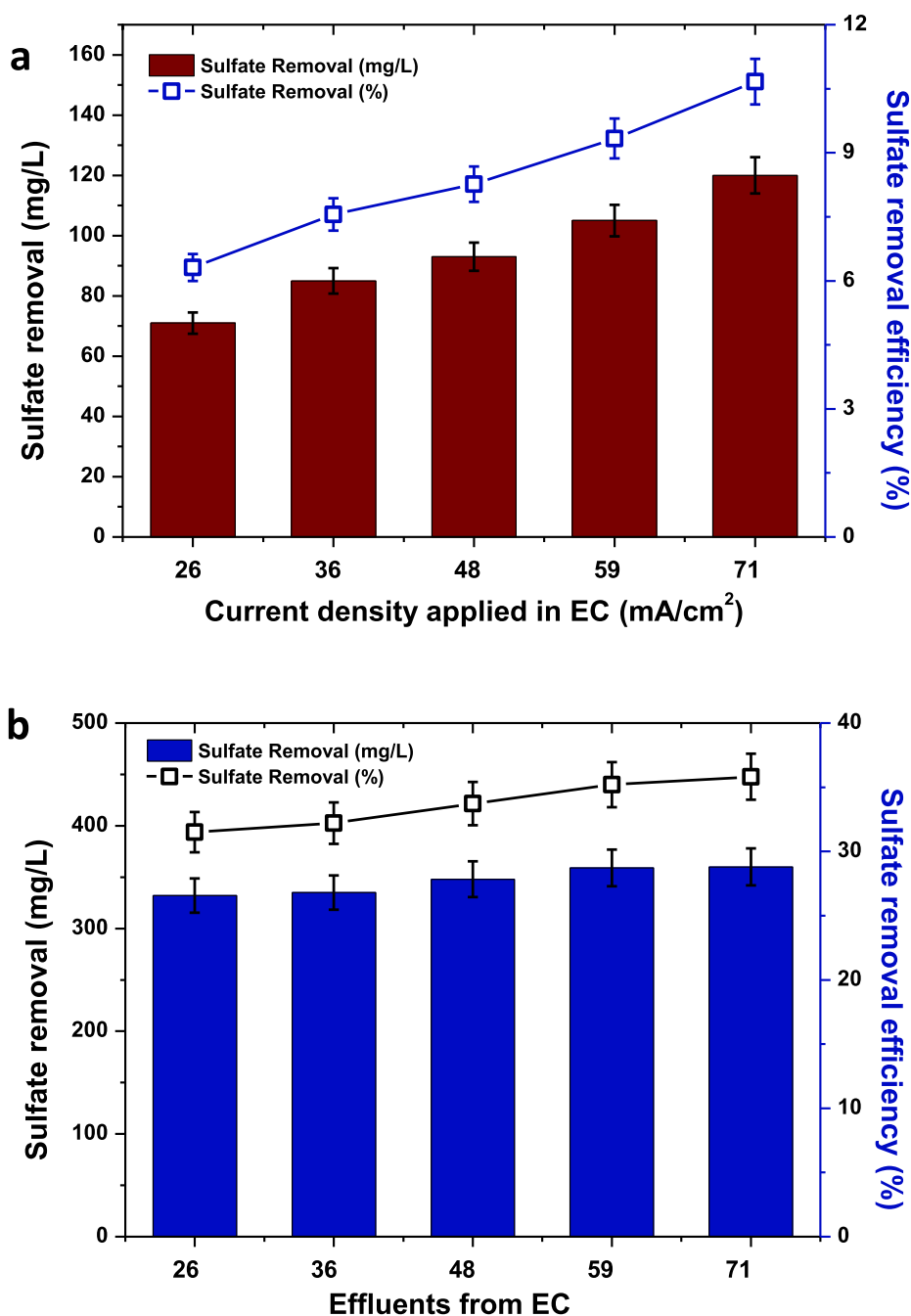


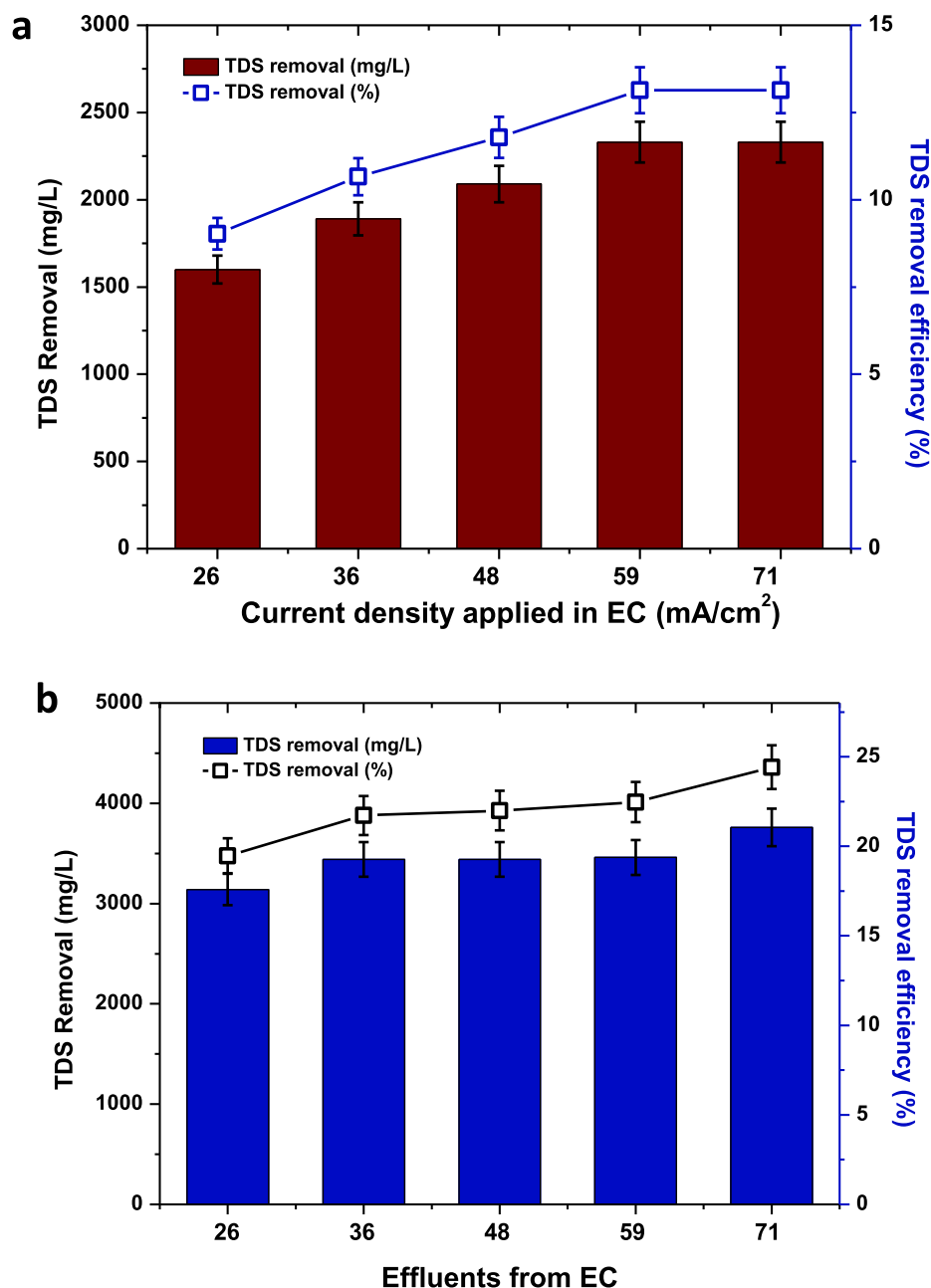
Fig. 5. Individual performance of electrochemical process (a) Sulfate removal and removal efficiency in electrochemical cell (EC) in 4 h, and (b) Sulfate removal and removal efficiency in microbial fuel cells (MFC) in 10 days.

