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Degradation of phenolic compounds in wastewater using a conical-shaped packed-bed microbial fuel cell in continuous flow with recycling†

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A unique conical-shaped single-chamber (SC) microbial fuel cell (MFC) set-up was used to demonstrate the feasibility of continuous mode operation with recycling for the enhanced degradation of phenolic compounds in wastewater. Here, 1,2-propanediol/propylene glycol (1-2-PD, a phenolic compound) was used as the model phenolic compound, which is commonly found in pharmaceutical and cosmetic industrial effluents. Different flow rates (Q = 1, 3, and 5 cc min^{-1}) and recycling ratios (RQ = 0.5, 1, 1.5 cc min^{-1}) were used to study the effect of recycling on wastewater treatment in the continuous mode. The effects of the 1-2-PD concentration (1000, 5000, and 10 000 ppm) and solution pH (6.23, 7.84, and 8.32) on the efficacy of SCMFC were determined. The maximum voltage generation (~380 mV), chemical oxygen demand reduction (~80%), and 1-2-PD degradation (~84%) were measured at the optimized effluent and with a recycling flowrate of 1 cc min^{-1} each. The 16s rRNA sequencing confirmed the abundance of *Paenibacillus* and *Pseudomonas* genera in the mixed bacterial culture of the effluent. This study emphasizes the necessity of recycling during wastewater treatment in an SCMFC operated in the continuous mode, which may be further useful for designing new types of effluent treatment plants integrated with MFC for efficiently treating industrial wastewater effluent contaminated with organic compounds.

1. Introduction

There is increasingly continued pressure applied by government agencies globally on chemical manufacturing plants to comply with the prescribed effluent water quality parameters before discharging effluent to local water bodies. Consequently, the installation of onsite wastewater treatment plants (WTPs) has gained importance.[1,2] The single-chamber microbial fuel cell (SCMFC), using the idea of an air cathode, is a spontaneous bioelectrochemical system that is capable of treating the organic compounds contained in wastewater (COD 1000–6000 mg L^{-1}) under continuous-flow conditions and simultaneously generating bioenergy (424–3000 mW m^{-3}). Pharmaceutical industries, petrochemical plants, dye processing plants, and textile industries are the potential users of such a device for treating their aqueous organic effluents.[3,4]

The use of expensive noble or precious metal-based electrodes and the Nafion proton-exchange membrane (PEM) are the major hindrances in scaling up SCMFCs. In this context, the focus of many recent studies is on the development of new electrode materials, including transition metal–carbon nanocomposites, as a potential substitute for the expensive noble metal-based electrodes.[5–8] Similarly, various materials, including conducting polymers, have been studied as potential substitutes for the expensive Nafion as a PEM.[9,10] Biocompatibility of the anode materials with the microbes present in the industrial wastewater effluents, and a dense and stable growth of biofilm on the anode during the operation of a microbial fuel cell (MFC) are critical for the continuous and long-term sustainability of MFCs, and therefore, these aspects are also the focus of many recent studies.[11,12]

Packed-bed reactors are widely used in a variety of chemical engineering applications, including absorption, adsorption, and reactions. A recent study successfully developed a unique conical configuration of the packed-bed membraneless SCMFC to treat wastewater (COD loading of ~20 000 mg L^{-1}) in the continuous-flow mode.[13] In such a device, cerium oxide (CeO_2)-doped activated carbon beads (ACBs) packed in the column served as the anode, while the same material, *i.e.* CeO_2, dispersed in activated carbon fabric (ACF) served as the air cathode. The air-cathode material consisted of polydimethylsiloxane coated on the air-side of ACF, whereas the anolyte-side of ACF was coated with the polymethyl vinyl ether-

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alt-maleic anhydride copolymer for the permeation of atmospheric oxygen and cation exchange, respectively. A mixture of wastewater and *E. coli* was used as an anolyte. The as-fabricated SCMFC operating at ~50 min hydraulic residence time generated ~426 mW m^{-3} power density with a COD removal efficiency of ~76.0%.

This study was performed to explore the feasibility and advantages (reduction in COD values) of recycling the treated or partially treated wastewater in a conical-shaped packed-bed single-chamber MFC. In particular, the present study is a step forward in operating SCMFCs under recycle-flow conditions to treat wastewater laden with recalcitrant phenolic derivatized organic compounds, namely 1-2-propanediol/propylene glycol (1-2-PD) here. This organic compound is a common precursor for synthesizing various chemicals, including adhesives, laminates, resins, detergents, cosmetic antifreeze, pharmaceutics, and paints.[14] However, the overuse of 1-2-PD has been recognized to cause severe diseases, categorized in biomagnification, such as depression, bradycardia, arrhythmia, and dermatitis.[15,16] First, the development and operation of the SCMFC, including the synthesis of anode beads and the air-cathode disc, are described. The effects of the water flow rate, concentration of 1-2-PD, and recycling ratio on the performance of the device, such as the power generation and the degradation of the phenolic compound, are described next. Importantly, a mixed culture isolated from the wastewater of a local chemical-producing plant was used in this study to grow a biofilm on the anode, and the 16s rRNA metagenomics technique was used to identify the microbes present in the wastewater.

