



Original Research Article

Employment of microbial fuel cell technology to biodegrade naphthalene and benzidine for bioelectricity generation

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ABSTRACT

Microbial fuel cells (MFCs) have gained a lot of attention as a mode of converting organic matter into electricity, and potentially enhancing biodegradation of recalcitrant pollutants. In this study, MFC technology with prolonged fed-batch operation (30 days) has been used to investigate biodegradation of mixture of naphthalene and benzidine and electricity generation simultaneously. The effect of salinity (0.5–5.0%, w/v, of NaCl), temperature (10–60°C), and the using of five redox mediators as Riboflavin (RI), Neutral red (NR), Prechlorate (PR), Thionine (TH) and Anthraquinone-2-Sulfonate (AQS) on biodegradation of naphthalene and benzidine in MFCs has been investigated. The performance criteria were biodegradation efficiency, % COD removal and electrochemical performance. Good electrochemical and biodegradation performance were maintained up to a salinity of 2.5% (w/v), but deteriorating was observed when salinity was raised to 3.0 % (w/v). The optimum was 2.0% (w/v) with a maximum voltage, power density, biodegradation efficiency of naphthalene, benzidine and COD removal of 306 mV, 156.06 mW/m², 100, 98 and 85%, respectively, namely improvement significantly by about 172.88, 298.91, 3.1, 1.03 and 2.41%, respectively, compared to initial salt concentration(0.5). A temperature of 40°C was found optimal giving a maximum power density of 292.60mW/m², a COD removal of 90%, and a biodegradation efficiency of naphthalene and benzidine 100 and 100%, respectively. Biodegradation rates (naphthalene, benzidine and COD) per day, maximum power density and CE were all improved by approximately 178.78, 196.29, 215.78, 185.07 and 120.63%, respectively, at 40°C compared to initial temperature (30°C), but decreasing sharply was noted when operating temperature was raised to 50°C. MFC performance in terms of electricity generation was enhanced 344.77% when the redox mediator riboflavin (30 μM) was added exogenously. This work suggests the possible application of MFC technology in the effective treatment of petroleum hydrocarbons contaminated site and refinery effluents.

Keywords

Microbial fuel cell,
Naphthalene,
Benzidine,
Biodegradation,
Bioelectricity generation.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are serious problems and global pollutants in the environment (Yucheng *et al.*, 2008; Driscoll *et al.*, 2010) due to their toxicity,

carcinogenicity and persistent organic pollutant properties (Yucheng *et al.*, 2008; Amezcua-Allieri *et al.*, 2012). Removal of PAHs from the environment is a necessity for ensuring human health and ecosystems

(Yucheng *et al.*, 2008; Haritash and Kaushik, 2009). Many strategies have been developed to remove PAHs from the environment, including volatilization, photo oxidation, chemical oxidation, adsorption, and biodegradation (Haritash and Kaushik, 2009; Lin *et al.*, 2010; Run *et al.*, 2010). Of these, biodegradation techniques have received considerable attention, particularly in the context of cleaning up contaminated sites, due to their efficacy, environmental safety and comparatively lower cost (Yang *et al.*, 2009; Lin *et al.*, 2010; Run *et al.*, 2010).

Microbial fuel cells (MFCs) are electrochemical devices that are able to convert chemical energy into electricity with the aid of exoelectrogenic bacteria as biocatalysts (Liu and Logan, 2004; Patil *et al.*, 2009). The application of MFCs to wastewater treatment with concomitant electricity generation has been reported extensively (Liu and Logan, 2004; Rozendal *et al.*, 2008; Patil *et al.*, 2009; Hawkes *et al.*, 2010). However, MFC technology could be further extended to treatment of more recalcitrant compounds such as PAHs (e.g. naphthalene and benzidine) in sub-surface environments where existing technologies are unsustainable in terms of treatment costs and ease of deployment.

Anaerobic biodegradation of PAHs has previously been reported extensively (Galushko *et al.*, 1999; Karl and Stuart, 2001; Rainer *et al.*, 2004; Meckenstock *et al.*, 2005; Michael and Rainer, 2006; Florin *et al.*, 2009; Rita and Rainer, 2011). To test for the robustness of microbial fuel cells during treating recalcitrant pollutants is necessary to investigate the response of the system under various levels of operating conditions e.g. salinity and temperature. The few workers (Morris *et al.*, 2009; Chandrasekhar and Venkata Mohan, 2012;

Morris and Jin, 2012) that investigated the treatment of PAHs in MFCs did not consider the impact of variations in environmental conditions. Morris *et al.* (2009) investigated the biodegradation of diesel in a dual MFC at 30°C; they achieved 82% removal over 21 days compared to an anaerobic incubated control, which achieved 31% removal.

Chandrasekhar and Venkata Mohan (2012) investigated the effect of substrate concentration on degradation of real field petroleum sludge with concomitant bioelectricity generation by varying the organic loads operated at ambient temperature (29°C). Highest total PAHs removal of 35% was obtained at lower organic loads (0.76 g/L PAHs). Knowledge of the robustness of MFCs to different operating conditions is important in assessing the technical feasibility of these systems. A change in operating temperature could adversely affect the nature and the distribution of the microbial population present in the anodic chambers of MFCs (Larrosa-Guerrero *et al.*, 2010). Low temperatures may inhibit the growth of methanogenic bacteria but favor electrogenesis.