osmosis, adsorption, membrane filtration etc., were being evaluated. The efficiency of TDS removal was achieved in the range of 80–95% [20]. However, the energy input required for the TDS removal is huge and impractical for large quantities of PW. On the other hand, chemical processes like dosage of coagulants such as hot lime, calcite and ferric ions have been used, which reported to remove more than 10000 mg TDS/L [8,52]. Compared to these processes, the present study reported reasonably less TDS removal. As bioelectrochemical systems generate additional energy from the treatment, an integrated approach with other processes will certainly develop an economic process for TDS removal from PW. Sequential bio-electrochemical reactor that fed with oilfield-produced water was used to evaluate the integration of EC and biofilter. This system reported removal of TDS along with sulfates, chemical oxygen demand and TPH [53]. However, the removal of TDS

was limited to 1.43% only, despite good performance towards TPH removal (75%), sulfate removal (25.3%) and COD removal (22.3%).

### 3.5. Change in pH

When PW used as feed in EC, the pH was not adjusted. The pH of PW was  $8.75 \pm 0.08$ . After electrochemical oxidation at different current densities, the pH of the effluent dropped to values in the range of 8.29 to 8.02. Higher drop in the effluent pH was identified with higher current densities used in EC, compared to lower current densities. Maximum drop was reported with 71 mA/cm<sup>2</sup> current density (pH 8.02), followed by 59 mA/cm<sup>2</sup> (pH 8.13), 48 mA/cm<sup>2</sup> (pH 8.29) (Fig. 7b). In the case of 26 and 36 mA/cm<sup>2</sup>, the drop in pH was registered in narrow difference (36 mA/cm<sup>2</sup>, pH 8.29; 26 mA/cm<sup>2</sup>, pH



**Fig. 6.** Individual performance of electrochemical process (a) Total dissolved solids (TDS) removal and removal efficiency in electrochemical cell (EC) in 4 h, and (d) TDS removal and removal efficiency in microbial fuel cells (MFC) in 10 days.

**Table 4**

Evaluation of salts deposited on anode surface during electrochemical cell operation using five different applied current densities for produced water treatment.

Current density used in EC (mA/cm <sup>2</sup> )	Total removal (g/L) in 6 cycles (average)	Scrapped salts from the electrode	Percentage recovery (%) on anode
26	3.36	1.32	39.29
36	3.97	1.85	46.61
48	4.39	2.06	46.94
59	4.89	2.13	43.53
71	4.89	2.21	45.17

8.25). The trend identified for pH drop in electrochemical oxidation process is correlating with the increase trend of TPH degradation identified in the same process. Even though the drop in pH was significant, the range was found to be suitable for bioelectrochemical activity in MFCs. MFCs found to treat waste organics in a broad anolyte pH range such as 5.5 to 8.5. So, all the effluents were readily fed to MFCs without adjusting the pH. After 10 days of bioelectrogenesis, the pH of the MFC effluents was further dropped to the narrow range of 7.89 to 7.71. Higher drop in pH was registered with EC effluents obtained from the current densities of 26 mA/cm<sup>2</sup> (from 8.25 to 7.74) and the least drop was registered with effluent obtained from 71 mA/cm<sup>2</sup> (from 8.02 to 7.80). In the case of other effluents, the pH drop was found to be inconsistent (36 mA/cm<sup>2</sup>, from 8.29 to 7.83; 48 mA/cm<sup>2</sup>, from 8.19 to 7.89; 59 mA/cm<sup>2</sup>, from 8.13 to 7.71). The pH of the final effluent is also determines the application of the treated PW. When the pH optimization was carried out by Liang et al., [54] in the range of 2.5