2. Materials and methods

All the chemicals used for the synthesis of the electrodes (CeO_2–CNF/ACB anode and CeO_2–CNF/CNF cathode) were as mentioned in a previous study.[13] Agar powder, tryptone, yeast extract powder, sodium chloride (NaCl), eosin methylene blue (EMB) agar, tryptic soy agar (TSA), mannitol salt agar (MSA), and nutrient agar (NA) were purchased from Himedia Pvt Ltd (India) for preparing the bacterial culture broth. 1-2-PD (purity > 99%) was purchased from Loba Chemie Pvt Ltd (India). The wastewater sample was collected

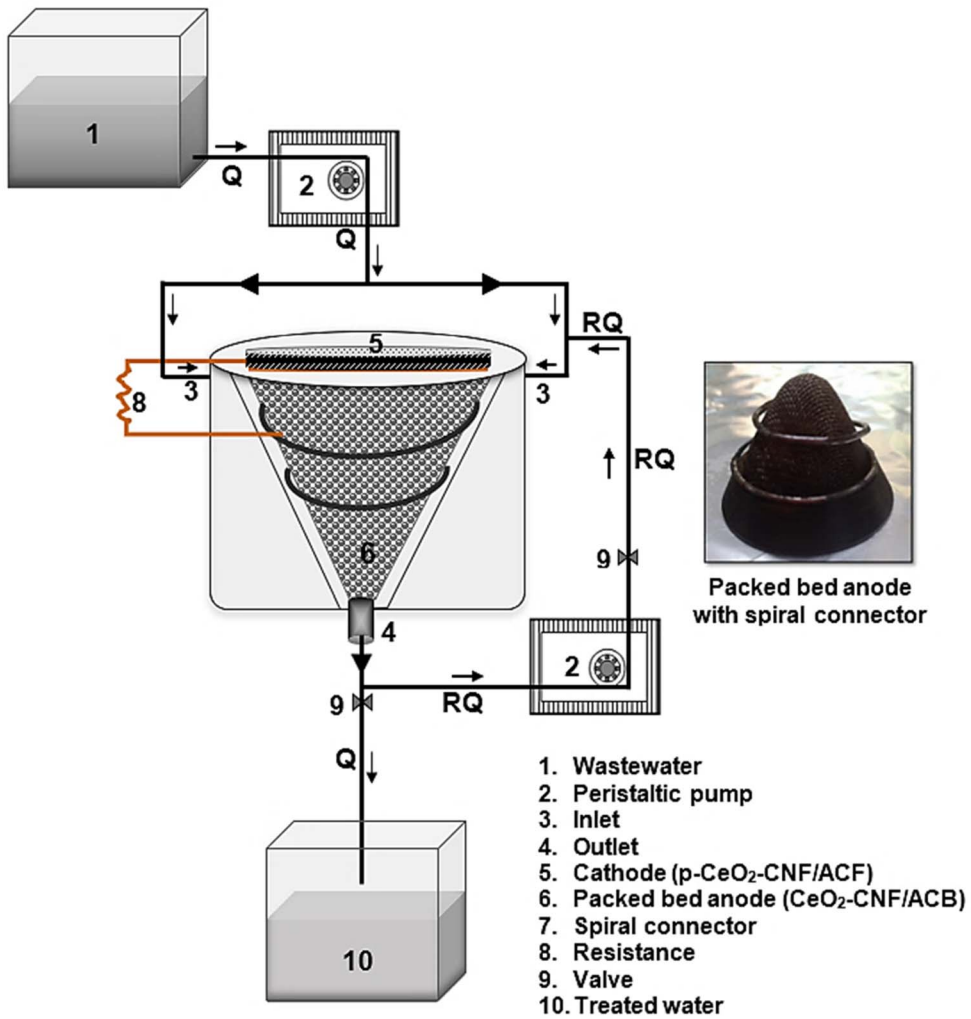

Fig. 1 Schematic of the recycle-SCMFC set-up with the inverted cone-shaped packed-bed anode basket and disc cathode, used under continuous-flow conditions.

from a local chemical-producing factory in Kanpur (India). The wastewater effluent predominantly contained phenolic compounds (~2000 mg L^{-1}) with COD values between 3000–4000 mg L^{-1}, and a TOC value of ~2500 mg L^{-1}.