An increase in temperature may increase biokinetics (mass transfer coefficient, activation energy, etc.), the system's thermodynamics and rate of substrate utilization (Larrosa-Guerrero *et al.*, 2010). Redox mediator is one of the key mechanisms that have been suggested for the transfer of electrons from the electrochemically active bacteria to the anode. The use of exogenous redox mediators could enhance electrochemical performance of MFCs system by improving electron transfer rates (Keck *et al.*, 2002). The key factors to consider are the redox potential of the mediator in relation to that of substrate oxidation and the anode potential are the

permeability of the cell membrane for the redox mediator molecules and the toxicity of the redox mediator. The addition of sodium chloride to increase salinity could increase the conductivity of the anodic solution and may also decrease the internal resistance within the MFCs (Lefebvre *et al.*, 2012). Salinity may induce contradictory effects, e.g. while increasing conductivity of the anolyte, the physiology of the microbial population present in the anode may be adversely affected (Minai-Tehrani *et al.*, 2009). Therefore, the purpose of the studies reported here was to investigate the performance of MFCs subjected to variation in operating temperature, redox mediator type and salinity, with respect to biodegradation of mixture of two PAHs (naphthalene and benzidine). The performance of the system was evaluated in terms of its degradation performance (substrate's degradation rate and COD removal efficiency) and electrochemical performance (voltage outputs, maximum power density and coulombic efficiency).

Materials and Methods

Inoculum and media

Anaerobic sludge was obtained from Makkah Sewage Treatment Plant (KSA). Anaerobic sludge inoculums was initially acclimated at 30°C for a month in a Winogradsky column (65 cm long, 12 cm wide) containing BTEX (Benzene, Toluene, Ethylbenzene, Xylene) and two PAHs compounds including naphthalene and benzidine (each at 250 mg/L) supplemented with microcrystalline cellulose (1% w/v), calcium carbonate (0.25% w/v) and calcium sulphate (0.5% w/v).

The Defined Minimal Medium (DMM) for bioelectrochemical experiments was (per L of deionized water): 8.24 g Na₂HPO₄, 5.08 g

NaH₂PO₄, 1.0 g NH₄Cl, 0.5 g NaCl, 0.25 g MgSO₄, 12.5 mL Wolfe trace mineral solution and 12.5 mL Wolfe vitamin solution.

MFCs construction and operation

Single-chamber air cathode MFCs were constructed as described previously (Liu and Logan, 2004) with some modification. Briefly, the anode and cathode were placed in parallel on the opposite side of the chamber (total volume is 200 mL, working volume is 100 mL) with distance of 5cm. Non – wet proofed carbon cloth (type A,E – TEK, Somerset, NJ, USA, 4cm²) which was used as anode.

Wet – proofed (30%) carbon cloth (type B, E – TEK, Somerest, NJ, USA, 10cm²) was used as cathode pressed to proton exchange membrane (Nafion 117, Dupont CO., USA) on the water-facing side. The anode chamber was filled with anolyte medium (DMM) (pH 7.0). The MFCs were sterilized by autoclaving at 121°C for 15 min, followed by addition of anolyte to the anode chamber which was done aseptically.

All experiments conducted in this study were operated in fed-batch mode whereas the MFCs were inoculated with 10 mL of the acclimated anaerobic sludge inoculum. Anaerobic conditions were maintained in the anode chambers by purging them with 100% N₂ for 15 min before MFC operation began. The pH was adjusted by adding NaOH or HCl. The temperature was controlled in an incubator (LAB – LINE ® AMBI – USA). The net volume of the anolyte was 100 mL for each experiment. Immediately after adding the fuel and inoculum, MFCs were hooked up to a data acquisition system to start monitoring the voltage generation (150Ω).

Experimental design

Fed-batch operation of the MFC system containing PAHs was conducted at 30°C for 30 days (i.e. over seven cycles). The anolyte medium consists of 100 mg/L naphthalene, 80 mg/L benzidine and DMM.

A cycle was deemed to have ended when MFC voltage fell below 7 mV and a new cycle was immediately initiated by removing 90% anode content. Subsequently, the anode chamber containing 10% (v/v) of preceding cycle (as inoculum) was replenished with fresh anolyte medium. Similar operation was performed for a control (devoid of inoculum). The effect of operating temperature on MFC performance was also evaluated by increasing the temperature of the MFC system from 10°C to 60°C.

The effect of salt concentration on degradation efficiency of PAHs and power generation in the anode of the MFC system was investigated, NaCl ranging from 0.5% to 5.0% w/v. For the salinity experiment, a temperature of 30°C was maintained throughout salt concentrations tested. The controls in all sets of experiments described above contained the same anolyte medium as the test, but were not seeded with inoculum.

The effect of five redox mediators, namely Riboflavin (RI), Neutral red (NR), Prechlorate (PR), Thionine (TH) and Anthraquinone-2-Sulfonate (AQS), on MFC performance with respect to degradation of PAHs and electricity generation was investigated. For this experiment, 30µM redox mediator was added to the anolyte medium, and MFCs were at operating temperature 40°C. The control was free of redox mediator.

Analytical methods

Chemical analysis: Anolyte samples containing PAHs were analyzed by high performance liquid chromatography (HPLC Agilent 1100) using a Photo-Diode Array (PDA) detector (DIONEX, PDA-100) at 254 nm. The injected volume was 25µL with column oven temperature (25°C), and the HPLC was operated at isocratic conditions. The analytical column was a reverse phase column, Supelcosil™ LC-PAH column (150 mm × 4.6 mm). The mobile phase was 80% methanol and 20% deionized water. The flow rate was 1.0 mL/min. Naphthalene and benzidine concentrations were quantified against external standards.

The minimum detectable concentration for naphthalene and benzidine was 20 µg/L and 5µg/L respectively. Extractions of PAHs present in the anolyte samples and on the electrode (at the end of each cycle) were carried out as follows. Approximately 1 mL of aliquots were withdrawn at intervals from the MFC and transferred to a 2 mL eppendorf tube. Subsequently, 1 mL of methanol was added to make 2 mL, and these were incubated on a shaker for 1 h at 25°C and 150 rpm. Tubes were immediately centrifuged at $13.2 \times g$ for 10 min and 1 mL of supernatant was carefully transferred into 1.5 mL HPLC glass vials prior to analysis by HPLC. The amount of PAHs present on the electrode was determined by soaking the anode electrodes in 10 mL methanol at the end of each experiment and subsequently placed on a shaker for 1 h at 200 rpm. Aliquots were transferred into 2 mL Eppendorf, immediately followed by centrifugation at $13.2 \times g$ for 10 min.