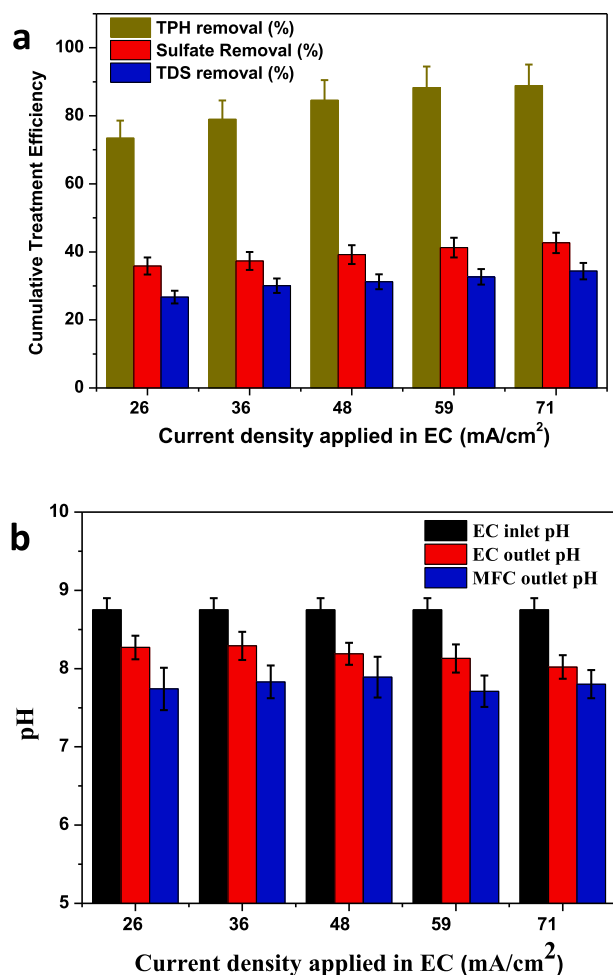


Fig. 7. (a) Consolidated representation of different parameters evaluated for treatment of produced water through integrated approach (b) pH values of the inlet produced water and pH values at the end of operation of electrochemical and microbial fuel cell system during produced water treatment.

and 10.5, it was identified that pH 4.5 as an optimum. Under this condition, *Paludibacter* sp. was found to be dominant and this species might be involved in sulfate reduction in MFCs at pH 4.5 [54]. However, under about neutral conditions (pH range 6 to 8) sulfate reducing bacteria was found to treat pollutants from wastewater [55]. In the present study, the pH of MFC system was sustained between 7.5 and 8.0, which might be favorable for sulfate reduction to exhibit in the range of 332 to 360 mg SO<sub>4</sub><sup>2-</sup>/L (Fig. 5b).

### 3.6. Electrochemical and bioelectrochemical behavior

In the present study, both EC and MFC systems were embedded with carbon brush as anode and carbon cloth as cathode electrodes which are suitable for harsh conditions prevailing due to PW. The electrochemical response of EC was found to be stable during operation with different current densities such as 26, 36, 48, 59 and 71 mA/cm<sup>2</sup> (Fig. 8a). Electrochemical and bioelectrochemical response of anode under different conditions can be identified by CV [56–58]. In the EC, no biological catalyst was used, and similar electrolyte conditions maintained. So, the treatment response against different current densities was largely influenced by electrode and electrolyte nature only. Due to this, the recorded current density (by CV analyses) was similar with all five current densities used for EC. Fig. 8a depicts the CV behavior of EC system with 26, 48 and 71 mA/cm<sup>2</sup> current densities (36 and 59 mA/cm<sup>2</sup> not represented to avoid overcrowded CVs). All CVs

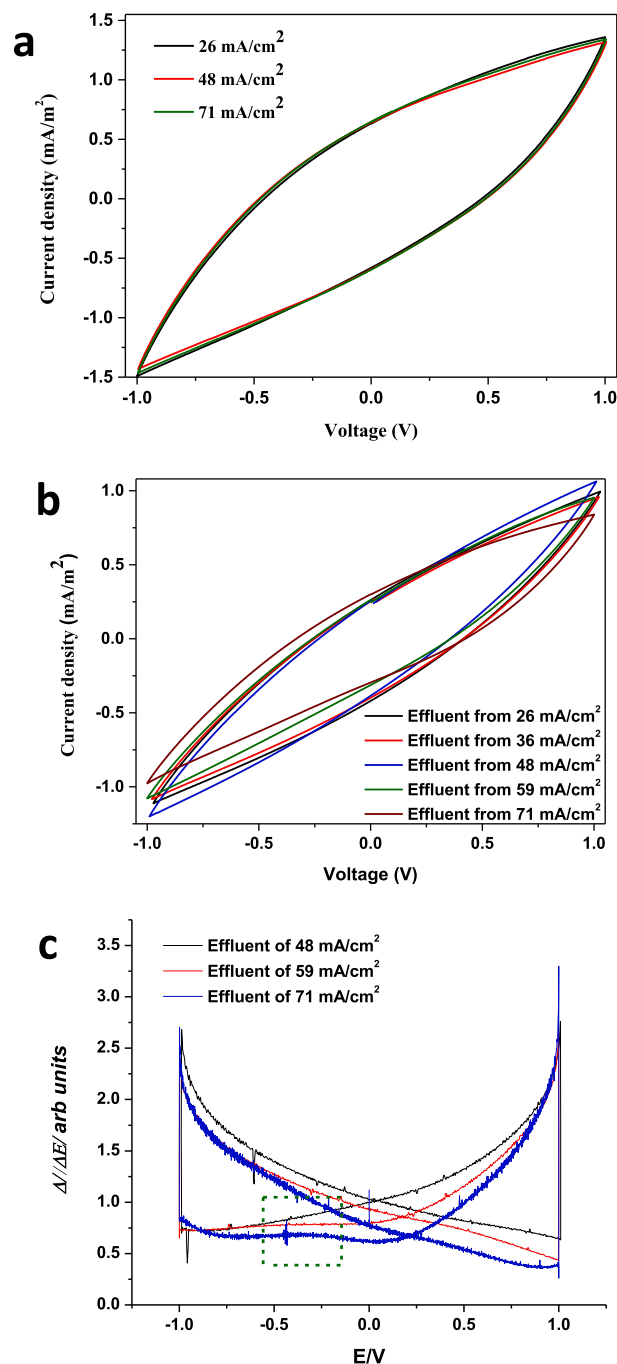


Fig. 8. Cyclic voltammetric (CV) analysis of (a) Electrochemical cell with 26, 48 and 71 mA/cm<sup>2</sup> experiments (CVs with 36 and 59 mA/cm<sup>2</sup> also showed very similar behavior. So, to avoid overcrowded data lines, only alternate experimental variations represented herewith) (b) CVs obtained from microbial fuel cell operated using effluents from EC under different conditions. (c) first derivative analysis of MFC data with 48, 59 and 71 mA/cm<sup>2</sup>. The section highlighted in green dotted box representing electron mediator signals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

recorded current density peak values in a narrow range. The case of 71 mA/cm<sup>2</sup> variation showed maximum current density of 1.34 mA/m<sup>2</sup> (forward scan) that was depicted as oxidation peak and -1.47 mA/m<sup>2</sup> (reverse scan) as reduction peak. Similarly, in the case of 26 mA/cm<sup>2</sup> of current density, oxidation and reduction peaks were identified respectively at 1.36 mA/m<sup>2</sup> and -1.49 mA/m<sup>2</sup>. The narrow change in the oxidation and reduction current densities evidenced stable behavior of