The syntheses of both electrode materials (anodic beads and cathodic disc) were as described in a previous study.[13] A conical-shaped SCMFC set-up (53 mL) of a similar design as used in the previous study was fabricated; albeit, with the following modifications: (1) the outer walls of the anodic graphite shell were wrapped with a spiral stainless steel wire to improve the electrical connectivity of the shell material; (2) provision was made for recycling of the treated stream. Fig. 1 is a schematic of the fabricated SCMFC; where the arrows represent the direction of the main (feed/wastewater) flow and that of the recycled stream. A digital image of the operational SCMFC is provided in the ESI (Fig. S1†). As shown, two peristaltic pumps (Miclim Ltd, India), one mounted at the top and the other in the middle, were used to control the flow rates. The wastewater to be treated entered the SCMFC from the top, and a fraction of the treated stream coming out from the bottom of the packed bed was recycled to the anode chamber. Isolated mixed bacterial cultures were used to form a biofilm on the packed-bed anode. The operating conditions for the performance study of the SCMFC included three flow rates (Q = 1.0, 3.0, and 5.0 cc min^{-1}) of the feed stream, three recycled flow rates (RQ = 0.5, 1.0, and 1.5 cc min^{-1}), and three different inlet concentrations (10 000, 5000, and 1000 mg L^{-1}) of 1-2-PD solution. Finally, the MFC was also tested using industrial wastewater effluent at three COD values (3000, 1500, and 200 mg L^{-1}). The SCMFC was operated for 10 h in all cases, using 1000 Ω external resistance. The samples were collected from the exit (treated) stream at 1 h intervals for the measurements of the pH, COD, and 1-2-PD solution concentrations. The concentration of 1-2-PD in the water samples was determined using a gas chromatography (GC) system equipped with a flame ionization detector (GC-FID, Nucon Gas Chromatograph-5700, India) with a Ch. W. hp column. The oven, injector, and detector temperatures were maintained at 185 °C, 290 °C, and 300 °C, respectively. Nitrogen gas was used as a carrier gas at a flow rate of 30 mL min^{-1} for transferring 1-2-PD to the column of the GC system. A mixture of hydrogen (30 sccm) and air (300 sccm) was used for flame ionization. Approximately 1 μL of the sample was taken using a precise glass syringe for the GC analysis.

A standard protocol was used to prepare Luria Bertani broth (LB).[17] Briefly, tryptone (10 g L^{-1}), NaCl (10 g L^{-1}), and yeast extract (5 g L^{-1}) were mixed in sterilized Milli-Q water (1 L). LB agar was prepared by adding agar (15 g L^{-1}) to the prepared broth medium. Different media were also prepared by separately adding EMB (35.96 g L^{-1}), MSA (51.53 g L^{-1}), NA (13.0 g L^{-1}), and TSA (30.0 g L^{-1}) in sterilized Milli-Q water (1 L) to check the maximum growth of bacteria. The prepared media were sterilized for 20 min in an autoclave (1 bar, 121 °C). For the isolation of the mixed bacterial consortium, 100 mL of diluted (40 times) industrial wastewater was incubated for 48 h at 37 °C. The bacterial consortium was isolated from the incubated samples using the standard serial dilution method.[17] A small amount (~100 μL) of inoculum of the diluted samples was evenly spread over the different solidified agar media in Petri dishes to identify the best medium for the growth of the mixed culture. The inoculated plates were further incubated at 37 °C for 24 h. The optimized medium was used for further study. Then, 16s rRNA sequencing was performed for the