Biodegradation efficiencies and rates were determined based on the remaining PAHs in solution and those adsorbed on the electrode at the end of MFC operation. The chemical

oxygen demand (COD) of the samples was determined using the closed reflux titrimetric method as described in the Environment Agency (USA) Standard method 5220D (APHA, 1997). Appropriately diluted 1 mL samples were used for each determination. COD removal was calculated as: $\text{COD (mg/L)} = (K_b - K_s) * DF * M * 8000$, where: K_b and K_s are ferrous ammonium sulphate (FAS) titrant volumes for blank and the sample, respectively. DF is the sample dilution factor, and M is the molarity of the FAS solution. The COD of samples was expressed as percentage COD removal and COD removal rate. The percentage COD removal was calculated as: $\text{percentage COD removal (\%)} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} * 100$, where: COD_i and COD_f are initial COD and final COD values respectively.

Electrochemical analysis: Voltage was measured after the MFC has reached the steady state by a digital multimeter (Sanwa CD800a, Japan) which was connected to a personal computer. Data was automatically recorded every second via Picolog software (Pico Technology Limited). The corresponding current was based on equation $I = E/R_{ext}$, where: I is current (mA), E is voltage (mV), and R_{ext} is external resistance. The power (P) was obtained by $P = IE$.

The current density and the power density have been normalized based on the projected surface area of the anode via equations $I_{An} = I/A_{An}$, where I_{An} is current density and A_{An} is the surface area of anode, $P_{An} = E^2/A_{An}R_{ext}$, where P_{An} is power density. The polarization curve was obtained at different external resistance (50 - 1000 Ω). Internal resistance was derived from the polarization curve as the slope. Coulombic efficiency (CE) was derived from the equations $C_p = It$, $C_{max} = FfS_{COD}V_{An}$, and $CE = C_p/C_{max}$, where

C_p is the coulombs of energy produced, t is the time of stable voltage output, C_{max} is the theoretical maximum coulombs, F is Faraday's constant (96.485 C/mol of electrons), f is a factor of 1 mol electrons/8g COD, S_{COD} is substrate concentration g COD/l, and V_{An} is a net volume of anolyte (mL).

Each experiment was performed in duplicate. Statistical analyses were performed with $\alpha = 0.05$. The standard deviation of the mean (SD) ranged between 0.1–0.5%.

Results and Discussion

Performance of PAHs degradation and electricity generation in MFC

The degradation performance of PAHs in MFCs operated in fed-batch mode was conducted over seven cycles in terms of degradation efficiency and COD removal efficiency of the individual PAHs (i.e. naphthalene and benzidine). The degradation efficiency of naphthalene, benzidine and COD removal was ranged 93–97, 91–97 and 80–83, respectively, in all of the cycles as shown in Fig. 1. There was a statistically significant difference ($p < 0.05$) between the experiments and the control over the seven cycles. Electrochemical performances of the fed-batch MFC operated over seven cycles were stable as shown in Fig. 2.

There was no significant difference ($p < 0.05$) in the voltage, power density and coulombic efficiency (CE) outputs over the cycles of operation. Values of the voltage, power density and coulombic efficiency were ranged 172–177, 49.30–52.21 and 7.81–7.92, respectively. The observed results in this study are better than those were reported by several authors that have

investigated the treatment of pollutants hydrocarbons in MFCs (Chandrasekhar and Venkata Mohan, 2012; Morris and Jin, 2012; Wu *et al.*, 2013). In a study on the anaerobic biodegradation of diesel in MFCs, Morris *et al.* (2009) reported peak voltage output of 50–65 mV, with degradation efficiency of 82%. Wu *et al.* (2013) reported maximum power density of 0.028 to 2.1 mW/m² and complete degradation of benzene (21.74 mg/L) was achieved. The obtained results in this study have proven success using of MFC technology to biodegrade recalcitrant pollutants, and generate electricity simultaneously.

Few studies have reported using MFC technology for similar purpose (Luo *et al.*, 2009; Zhang *et al.*, 2009; Nimje *et al.*, 2011; Huang *et al.*, 2013; Wua *et al.*, 2014; Adelaja *et al.*, 2015). Good degradation efficiency (PAHs) and electrochemical performance in MFCs was obtained when an adapted anaerobic microbial consortium was employed in the present study. High degradation rates and removal efficiency observed both in this study could be attributed to the presence of aromatic degrading enzymes present in the adapted microbial consortia and the availability of an insoluble electron acceptor present in the anodic chamber.

The presence of these enzymes could have facilitated increased cell metabolic rate that might have resulted into higher substrate utilization. The continuous availability of the anode (serving as an inexhaustible electron acceptor) for microbial respiration coupled with substrate degradation over seven cycles give credence to its choice as a sustainable and affordable bioremediation technology for groundwater treatment over the maintenance cost of supplying alternative electron acceptors such as nitrates, sulphates or metallic oxides into

such environments. Biodegradation of mixtures of PAHs by microorganisms could be affected by substrate interactions such as competitive inhibition (Mathura and Majumder, 2010). Therefore, interaction of two compounds of hydrocarbons (naphthalene and benzidine) has been investigated in the present study.

Degradation efficiency of about 97% was achieved. This suggests that the effect of co-substrates interactions on microbial uptake was not inhibitory but rather promotes simultaneous degradation of both substrates. This reason for the positive effect could be underpinned by the fact that the adapted anaerobic consortia possess versatile aromatic degrading enzymes that are capable of metabolizing both substrates. Biodegradation studies of hydrocarbon mixtures have rarely been reported in the literature (especially in MFC systems) even though few studies have reported the effect of competitive inhibition on degradation of substrate mixtures.