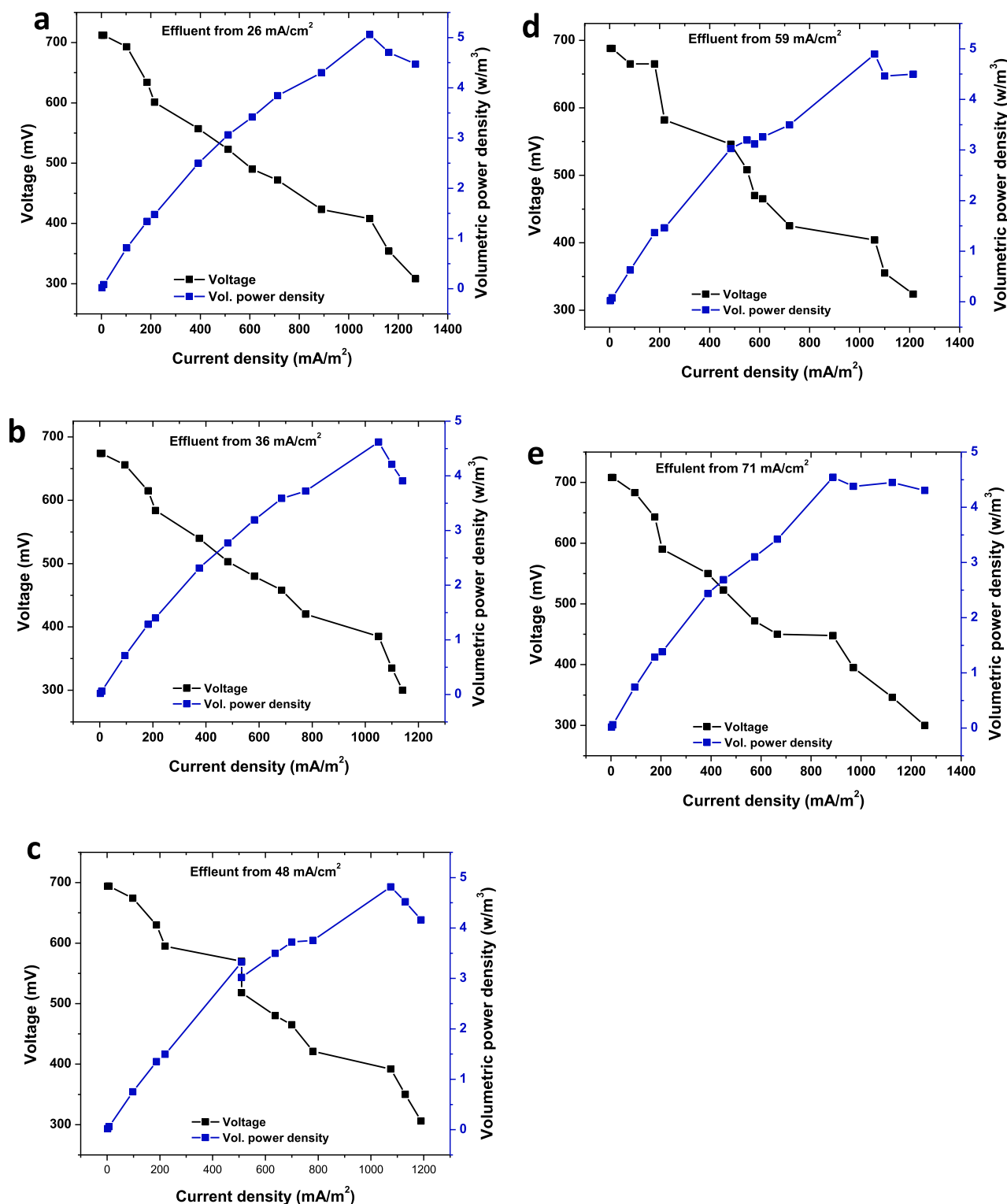


Fig. 9. Polarization behavior of MFC under 5 different effluents collected from (a) 26, (b) 36, (c) 48, (d) 59 and (e) 71 mA/cm<sup>2</sup> electrochemical cell.

electrodes used in EC system over different experimental variations. The narrow variation in oxidation and reduction currents exhibited over a range of variations in EC also suggesting stability of carbon brush that used as anode.

Contrary to the EC system, electrochemical behavior of MFC showed difference with respect to the concentration of treated PW used as substrate for electricity generation. Among the five substrates collected from five different EC processes, MFC operated with effluent from EC

showed the highest current density (by CV analyses). Maximum current density was identified with effluents from 48 mA/cm<sup>2</sup> EC operation (oxidation peak, 1.06 mA/m<sup>2</sup>; reduction peak, -1.20 mA/m<sup>2</sup>). In the case of 71 mA/cm<sup>2</sup> operation, the minimum response was recorded (oxidation peak, 0.84 mA/m<sup>2</sup>; reduction peak, -0.98 mA/m<sup>2</sup>). In the case of other effluents from 26, 36 and 59 mA/cm<sup>2</sup>, oxidation and reduction peaks were registered in narrow range (Fig. 8b). The bioelectrochemical response that observed through CVs is correlating well with

**Table 5**  
Polarization behavior of the MFC using five different EC effluents as substrate and cell design point of each variation.

Substrate for MFC operation (Effluent of EC, mA/cm <sup>2</sup> )	Cell design point ( $\Omega$ )	Volumetric power density (w/m <sup>3</sup> )	Current density (mA/m <sup>2</sup> )
26	300	5.06	443
36	300	4.62	404
48	300	4.82	421
59	300	4.89	428
71	400	4.54	398

the bioelectricity generation recorded from the MFC operation (Fig. 3). The effluent from 48 mA/cm<sup>2</sup> has shown the highest bioelectricity generation and the lowest with effluent from EC of 71 mA/cm<sup>2</sup>. Similar trend was also registered with CV analysis. This clearly shows that bioelectricity generation potential depends on the nature of the substrate used in the anolyte. However, the mediators involved in the electron transfer were not identified clearly through CV graphs. The first derivative analysis was performed for MFCs recorded in 48, 57 and 71 mA/m<sup>2</sup> experiments. A signal in the range of  $-0.4$  and  $-0.5$  was identified, which is optimum potential range for NADH [59,60]. This denotes that NADHs might be involved in the electron transfer mechanisms of electroactive biofilms. Electron discharge phenomenon of electroactive biofilms can be evaluated with polarization analysis. Electron discharge was evaluated at various external potentials (100  $\Omega$  to 30 k $\Omega$ ) and recorded current and volumetric power density. Polarization behavior also helps to identify the cell design point of the system under particular operating conditions [61]. Among the five different effluents used as MFC feed, maximum volumetric power density (VPD<sub>max</sub>) of 5.06 w/m<sup>3</sup> was registered with effluent from 26 mA/cm<sup>2</sup> (Fig. 9). During stable phase of operation, this effluent showed cell design point at 300  $\Omega$ . Among all the 5 EC effluents studies, only 71 mA/cm<sup>2</sup> effluent showed 400  $\Omega$  as cell design point, all other effluents showed 300  $\Omega$ . Current densities, volumetric power densities and respective cell design of all the variations studied were mentioned in Table 5.