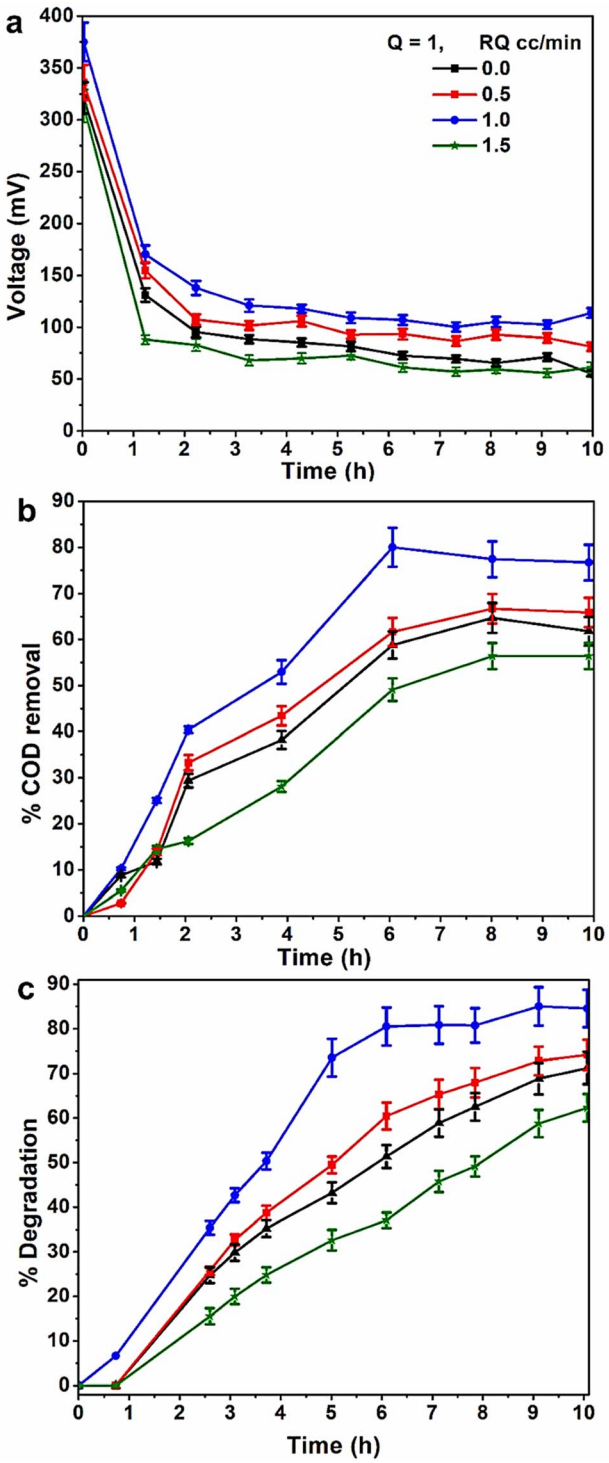

Fig. 2 Effect of the recycle flowrates: RQ = 0, 0.5, 1.0, 1.5 cc min^{-1} (Q = 1 cc min^{-1}) on (a) voltage generation, (b) % COD reduction, and (c) % degradation of 1-2-PD (1000 ppm) with respect to the time (h).

identification and taxonomical classification of the genus present in the mixed culture. Before analysis, the isolated bacterial consortium was grown in freshly prepared MSA broth and incubated for 24 h. The bacterial consortium identification and classification were performed by Triyat Genomics Pvt. Ltd (Nagpur, Maharashtra, India).

3. Results and discussion

Both materials, namely CeO_2–CNF/ACB and CeO_2–CNF/CNF, were thoroughly characterized for their physicochemical and electrochemical characteristics in the previous study, using several analytical techniques, including field-emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Raman spectroscopy analysis, cyclic voltammetry (CV), and linear sweep voltammetry (LSV), and recommended as efficient electrodes, specifically CeO_2–CNF/ACB as the anode and CeO_2–CNF/CNF as the cathode.[13] Briefly, a uniform and dense growth of CNF was observed on both electrodes (CeO_2–CNF/ACB and CeO_2–CNF/CNF). The average diameters of ACB and CNF were measured to be ~0.8 mm and ~70 nm, respectively. The specific surface areas of the anode and cathode were determined to be ~540 and ~370 $m^2\ g^{-1}$, respectively, using a BET area measurement instrument (Quantachorme, Autosorb model, USA). Both materials showed a high specific surface area with mesoporosity characteristics. They were also found to be graphitic, electroconductive, electroactive, and stable. Overall, all these physicochemical and electrochemical features indicated the synthesized electrode materials were capable of sustaining a dense and uniform biofilm formation, along with a fast charge transfer on the electrode surface.

Initial control experiments on the fabricated SCMFC in this study were performed under flow conditions (Q = 1, 3, 5 cc min^{-1}), and the corresponding hydraulic times (HRTs) of 50, 16, and 9 min, respectively, however, without recycling (RQ = 0). Fig. S2(a–c)† show the data for the open circuit potential (OCP) of the MFC operated for 10 h. The OCP values were expectedly found to be approximately the same (~300 mV) in all cases. However, the total COD and 1-2-PD degradation were measured to be the highest (~65% and ~70%, respectively) at Q = 1 cc min^{-1} (HRT ~ 50 min), thus Q was set at 1 cc min^{-1} for the next experiments. It was clear that an optimized HRT (or contact time between the packed-bed anodic beads and the wastewater trickling from the top) was required for the maximum treatment (COD reduction) of water.