In one study, Lee *et al.* (2002) quantified the competitive inhibition kinetics of BTEX mixtures using *Stenotrophomonas maltophilia* T3-c. They found that the presence of toluene or xylene in binary mixtures with benzene increased the specific degradation of benzene while benzene degradation was inhibited in binary mixtures with ethylbenzene. Similarly, Mathur and Majumder (2010) investigated the degradation kinetics of BTEX compounds and phenol as a single and mixed substrate using *Pseudomonas putida*. The authors observed a similar negative effect of competitive inhibition on the degradation of benzene in the presence of other BTEX compounds. In the two previous studies reported above, pure cultures were used which could have contributed to the negative effect reported by these authors. A possible

reason might be due to the lack of highly versatile aromatic degrading enzymes that was capable of degrading the mixed substrates efficiently, considering the degree of recalcitrance, molecular structure and molecular weight of substrates involved. Other performance factors such as increased performance stability, resistance to bacteriophage and others could be associated with adapted mixed cultures. This suggests the added advantage of adapted anaerobic microbial consortia over pure cultures from an operational standpoint in the effective treatment of oil contaminated environments. The result of this study indicates the possibility of achieving over 96% degradation efficiency of PAHs mixture, using adapted anaerobic microbial consortium, in a repeatable and consistent fashion during fed-batch MFC operation. Findings from this study recommend the potential use of MFC technology in enhancing biodegradation efficiency of PAHs in contaminated environments in a cost effective and sustainable manner.

Effect of salinity

Effect of salinity on overall system performance has been investigated in current study. Salt concentrations between 0.5% and 5.0% of NaCl (w/v) were varied in the anodic chamber of the MFCs in order to evaluate its influence on system performance. Results indicated that good electrochemical and degradation performance can be maintained up to 2.5% of NaCl. Optimum MFC performance was recorded at moderate salinity, 2.0% of NaCl (w/v), with maximum voltage and power density outputs, 306 mV and 156.06 mW/m², respectively, namely improvement significantly by about 172.88 and 298.91%, respectively, ($p < 0.05$) compared to initial salt concentration (0.5), rapid decreasing was observed when salinity was increased to

3.0% (w/v) (Fig. 3). There was also a strong correlation between the power density and salinity ($r = 0.98$, $p < 0.01$) which implies a significant impact that changes in salinity could have on MFC performance. It further suggests that salinity could be one of the most critical environmental parameters that could significantly influence operational conditions. Biodegradation of naphthalene and benzidine, as well as COD removal increased gradually with increase in salinity till it peaked as 100, 98 and 85%, respectively, at 2.0% of NaCl (w/v), by about 3.1, 1.03 and 2.41% increasing, respectively, compared to initial salt concentration, then dropped afterwards was recorded after 3.0% of NaCl (w/v), (Fig. 4).

The observed decrease in MFC performance when salinity was raised to 3.0% (w/v) could likely be due to the dehydration of anodophilic cells at such relatively high saline condition (Lefebvre *et al.*, 2012). This appears to have adversely affected the physiology of the anaerobic microbial consortia and thus resulted into slower electron transfer rates at such high ionic strengths. In a previous study (Minai-Tehrani *et al.*, 2009), the authors reported a sharp decrease in PAH removal efficiency in oil contaminated samples when salt concentration was raised from 1% to 5% NaCl.

In another study, Lefebvre *et al.* (2012) reported that higher NaCl concentration above 2% was detrimental to overall system performance of an MFC fed with acetate. Increasing salt concentrations in MFCs are expected to result into corresponding rise in the ionic conductivity of the anolyte thereby decreasing the internal resistance and over potential of the anode (Logan, 2008; Lefebvre *et al.*, 2012). These changes could result into improvement in electrochemical performance of the system; however, at high

saline condition microbial metabolism is inhibited thus resulting into low MFC performance as reported in this study. Findings from this study suggest that optimum MFC performance could be achieved when the MFC is operated at such moderate saline conditions 2.0% of NaCl (w/v).

Effect of temperature

Effect of operating temperature ranging from 10 to 60°C on biodegradation and electrochemical performances in MFCs was investigated. Biodegradation efficiency (naphthalene and benzidine), COD removal, maximum voltage, maximum power density, current density, coulombic efficiency (CE) and Degradation rates (naphthalene, benzidine and COD) per day increased with increasing temperature till it peaked at 40°C as 100, 100 and 90%, 419mV, 292.60mW/m², 0.69mA/m², 13.21%, 5.9, 5.3 and 4.1%, respectively, (Fig. 5–7), afterwards, a sharp decrease in MFC performance was observed at 50°C. Degradation rates (naphthalene, benzidine and COD) per day, maximum voltage, maximum power density and CE were all improved by approximately 178.78, 196.29, 215.78, 136.04, 185.07 and 120.63%, respectively, at 40°C, compared to initial temperature (30°C).

Correlation studies also indicated a good relationship ($r = 0.97$, $p < 0.01$) between change in temperature and the performance parameters (degradation rates, maximum voltage, maximum power density and CE). Decline in MFC performance at temperature higher than 40°C may be due to loss of microbial activity resulting from hostile MFC operating condition. This implies that the adapted microbial consortium used in this study could not tolerate thermophilic conditions. The adapted microbial

consortium probably prefers MFC operated at mesophilic condition for PAHs degradation to thermophilic operation. Hence, would not recommend its technical applications beyond the tolerable temperature limit (i.e. 40°C). At higher temperatures, activation energy required to drive the oxidation process is lowered. Increase in operating temperature could have multiple effects including the enhancement of microbial kinetic rates, an increase in the conductivity of the anolyte medium which may have contributed to reduction in internal resistance of the cells (Liu and Logan, 2004; Kim *et al.*, 2005; Logan, 2008). All these generally have a positive effect on the system performance regarding degradation rates, power generation and CE% as observed in this study. In the present work, MFC performance was optimized at an operating temperature of 40°C. This suggests a potential application of MFC technology to decontaminate polluted environments in tropical and hot climate regions (like Saudi Arabia).