#### 4. Energy efficiency of the individual processes and integration

Bio-refineries integrate different processes to harness the advantage of each process and achieve improved overall performance. Here, electrochemical process and MFC were integrated to treat recalcitrant PW. One of the major concerns of wastewater treatment is energy consumption, so energy balance between consumption and generation will decide the practical applicability of the overall integration. In this direction, an attempt was made to evaluate the total power consumed for electrochemical process and total energy generated from MFCs using the five different current densities evaluated for treatment. The total power consumption (TPC) was calculated by integrating time and power consumed. Power was calculated from voltage applied and

**Table 6**  
Energy balance calculations for net energy production. The calculations are based on energy consumption through electrochemical process and energy generation in microbial fuel cell system from the treatment of produced water.

Current density (mA/cm <sup>2</sup> )	Electrochemical Cell (EC)		Microbial Fuel Cell (MFC)		Net Energy Production	
	Total power consumption (TPC) (mWh)	Volumetric power consumption (VPC) (Wh m <sup>-3</sup> )	Total power production (TPP) (mWh)	Volumetric power production (VPP) (Wh m <sup>-3</sup> )	Net power production (NPP) (mWh)	Net volumetric power production (NVPP) (Wh m <sup>-3</sup> )
26	34	96	555	1586	521	1490
36	58	166	567	1620	509	1454
48	91	261	656	1876	565	1615
59	150	430	553	1580	403	1150
71	228	651	471	1346	243	695

current recorded during the power supply. Similarly, the total power produced (TPP) was calculated. Here, due to the fluctuations in power generation, average values were considered and integrated with time of operation. Resulting power consumption and generation were normalized to m<sup>3</sup> to determine the volumetric power consumption (VPC) and volumetric power production (VPP) respectively. Volumetric calculations guides preliminary notion for larger scale studies. Further, this evaluation was used to calculate the net energy generated or consumed from each integration process.

Referring to Table 6, the highest TPC of 228 mWh was registered with 71 mA/cm<sup>2</sup> and the minimum was identified with 26 mA/cm<sup>2</sup> (34 mWh) in ECs. It is obvious that the highest consumption was recorded with high current densities. Similarly, the highest and the lowest VPC were recorded with 71 mA/cm<sup>2</sup> (651 Wh m<sup>-3</sup>) and 26 mA/cm<sup>2</sup> (96 Wh m<sup>-3</sup>) respectively. A clear increasing trend was identified with increase in current densities used for electrochemical treatment. However, the net energy of the treatment process can be identified when power consumption in electrochemical process (primary stage) is clubbed with power generation in MFC operation (secondary stage). In the case of MFC, the highest TPP of 656 mWh was recorded with effluent generated from 48 mA/cm<sup>2</sup> EC variation. The lowest TPP was recorded with effluent generated from 71 mA/cm<sup>2</sup> condition (471 mWh). The trend of energy generated with MFC was influenced by the concentration and the extent of degradation/treatment that occurred during primary process (electrochemical reactors). Similar to TPP, VPP was also registered the highest energy recovery with 48 mA/cm<sup>2</sup> (1876 Wh m<sup>-3</sup>) and the lowest energy recovery with 71 mA/cm<sup>2</sup> (1346 Wh m<sup>-3</sup>). Based on the balance of energy recovery and consumption, energy from the integration resulted in net positive values in all the integrations. However, the amount of net energy production was found to vary with each integration combination.

The highest net energy production was registered with 48 mA/cm<sup>2</sup> condition, which showed 565 mWh of positive energy from the primary and secondary treatment processes (Table 6). Compared to the energy consumption in EC, almost 5 times more net energy was produced through MFC as secondary process. In the case of 71 mA/cm<sup>2</sup> of EC process, the highest energy consumption was recorded (228 mWh) and the lowest power generation was identified from MFC process. This resulted in lowest net energy production from the EC and MFC balance. From the present study, the net energy balance was normalized to cubic meter (m<sup>3</sup>) to identify the energy efficiency of process integration. The calculations were made considering the energy consumption and generation from EC and MFC only. The energy consumption for operation of treatment process and plant maintenance were not considered. The energy values acquired from 350 mL reactor were extrapolated to cubic meter (m<sup>3</sup>), which is almost 2857 times the present volume of EC and MFC reactors. Maximum net energy production of 1615 Wh m<sup>-3</sup> was registered with the integration of 48 mA/cm<sup>2</sup> (EC) and its effluents in MFC operation. In the case of 26 and 36 mA/cm<sup>2</sup>, net energy production was registered respectively as 1490 and 1454 Wh m<sup>-3</sup>, whereas, 71 mA/cm<sup>2</sup> showed the lowest net energy production of 695 Wh m<sup>-3</sup>.

This is in contrast to the substrate degradation rates registered. However, the extent of the net energy recovery varies in each integration process. Net energy balance is not the only factor for the selection of integration process. It must be consolidated with time and substrate degradation rate along with energy expenses in the operation processes.