Fig. 2 shows the performance of the SCMFC at a constant feed flowrate of 1 cc min^{-1} at different recycle flowrates (RQ = 0.5, 1.0, and 1.5 cc min^{-1}). Similar trends were observed in the

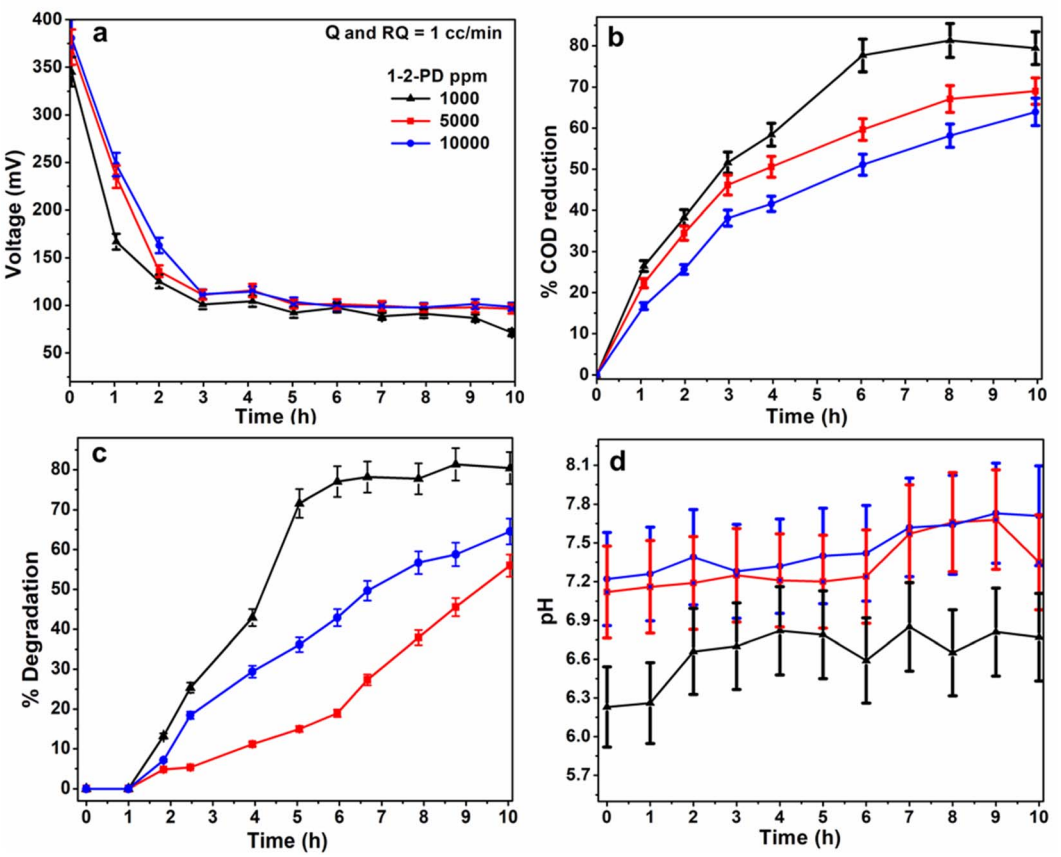

Fig. 3 Effect of the inlet concentrations of 1-2-PD (1000, 5000, and 10 000 ppm) on (a) voltage generation, (b) % COD reduction, (c) % degradation, and (d) pH with respect to the time (h) at Q = RQ = 1 cc min^{-1}.

OCP values (Fig. 2a), *i.e.* there was no significant effect of Q and RQ on the OCP (~350 mV). However, COD reduction was measured to be significantly higher (84%) at RQ = 1 cc min^{-1} than at 0.5 cc min^{-1} (~65%) and 1.5 cc min^{-1} (~56%) (Fig. 2b). Notably, the maximum COD reduction occurred within 6 h of the operation. The positive effects of recycling the partially or incomplete treated wastewater to the MFC on the COD reductions were clear; for instance, recycling at 1 cc min^{-1} improved the COD reduction by approximately 35% relative to the no-recycle case at the same feed flowrate. On the other hand, a relatively higher recycle ratio or recycle flowrate created an extra load on the microbes in the biofilm on the packed-bed beads, resulting in a reduced or decreased degradation of the organics in water. A high recycle-flowrate also resulted in a short contact time or decreased HRT, adversely affecting the treatment efficiency. The results, therefore, indicated the necessity of using an optimized recycle ratio relative to the volume or amount of the packed-bed materials used in the MFC to ensure the maximum reduction of the COD values in the exit stream. In a practical situation (pilot or large-scale plant), a mathematical model is required for the scale-up analysis and optimizing the recycle ratio prior to designing, fabricating, and operating an MFC. The data presented in Fig. 2b also confirmed the successful operation of the SCMFC developed in this study, under continuous-flow conditions with a provision for recycling. The percentage degradation of 1-2-PD is shown in Fig. 2c for different RQ values. Similar to the trend observed in the COD reductions, the decrease in 1-2-PD concentration was measured to be highest (~85%) at RQ = 1 cc min^{-1}, which was higher than that at the other recycle flowrates, *i.e.* 0.5 (68%) and 1.5 cc min^{-1} (62%). Additional experiments were carried out at different feed flowrates (Q = 1, 3, and 5 cc min^{-1}) but at a constant recycle flowrate (RQ = 1 cc min^{-1}) to establish each flowrate, with RQ and Q at 1 cc min^{-1} showing the maximum performance (COD reduction ~82% and 1-2-PD degradation ~86%) for the SCMFC used in the present study (Fig. S2(d–f).† Next, experiments were, therefore, carried out at Q = RQ = 1 cc min^{-1}.