Effect of redox mediators

The effect of five redox mediators (RI, NR, PR, TH and AQS) on degradation efficiencies of PAHs in MFC and its performance is shown in Fig. 8 and 9. In the presence of redox mediators, the degradation performance could be maintained while improving electrochemical performance of the MFC technology. Notably, one of the redox mediators, riboflavin (RI), positively impacted power generation and CE significantly ($p < 0.05$). The maximum voltage, power density, current density and CE were 778 mV, 1008.80 mW/m², 1.29 mA/m² and 39.75%, respectively, with enhancement up to 185.68, 344.77, 186.95, 300.9%, respectively compared to mediator-free incubation when anolyte medium was

supplemented with riboflavin (RI). The next redox mediator in the results was AQS then TH followed by NR, while PR was the worst (Fig. 8 and 9). Addition of redox mediator has been shown to enhance electron transfer (Keck *et al.*, 2002; Hawkes *et al.*, 2010). In a related study, Park and Zeikus (2000) have demonstrated that electricity generation in a glucose fed MFC was enhanced by about 10-fold than mediator-free MFC when neutral red (a redox mediator) was added to the anolyte medium. Santos *et al.* (2004) demonstrated that decolorization rates of dyes in synthetic wastewater at thermophilic conditions could be increased by 8-fold in the presence of riboflavin compared with mediator-free control. High decolorization rates were achieved due to enhancement in electron transfer to the dyes (in the presence of the redox mediator), thus increasing color removal.

Based on results of this study, riboflavin was better than the others with regards to their electrochemical performances. This could be explained by the differences in their redox potentials and chemical structures. Riboflavin, a flavin-based compounds (having diverse functional groups such as ketones and hydroxyl groups), has redox potential of -208 mV (vs. NHE). For effective electron transfer, a higher redox potential of the redox mediator would thermodynamically favor the microorganism for its growth and maintenance (Logan, 2008). The obtained results suggest the use of riboflavin as the preferred redox mediator in optimizing power generation while maintaining good degradation efficiency of PAHs.

Conclusion

In the present study, the performance of MFC technology for biodegradation a mixture of naphthalene and benzidine at operating conditions such as salinity, temperature and mediator types was investigated. The optimal salinity was 2.0% of NaCl (w/v), giving a maximum voltage, power density, biodegradation efficiency of naphthalene, benzidine and COD removal of 306 mV, 156.06 mW/m², 100, 98 and 85%, respectively, namely improvement significantly by about 172.88, 298.91%, 3.1, 1.03 and 2.41%, respectively, ($p < 0.05$) compared to initial salt concentration (0.5).

A temperature of 40°C was found optimal giving a maximum power density of 292.60 mW/m², a COD removal of 90%, and a biodegradation efficiency of naphthalene and benzidine 100 and 100%, respectively. Degradation rates (naphthalene, benzidine and COD) per day, maximum power density and CE were all improved by approximately 178.78, 196.29, 215.78, 185.07 and 120.63%, respectively, at 40°C, compared to initial temperature (30°C). MFC performance in terms of electricity generation was enhanced 344.77% when the redox mediator riboflavin (30 μM) was added exogenously. This work suggests the potential use of MFC technology in enhancing the degradation efficiency of PAHs especially in tropical subsurface environments with concomitant bioelectricity generation.

Fig.1 Cycles of MFCs Fed-Batch operation show percentage COD removal and biodegradation efficiencies of PAHs (naphthalene and benzidine)

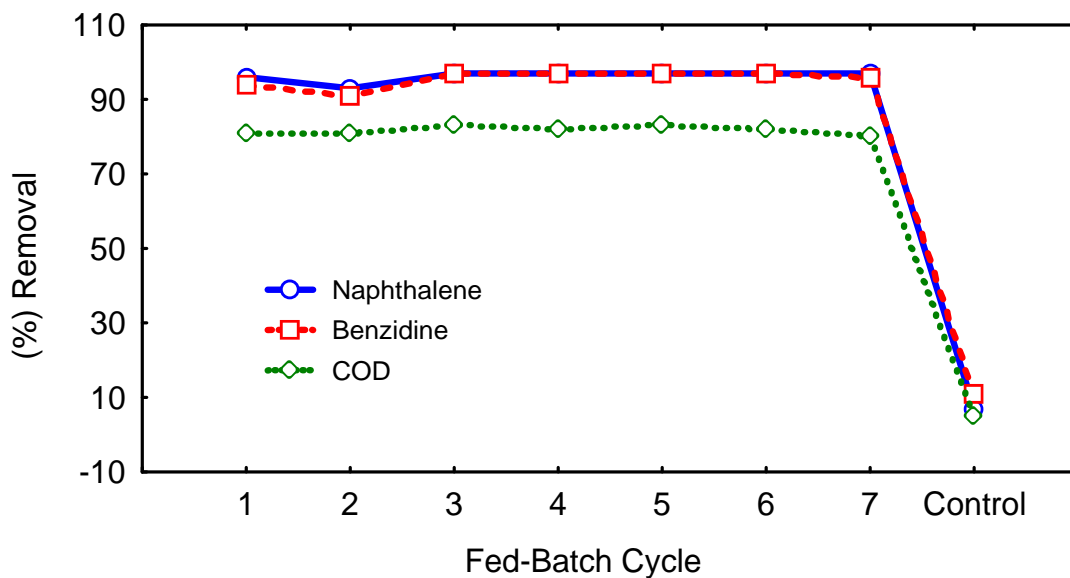


Fig.2 Cycles of MFCs Fed-Batch operation show electrochemical performances (voltage, power density and CE) of PAHs (naphthalene and benzidine) biodegradation