Several researchers were studied scaling up of microbial fuel cells with different wastewaters and reactor configurations [62–66]. A study with submersible 255 L prototype MFC was operated using municipal sewage wastewater which is having high share from industrial activities. This MFC was operated with multi-panel stainless steel/activated carbons air cathode (85 × 85 cm). The study resulted in 176 mW/m<sup>3</sup> of power generation. After 77 days of operation, high salts concentration of 2.8 g TDS/L caused drastic decline in the power output to 35 mW/m<sup>3</sup> (56–77 days). The cause for decline in performance was due to the inorganic fouling, which can be improved by 22% upon mechanical cleaning of the cathode electrode [62]. In another study by Rossi et al. [63], multi-panel air cathode in which 15 small cathodes welded into one large cathode were used. This helps to maintain good electrical conductivity and high surface area. This study also evaluated three different cathode sizes (7 cm<sup>2</sup>, 33 cm<sup>2</sup> and 6200 cm<sup>2</sup>) to check the bioelectrochemical behavior with scaling-up of the MFC process. Both 7 and 33 cm<sup>2</sup> evaluated in single panel design, whereas the 6200 cm<sup>2</sup> evaluated in multi-panel cathode design. Increasing the size of the cathode electrode from 7 cm<sup>2</sup> to 33 cm<sup>2</sup> resulted in 5% increase in cathode potential. Further increase in cathode size to 6200 cm<sup>2</sup> resulted in 55% drop in cathode potential. Similar performance was observed with different numbers of anode brushes also in 85 L MFC reactor [63]. This suggest the possibility of drop in performance and energy production efficiency when scaled up to large volumes and different sizes of electrodes. In MFCs, type of electrodes (cathode/anode), type of cathodic reduction reaction, wastewater/substrate, composition of wastewater, design of MFC, etc. were found to influence MFC performance to a great extent. However, using PW as substrate with an efficient MFC design and electrode at large scale will provide more insights.

## 5. Conclusions

Integration of electrochemical and bioelectrochemical processes treating PW evidenced its function towards sustainable process development. The cumulative treatment efficiency of EC and MFC integration is promising. The integration resulted in TPH removal (89%) and COD removal (90%). The integration was also removed sulfates (42.6%) and TDS (34.3%). Integration offers extended treatment efficiency along with additional energy generation (bioelectricity). Balancing the energy consumption in EC and generation in MFC resulted in net energy production of about 1615 Wh m<sup>-3</sup>. Based on the results exhibited from the present integration study, a hybrid system can be developed through continuous mode of operation.

## CRedit authorship contribution statement

**Gunda Mohanakrishna:** Conceptualization, Methodology, Formal analysis, Writing - original draft. **Riyadh I. Al-Raoush:** Funding acquisition, Project administration, Resources, Conceptualization, Methodology, Writing - review & editing. **Ibrahim M. Abu-Reesh:** Resources, Conceptualization, Methodology, Writing - review & editing.

## 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.

## Acknowledgements

This publication was made possible by NPRP grant # 9-093-1-021 from the Qatar national research fund (a member of Qatar Foundation). The findings achieved herein are solely the responsibility of the authors. Open Access funding provided by the Qatar National Library.

## References

- [1] Jiménez S, Andreozzi M, Micó MM, Álvarez MG, Contreras S. Produced water treatment by advanced oxidation processes. *Sci Total Environ* 2019;666:12–21.
- [2] Acharya HR, Henderson C, Matis H, Kommepalli H, Moore B, Wang H. Cost effective recovery of low-TDS frac flowback water for re-use. DOE Report DE-FE0000784, (2011) 100.
- [3] Wang H, Lu L, Chen X, Bian Y, Ren ZJ. Geochemical and microbial characterizations of flowback and produced water in three shale oil and gas plays in the central and western United States. *Water Res* 2019;164:114942.
- [4] Jain P, Sharma M, Dureja P, Sarma PM, Lal B. Bioelectrochemical approaches for removal of sulfate, hydrocarbon and salinity from produced water. *Chemosphere* 2017;166:96–108.
- [5] Benamor A, Talkhan AG, Nasser M, Hussein I, Okonkwo PC. Effect of temperature and fluid speed on the corrosion behavior of carbon steel pipeline in Qatari oilfield produced water. *J Electroanal Chem* 2018;808:218–27.
- [6] Bagheri M, Roshandel R, Shayegan J. Optimal selection of an integrated produced water treatment system in the upstream of oil industry. *Process, Saf Environ Prot* 2018;117:67–81.
- [7] Khansari Z, Gates ID. Assessment of reservoir heterogeneity by using produced water chemistry in SAGD. *Int J Energy Res* 2016;40(10):1367–80.
- [8] Jiménez S, Micó MM, Armalos M, Medina F, Contreras S. State of the art of produced water treatment. *Chemosphere* 2018;192:186–208.
- [9] Arowshola L, Cope G, David V, Gasson C, González-Manchón C, Kelleher M, et al. Produced Water Market: Opportunities in the oil, shale and gas sectors in North America. Global Water Intelligence Publication. 1st ed., New York: Media Analytics Ltd.; 2011.
- [10] Al-Ghouti MA, Al-Kaabi MA, Ashfaq MY, Da'na DA. Produced water characteristics, treatment and reuse: a review. *J. Water Process. Eng.* 2019;28:222–39.
- [11] Gregory K, Mohan AM. Current perspective on produced water management challenges during hydraulic fracturing for oil and gas recovery. *Environ. Chem.* 2015;12:261–6.
- [12] Produced Water Report: Regulations, Current Practices, and Research Needs. Ground Water Protection Council 13308 N. MacArthur Blvd. Oklahoma City, OK 73142, June-2019 <http://www.gwpc.org/sites/default/files/files/Produced%20Water%20Full%20Report%20-%20Digital%20Use.pdf>.
- [13] Produced Water Reuse in Oklahoma: Regulatory Considerations and References, Ground Water Protection Council, Oklahoma, USA, 2015, pp. 1–47. <http://www.gwpc.org/sites/default/files/Oklahoma-Produced-Water-Project-Summary-Report.pdf>.
- [14] Blondes MS, Gans KD, Engle MA, Kharaka YK, Reidy ME, Saraswathula V, Thordson JJ, Rowan EL, Morrissey EA, U.S. Geological Survey National Produced Waters Geochemical Database (ver. 2.3, January 2018): U.S. Geological Survey data release, 2018. <https://doi.org/10.5066/F7J964W8>.
- [15] Lu J, Wang X, Shan B, Li X, Wang W. Analysis of chemical compositions contributable to chemical oxygen demand (COD) of oilfield produced water. *Chemosphere* 2006;62(2):322–31.
- [16] Butkovskiy A, Bruning H, Kools SA, Rijnaarts HH, Van Wezel AP. Organic pollutants in shale gas flowback and produced waters: identification, potential ecological impact, and implications for treatment strategies. *Environ. Sci. Technol.* 2017;51:4740–54.
- [17] Igundu ET, Chen GZ. Produced water treatment technologies. *Int. J. Low-Carbon Technol.* 2012;9:157–77.
- [18] Adham S, Hussain A, Minier-Matar J, Janson A, Sharma R. Membrane applications and opportunities for water management in the oil & gas industry. *Desalination* 2018;440:2–17.
- [19] Kardena E, Hidayat S, Nora S, Helmy Q. Biological treatment of synthetic oilfield-produced water in activated sludge using a consortium of endogenous bacteria isolated from a tropical area. *J. Pet. Environ. Biotechnol.* 2017;8:1–6.
- [20] Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biakl DR, Madaeni SS, Abidin ZZ. Review of technologies for oil and gas produced water treatment. *J. Hazard. Mater.* 2009;170:530–51.
- [21] Tavakkoli S, Lokare OR, Vidic RD, Khanna V. A techno-economic assessment of membrane distillation for treatment of Marcellus shale produced water. *Desalination* 2017;416:24–34.
- [22] Garcia-Segura S, Ocon JD, Chong MN. Electrochemical oxidation remediation of real wastewater effluents—a review. *Process Saf Environ Prot* 2018;113:48–67.
- [23] Kumar SS, Kumar V, Kumar R, Malyan SK, Pugazhendhi A. Microbial fuel cells as a sustainable platform technology for bioenergy, biosensing, environmental monitoring, and other low power device applications. *Fuel* 2019;255:115682.
- [24] Kumar SS, Kumar V, Malyan SK, Sharma J, Mathimani T, Maskarej MS, et al. Microbial fuel cells (MFCs) for bioelectrochemical treatment of different wastewater streams. *Fuel* 2019;254:115526.
- [25] Mohamed SN, Thomas N, Tamilmani J, Boobalan T, Matheswaran M, Kalachelvi P, et al. Bioelectricity generation using iron (II) molybdate nanocatalyst coated anode during treatment of sugar wastewater in microbial fuel cell. *Fuel* 2020;277:118119.