The effect of the inlet concentration of the anolyte (1-2-PD) on its degradation was studied at three different concentrations: 1000, 5000, and 10 000 ppm. The OCP value was slightly higher (~380 mV) at 10 000 ppm than at 5000 ppm (~365 mV) and 1000 ppm (~350 mV) (Fig. 3a), attributed to the relatively greater microbial activities and biofilm formation at the anode at high 1-2-PD concentrations (Fig. S3†). On the other hand, relatively greater reductions in COD (79%) and 1-2-PD (81%) were measured at low concentration levels of 1-2-PD, attributed to an increased consumption of the organics in the feed by

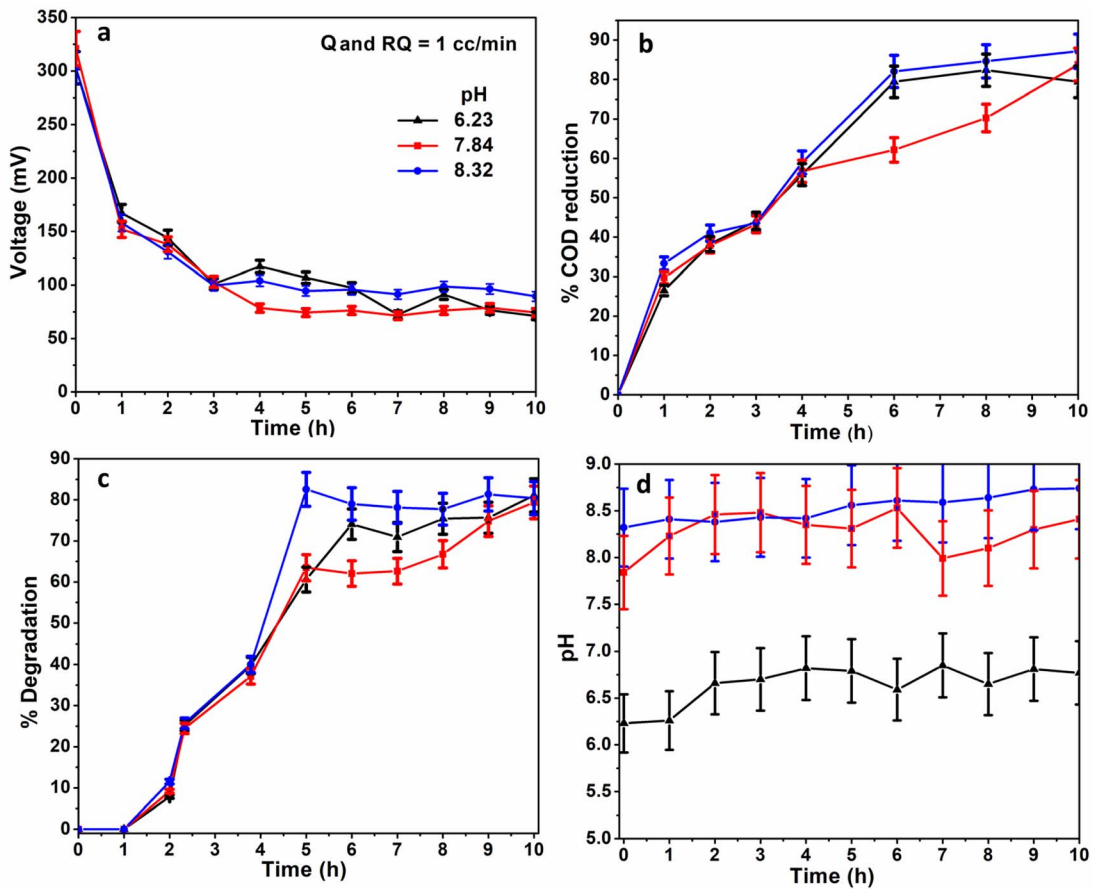

Fig. 4 Effect of the anolyte pH (Q and RQ = 1 cc min^{-1}, 1000 ppm) on (a) voltage generation, (b) % COD reduction, (c) % degradation of 1-2-PD, and (d) pH with respect to the time.

bacteria (Fig. 3b and c). Thus, the corresponding COD and analyte concentration values were low (<25%) at the 10 000 ppm inlet concentration, as the bacteria were unable to completely degrade the organics at high concentrations in the feed stream. The effect of the analyte concentrations on the pH of the spent water was also determined during SCMFC operation of 10 h (Fig. 3d). Though the pH slightly increased during the operation because of the formation of H^+, there was no significant change observed after 10 h. The recorded marginal changes in pH values (less than 5%) in this study are common during the continuous operation of an MFC.