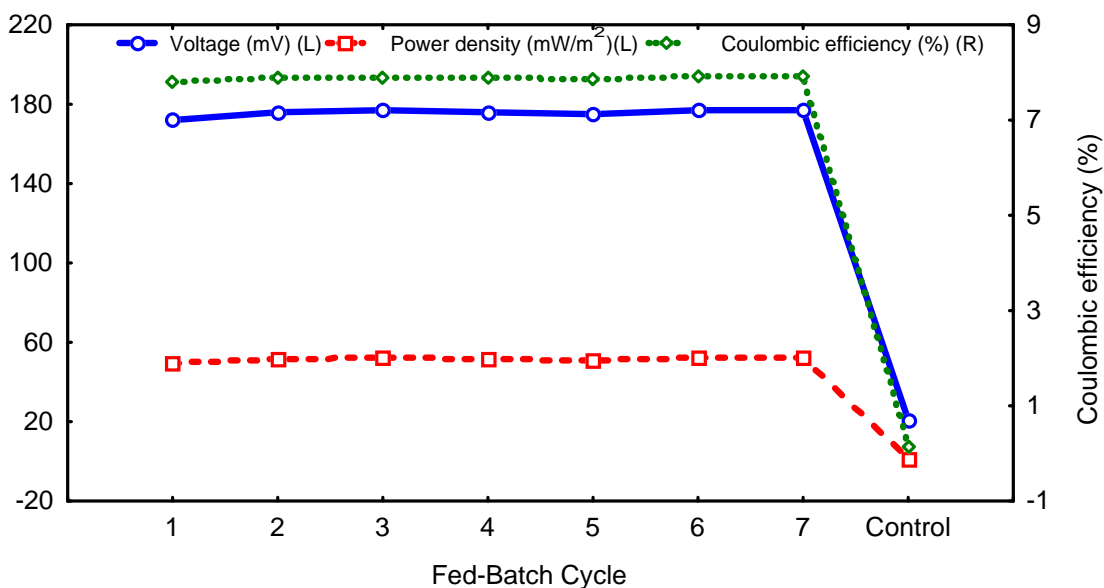


Fig.3 Effect of salinity on electrochemical performance (voltage and power density) of the MFC technology during PAHs biodegradation at temp. 30°C

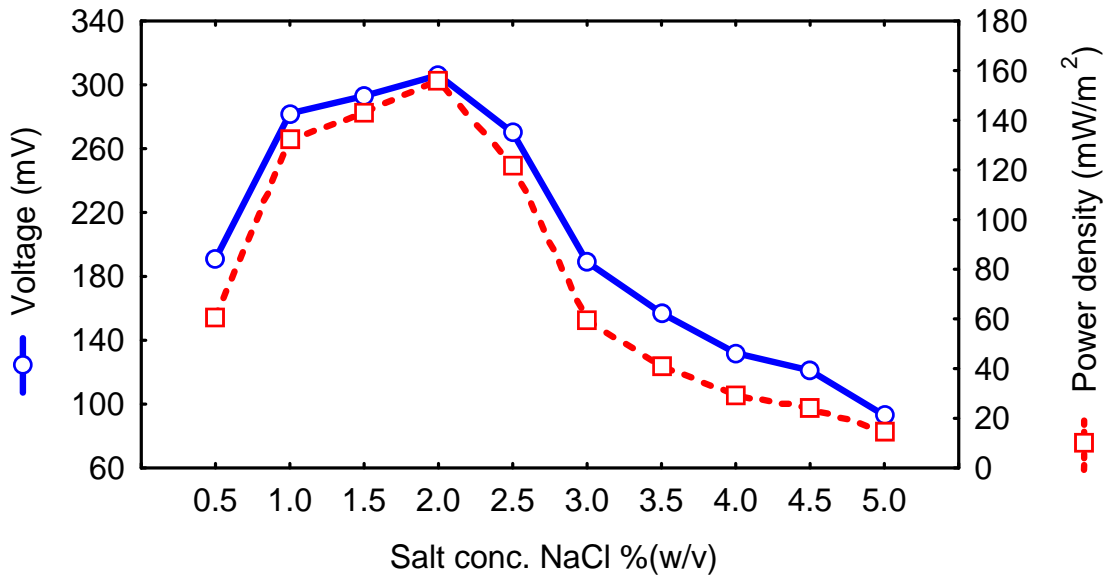


Fig.4 Effect of salt concentrations on biodegradation efficiencies and COD removal during MFCs operation (at 30°C)

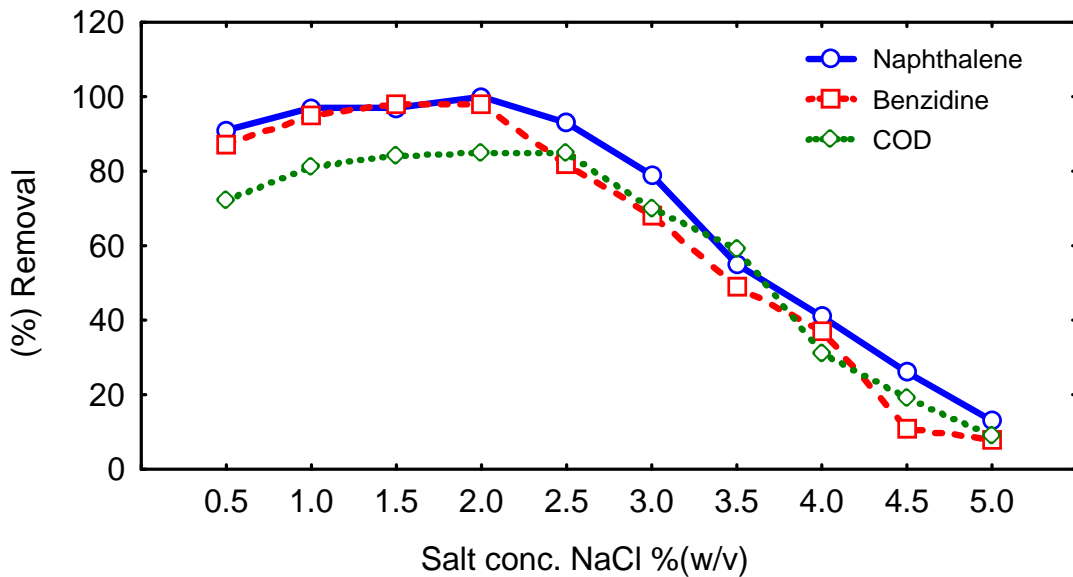


Fig.5 Effect of operating temperature on biodegradation efficiencies of PAHs and COD removal during MFC operation