- [26] Kumar SS, Kumar V, Gude VG, Malyan SK, Pugazhendhi A. Alkalinity and salinity favor bioelectricity generation potential of *Clostridium*, *Tetrathlobacter* and *Desulfovibrio* consortium in microbial fuel Cells (MFC) treating sulfate-laden wastewater. *Bioresour Technol* 2020;123110.
- [27] He Z, Angenent LT. Application of bacterial biocathodes in microbial fuel cells. *Electroanalysis* 2006;18:2009–16.
- [28] Mohanakrishna G, Mohan SV, Sarma PN. Bio-electrochemical treatment of distillery wastewater in microbial fuel cell facilitating decolorization and desalination along with power generation. *J. Hazard. Mater.* 2010;177:487–94.
- [29] Mohanakrishna G, Abu-Reesh IM, Al-Raoush RI. Biological anodic oxidation and cathodic reduction reactions for improved bioelectrochemical treatment of petroleum refinery wastewater. *J. Clean. Prod.* 2018;190:44–52.
- [30] Cao X, Huang X, Liang P, Xiao K, Zhou Y, Zhang X, et al. A new method for water desalination using microbial desalination cells. *Environ. Sci. Technol.* 2009;43:7148–52.
- [31] Khan N, Khan MD, Nizami AS, Rehan M, Shaida A, Ahmad A, et al. Energy generation through bioelectrochemical degradation of pentachlorophenol in microbial fuel cell. *RSC Adv.* 2018;8:20726–36.
- [32] Pant D, Van Bogaert G, Diels L, Vanbroekhoven K. A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. *Bioresour. Technol.* 2010;101:1533–43.
- [33] Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM, Aljaml K. Removal of petroleum hydrocarbons and sulfates from produced water using different bioelectrochemical reactor configurations. *Sci. Total. Environ.* 2019;665:820–7.
- [34] Mohanakrishna G, Abu-Reesh IM, Kondaveeti S, Al-Raoush RI, He Z. Enhanced treatment of petroleum refinery wastewater by short-term applied voltage in single chamber microbial fuel cell. *Bioresour. Technol.* 2018;253:16–21.
- [35] Shrestha N, Chilkoor G, Wilder J, Ren ZJ, Gadhamshetty V. Comparative performances of microbial capacitive deionization cell and microbial fuel cell fed with produced water from the Bakken shale. *Bioelectrochemistry* 2018;121:56–64.
- [36] Makhtar MMZ, Tajarudin HA. Electricity generation using membrane-less microbial fuel cell powered by sludge supplemented with lignocellulosic waste. *Int J Energy Res* 2020. <https://doi.org/10.1002/er.5151>.
- [37] Kadier A, Jain P, Lai B, Kalil MS, Kondaveeti S, Alabbosh KFS, et al. Biorefinery perspectives of microbial electrolysis cells (MECs) for hydrogen and valuable chemicals production through wastewater treatment. *Biofuel Res J* 2020;7(1):1128–42.
- [38] Saba B, Khan M, Christy AD, Kjellerup BV. Microbial phyto-power systems—A sustainable integration of phytoremediation and microbial fuel cells. *Bioelectrochemistry* 2019;127:1–11.
- [39] APHA, Rice A, Baird EW, Eaton RB. *Standard Methods for Examination of Water and Wastewater* (Washington: American Public Health Association, American Water Works Association, Water Environment Federation ISBN); 2017.
- [40] Gargouri B, Gargouri OD, Gargouri B, Trabelsi SK, Abdelhedi R, Bouaziz M. Application of electrochemical technology for removing petroleum hydrocarbons from produced water using lead dioxide and boron-doped diamond electrodes. *Chemosphere* 2014;117:309–15.
- [41] Medel A, Lugo F, Meas Y. Application of Electrochemical Processes for Treating Effluents from Hydrocarbon Industries. *Electrochemical Water and Wastewater Treatment*. 2018. p. 365–92.
- [42] Dos Santos EV, Rocha JHB, de Araújo DM, de Moura DC, Martínez-Huitle CA. Decontamination of produced water containing petroleum hydrocarbons by electrochemical methods: a minireview. *Environ Sci Pollut Res* 2014;21(14):8432–41.
- [43] Yan L, Wang Y, Li J, Ma H, Liu H, Li T, et al. Comparative study of different electrochemical methods for petroleum refinery wastewater treatment. *Desalination* 2014;341:87–93.
- [44] Zhao YG, Wang AJ, Ren NQ. Effect of carbon sources on sulfidogenic bacterial communities during the starting-up of acidogenic sulfate-reducing bioreactors. *Bioresour. Technol.* 2010;101:2952–9.
- [45] Mohanakrishna G, Mohan SK, Mohan SV. Carbon based nanotubes and nanopowder as impregnated electrode structures for enhanced power generation: evaluation with real field wastewater. *Appl. Energy* 2012;95:31–7.
- [46] Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, et al. Microbial fuel cells: methodology and technology. *Environ Sci Technol* 2006;40(17):5181–92.
- [47] Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM, Pant D. A microbial fuel cell configured for the remediation of recalcitrant pollutants in soil environment. *RSC Adv* 2019;9(71):41409–18.