Also, the low concentrations showed a slightly acidic pH value which was close to that of the Milli-Q water used in this study; the data clearly indicated that no post-treatment (adjustment of the pH) of the spent water was required in this case, and the same could be discharged safely to water bodies. The effect of the initial pH of the effluent or water to be treated on the performance of the SCMFC was also studied and the data are shown in Fig. 4. The MFC was operated at the earlier optimized conditions: Q = RQ = 1 cc min^{-1} and 1-2-PD concentration = 1000 ppm. Three different pH values (6.23, 7.84, and 8.32) were considered, varying from relatively less acidic to less basic.

No significant variations or differences were observed in the OCP (~310 mV), COD reduction (~82%), 1-2-PD degradation (~85%), or pH values after 10 h of operation (Fig. 4a–d), indicating that no pre-adjustment of the initial pH of wastewater was required. Post optimization of all the operating conditions, the fabricated SCMFC in this study was operated for 10 h using industrial wastewater to check its suitability for practical applications. Three COD values (200, 1500, and 3000 ppm) were considered in different effluent samples. Fig. 5 shows the results. The generated OCP and COD reduction were found to be

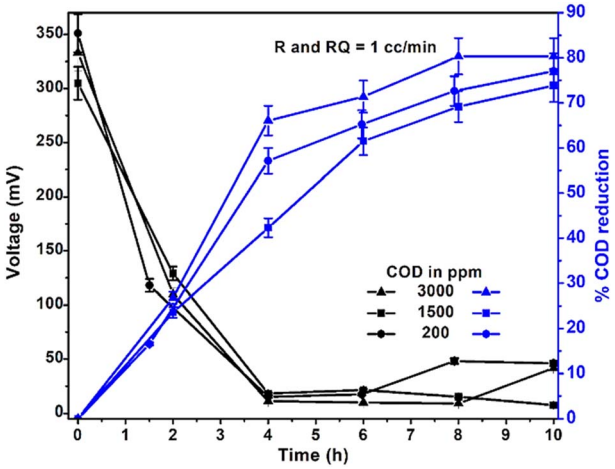

Fig. 5 Operation of the recycle-SCMFC used to treat the industrial wastewater samples (Q = RQ = 1 cc min^{-1}) at different initial COD values.