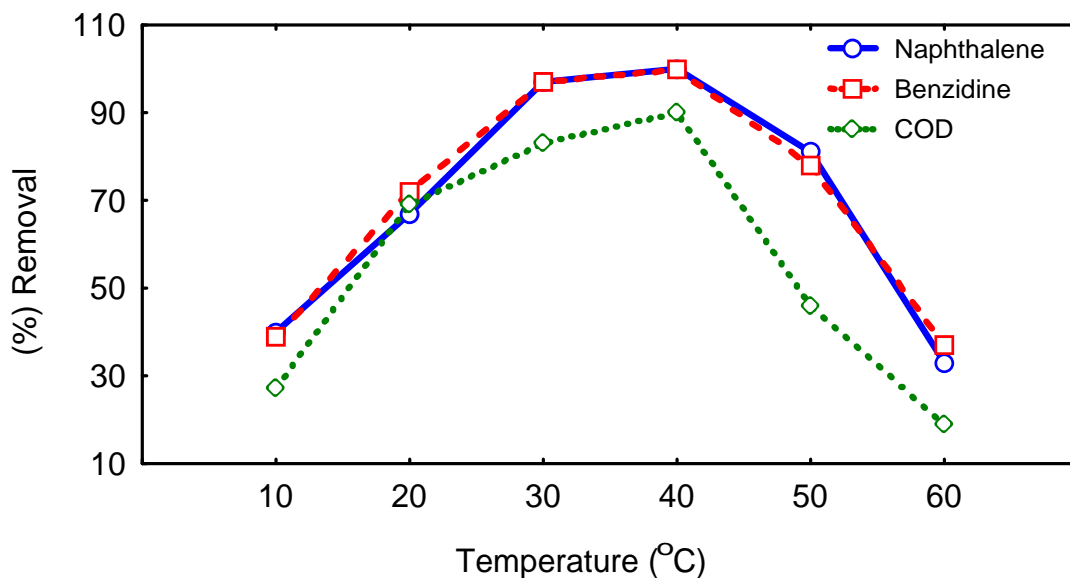


Fig.6 Effect of operating temperature on electrochemical performance (voltage, power density, current density and CE) of the MFC technology during biodegradation of PAHs

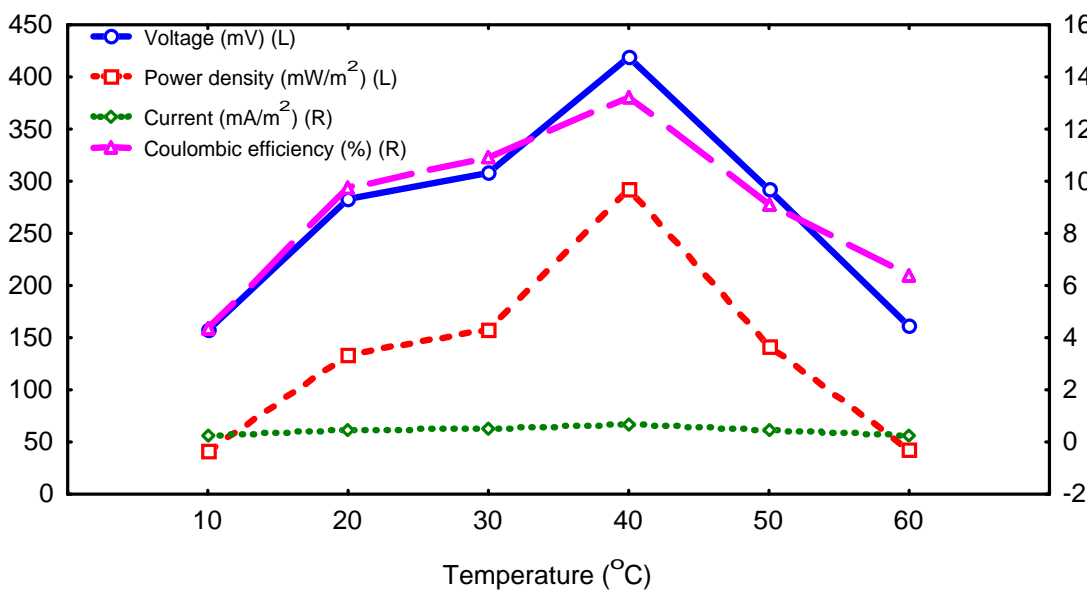


Fig.7 Degradation rate (mg/d) of PAHs in MFC technology at different operating temperature