- [48] Mohanakrishna G, Al-Raoush RI, Abu-Reesh IM. Induced bioelectrochemical metabolism for bioremediation of petroleum refinery wastewater: Optimization of applied potential and flow of wastewater. *Bioresour. Technol.* 2018;260:227–32.
- [49] Srikanth S, Mohan SV, Sarma PN. Positive anodic poised potential regulates microbial fuel cell performance with the function of open and closed circuitry. *Bioresour. Technol.* 2010;101:5337–44.
- [50] Nancharaiyah YV, Mohan SV, Lens PNL. Metals removal and recovery in bioelectrochemical systems: a review. *Bioresour Technol* 2015;195:102–14.
- [51] Mohan SV, Mohanakrishna G, Velvizhi G, Babu VL, Sarma PN. Bio-catalyzed electrochemical treatment of real field dairy wastewater with simultaneous power generation. *Biochem Eng J* 2010;51(1–2):32–9.
- [52] Zouboulis AI, Avranas A. Treatment of oil-in-water emulsions by coagulation and dissolved-air flotation. *Colloids Surf. A Physicochem. Eng. Asp.* 2000;172:153–61.
- [53] Mousa IE. Total petroleum hydrocarbon degradation by hybrid electrobiochemical reactor in oilfield produced water. *Mar. Pollut. Bull.* 2016;109:356–60.
- [54] Liang F, Xiao Y, Zhao F. Effect of pH on sulfate removal from wastewater using a bioelectrochemical system. *Chem. Eng. J.* 2013;218:147–53.
- [55] Madigan MT, Martinko JM, Parker J. *Brock biology of microorganisms*. Upper Saddle River 1997;vol. 11.
- [56] Modestra JA, Mohan SV. Microbial electrosynthesis of carboxylic acids through CO<sub>2</sub> reduction with selectively enriched biocatalyst: Microbial dynamics. *J CO<sub>2</sub> Util* 2017;20:190–9.
- [57] Zhu W, Gao H, Zheng F, Huang T, Wu F, Wang H. Electrodeposition of graphene by cyclic voltammetry on nickel electrodes for microbial fuel cells applications. *Int J Energy Res* 2019;43(7):2795–805.
- [58] Zhao Y, Ma Y, Li T, Dong Z, Wang Y. Modification of carbon felt anodes using double-oxidant HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> for application in microbial fuel cells. *RSC Adv* 2018;8(4):2059–64.
- [59] Park DH, Zeikus JG. Electricity generation in microbial fuel cells using neutral red as an electronophore. *Appl Environ Microbiol* 2000;66(4):1292–7.
- [60] Nikhil GN, Chaitanya DK, Srikanth S, Swamy YV, Mohan SV. Applied resistance for power generation and energy distribution in microbial fuel cells with rationale for maximum power point. *Chem Eng J* 2018;335:267–74.
- [61] Mohan SV, Mohanakrishna G, Srikanth S, Sarma PN. Harnessing of bioelectricity in microbial fuel cell (MFC) employing aerated cathode through anaerobic treatment of chemical wastewater using selectively enriched hydrogen producing mixed consortia. *Fuel* 2008;87(12):2667–76.
- [62] Hiegemann H, Littfinski T, Krimmler S, Lübken M, Klein D, Schmelz KG, et al. Performance and inorganic fouling of a submersible 255 L prototype microbial fuel cell module during continuous long-term operation with real municipal wastewater under practical conditions. *Bioresour Technol* 2019;294:122227.
- [63] Rossi R, Jones D, Myung J, Zikmund E, Yang W, Gallego YA, et al. Evaluating a multi-panel air cathode through electrochemical and biotic tests. *Water Res* 2019;148:51–9.
- [64] He W, Dong Y, Li C, Han X, Liu G, Liu J, et al. Field tests of cubic-meter scale microbial electrochemical system in a municipal wastewater treatment plant. *Water Res* 2019;155:372–80.
- [65] Liang P, Duan R, Jiang Y, Zhang X, Qiu Y, Huang X. One-year operation of 1000-L modularized microbial fuel cell for municipal wastewater treatment. *Water Res* 2018;141:1–8.
- [66] Hiegemann H, Lübken M, Schulte P, Schmelz KG, Gredigk-Hoffmann S, Wichern M. Inhibition of microbial fuel cell operation for municipal wastewater treatment by impact loads of free ammonia in bench-and 45 L-scale. *Sci Total Environ* 2018;624:34–9.
- [67] Pahlevani L, Mozdianfar MR, Fallah N. Electrochemical oxidation treatment of offshore produced water using modified Ti/Sb-SnO<sub>2</sub> anode by graphene oxide. *J Water Process Eng* 2020;35:101204.
- [68] Yavuz Y, Koparal AS. Electrochemical oxidation of phenol in a parallel plate reactor using ruthenium mixed metal oxide electrode. *J Hazard Mater* 2006;136(2):296–302.
- [69] Santos MR, Goulart MO, Tonholo J, Zanta CL. The application of electrochemical technology to the remediation of oily wastewater. *Chemosphere* 2006;64(3):393–9.
- [70] Abdel-Salam OE, Abou Taleb EM, Afify AA. Electrochemical treatment of chemical oxygen demand in produced water using flow-by porous graphite electrode. *Water Environ J* 2018;32(3):404–11.
- [71] Körbahti BK, Artut K. Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes. *Desalination* 2010;258(1–3):219–28.
- [72] Medel A, Bustos E, Esquivel K, Godínez LA, Meas Y. Electrochemical incineration of phenolic compounds from the hydrocarbon industry using boron-doped diamond electrodes. *Int. J. Photoenergy* 2012;2012:681875.