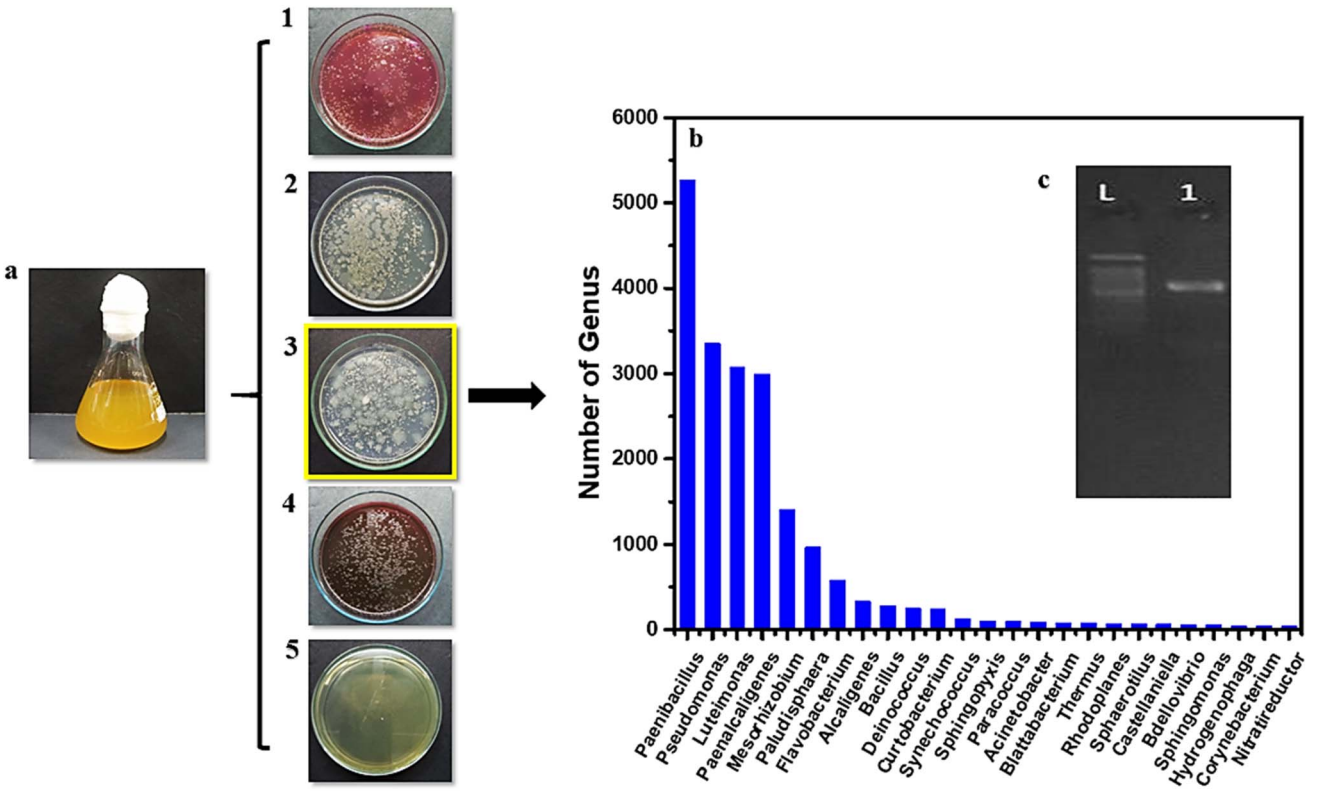

Fig. 6 Results of 16s rRNA metagenomics of isolated industrial wastewater: (a) mixed bacterial culture broth, (1–5) isolated bacteria in different media, where no. 3 (highlighted with yellow) showed the maximum and different bacterial colonies, (b) 16s rRNA metagenomics sequencing results of the top 25 enriched genus, and (c) the quality control ladder.

~325 mV and ~80%, respectively, in all cases. The maximum COD degradation was again measured in 6 h of SCMFC operation.

Fig. S4† shows the EIS data, indicating the relative overpotential losses in the SCMFC operated using both electrodes. The R_{ct} or charge-transfer resistance plays an important role in transferring the electrons over the electrode surface and it must be small in a material with good conductivity. A significantly low R_{ct} (18 Ω) value was calculated from the Nyquist plot in this study, which indicated that the electrodes used in this study had a relatively higher conductivity. The material's graphitic characteristics were also confirmed by the Raman, XRD, and SAED analyses.[13,18] A comparison table (Table S1) is available in the ESI† for continuous MFCs discussed in the literature for the biodegradation of phenol in wastewater, where the detailed parameters are tabulated. The comparative data confirmed the relatively superior performance of our SCMFC.

As mentioned earlier, a (non-specific) mixed bacterial culture was used in this study. The results of the 16s rRNA metagenomics of industrial wastewater are shown in Fig. 6, along with the digital images of the mixed bacterial culture broth and the different prepared media (1–5), *i.e.* MSA, NA, TSA, EMA, and LB, used for bacteria isolation. Plate no. 3 (TSA) showed the maximum as well as different bacterial colonies and CFU mL^{-1} counts, and was, therefore, considered for further study. Fig. 6b shows the tabulated results for the 16s rRNA metagenomics sequencing of the top twenty five enriched genera. As shown, the *Paenibacillus* genus of the *Bacillus* family and *Pseudomonas* were the top two enriched bacteria in the sequencing results and may be considered to be abundant in the biofilm formed over the packed-bed beads used as the anode for the fabricated SCMFC. The inset in Fig. 6 presents the quality control ladder, which confirmed the accuracy of the sequencing results.

4. Conclusions

A novel conical-shaped packed-bed SCMFC developed using CeO_2–CNF/ACB beads as the anode and a CeO_2–CNF/CNF disc as the air cathode was successfully used for the first time to treat 1-2-PD pharmaceutical organic compound-contaminated wastewater under continuous-flow conditions with a recycle stream. The recycle flowrate (RQ), relative to the feed flowrate (Q), was optimized for maximum COD reduction and bioelectricity generation. The results showed OCP generation of ~380 mV, COD reduction of ~80%, and 1-2-PD degradation of ~84% at Q = RQ = 1 cc min^{-1} for 1000 ppm of inlet concentration. The SCMFC was operated using the mixed bacterial culture, with a thick and dense growth of biofilm observed over the anode beads. The 16s rRNA metagenomic data showed the abundance of *Bacillus* and *Pseudomonas* genera in the culture. The findings of this study are likely to spark further research interest in the proposed SCMFC with the provision for recycling in the continuous-flow mode. Such MFCs can also be scaled up to the pilot plant as a standalone system, or integrated with the existing ETPs for treating organics-laden industrial wastewater. A mathematical model incorporating hydrodynamics and mass transfer will be developed for scaling up the SCMFC, and the results will be communicated in the future.

Conflicts of interest

There are no conflicts to declare.

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