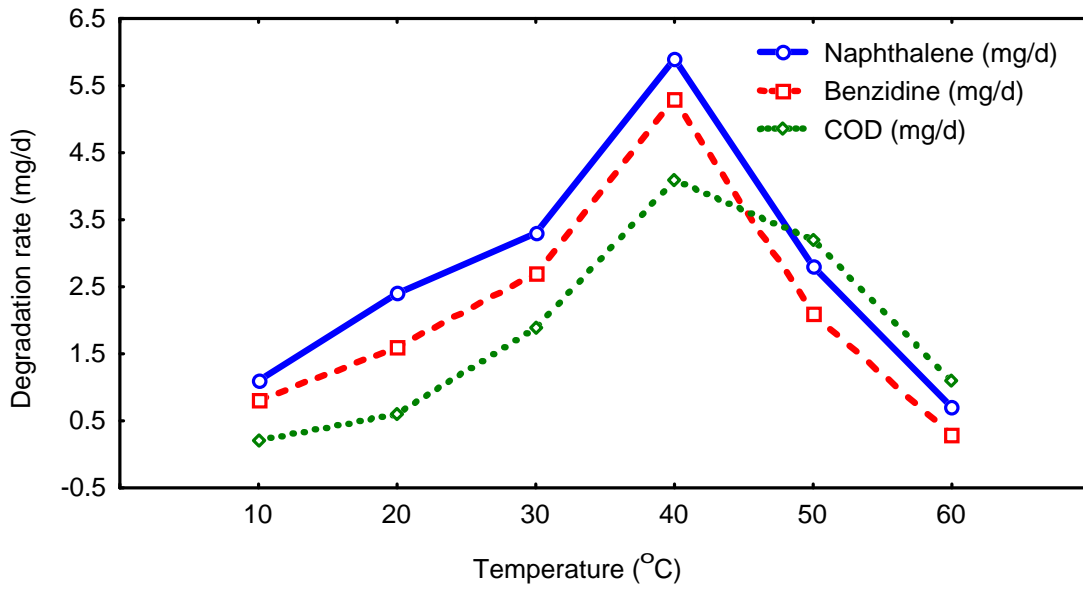


Fig.8 Effect of redox mediators on biodegradation efficiencies of PAHs and COD removal during MFC operation

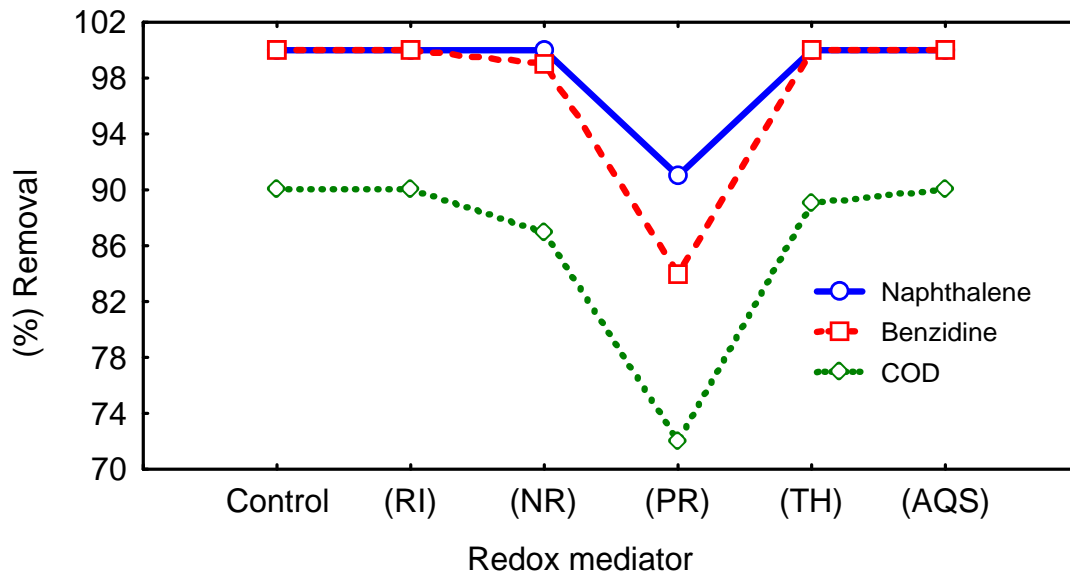
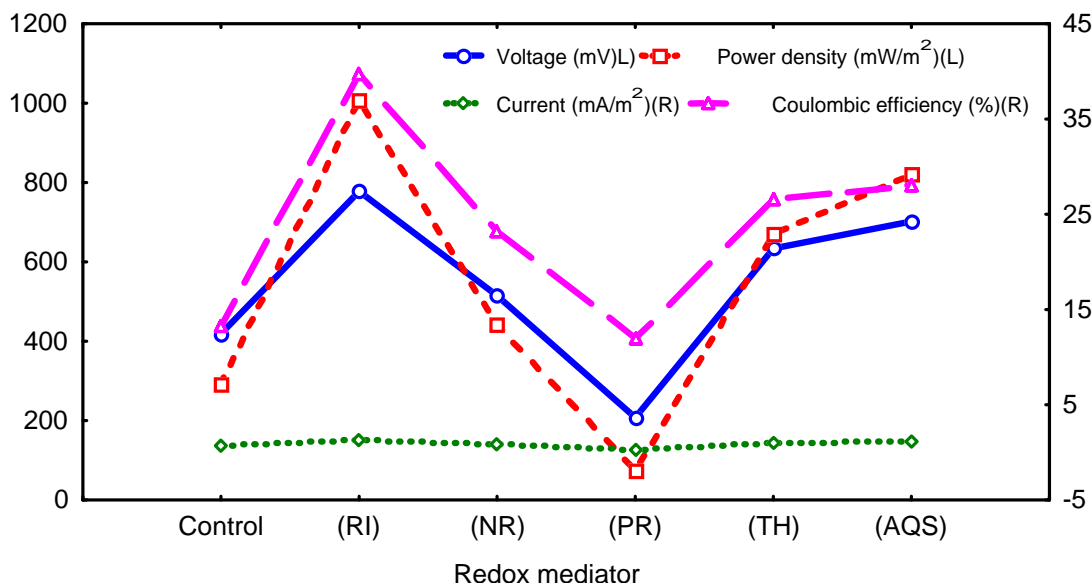


Fig.9 Effect of redox mediators on electrochemical performance (voltage, power density, current density and CE) of the MFC technology during biodegradation of PAHs



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