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Feasibility assessment of oil sands process water treatment in a flow-through microbial electrolysis cell

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ABSTRACT

This study examines the feasibility of oil sands process water (OSPW) treatment in a gravitational flow-through membraneless microbial electrolysis cell (MEC) using crushed metallurgical coke as an electrode material. Synthetic OSPW was composed of the water soluble fraction (WSF) of diesel, naphthenic acids (NAs), and metals with a total chemical oxygen demand (COD) concentration of 200 mg L^{-1} and total NA concentration of 9.4 mg L^{-1}. OSPW treatment under bioelectrochemical conditions (1.4 V applied voltage) was compared with a control system operated at 0 V. Furthermore, in an additional set of experiments, microaerobic conditions were applied to both MEC and control setups to facilitate NA biodegradation. Highest NA and COD removal rates were observed in the MEC with microaeration in electrode compartments, where total NA concentration decreased to 4.2 mg L^{-1} at a hydraulic retention time of 4 days. Furthermore, microtox and microalgae toxicological assays showed substantial toxicity decrease in this MEC.

1. Introduction

Petroleum bitumen reserves in the Athabasca region of northeastern Alberta in Canada represent one of the world's largest proven petroleum sources (Larter and Head 2014). However, extraction of this bitumen causes diverse environmental issues related, among other aspects, to the intensive use of river water and process-affected water toxicity. The extraction process requires huge volumes of hot and caustic water and a significant amount of oil sands process water (OSPW) is generated with toxicity that precludes its direct release into the environment. Large volumes of OSPW are currently impounded in oil sands tailings ponds (OSTP), waiting to be remediated. According to Foght et al. (2017), OSTP management and reclamation knowledge gaps include any approach applied as a pre-treatment to froth treatment tailings or the resulting OSPW that could contribute to pre-emptively biodegrade diluent hydrocarbons and other components prior to their deposition in OSPWs. These pre-treatments could decrease the toxicity of OSPW by removing low molecular mass hydrocarbons, as well as subsequent CH_4 emissions by decreasing labile carbon sources entering the tailings ponds.

Our understanding of complex bitumen-derived organic mixtures has greatly improved with the advancement of chemical characterization of organic compounds in OSPW (Bauer et al., 2019). Several analytical methods for qualitative and quantitative characterization of bitumen-derived organics exist (Bauer et al., 2019; Hewitt et al., 2020; Frank et al., 2021), including electrospray ionization high resolution mass spectrometry (ESI-HRMS), liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF/MS), gas chromatography - mass spectrometry (GC–MS), and synchronous fluorescence spectroscopy (SFS). A recent study by Frank et al. (2021) applying these methods to bitumen-influenced groundwater successfully isolated dissolved organics from both industrial and natural sources into three chemically distinct fractions (F1, F2, F3) without obvious differences between the sources. Comparison amongst fractions derived from each source consistently demonstrated that F3 contained compounds with greater polarity than F2, which was in turn more polar than F1. The abundance of O_2 species was confined to F1, including naphthenic acids (NAs) often cited for being the primary toxicants within bitumen-influenced waters. Bitumen extraction also liberates chemical by-products, such as major ions, dissolved metals, and polar organic compounds, primarily NAs, which may comprise almost half of the organic fraction of OSPW. Although NAs concentrations are relatively low (parts per million), they are recalcitrant and not efficiently removed by conventional aerobic and anaerobic biological treatment methods, which may require several years while still resulting in incomplete degradation.

Treatment methods for the recovery of NAs and polycyclic aromatic hydrocarbons (PAHs) from OSPW include reclaimed landscapes, such as end-pit lakes where liquid fine tailings are capped with a mixture of OSPW and fresh water, wetland filtering of organics, or adsorption utilizing cost effective and applicable adsorbents derived from petroleum coke (Brown and Ulrich 2015; Foght et al., 2017; Simair et al., 2021).

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Physical and chemical technologies available for NA removal (e.g. advanced oxidation, etc.) are currently limited by high costs and inefficient removal at relatively low NA concentrations.

New biotechnological approaches based on the principle of a bioelectrochemical system (BES) have recently emerged (Nancharaiah et al., 2016). BESs are important contributors towards emerging sustainable technologies for energy production from organic wastes, including wastewater (Logan et al., 2008; Wang et al., 2015; Escapa et al., 2016; Zhu et al., 2021). In BESs, living electroactive microorganisms exchange electrons with solid electrodes (Sydow et al., 2014). Biodegradable organic materials are oxidized by microorganisms in the anodic chamber to generate an electron flow (i.e., current) toward the cathodic compartment where electrons can be used in an oxygen reduction reaction resulting in the direct production of electricity in microbial fuel cells (MFC) (Rabaey and Verstraete 2005; Lovley 2008; Ardolino et al., 2021), or the production of hydrogen (Tartakovsky et al., 2011; Escapa et al., 2016), value-added chemicals and removal of contaminants, such as metal ions, in microbial electrolysis cells (MECs) (Qin et al., 2012; Ezziat et al., 2019).

Recently, bioelectrochemical anaerobic sewage treatment (BEAST) technology has been proposed as an energy-efficient municipal wastewater treatment (Tartakovsky et al., 2018). This technology is based on the MEC concept and uses a membraneless flow-through configuration to simplify the construction and operation of the setup. In a similarly designed MEC, removal of heavy metals and selenium oxyanions was achieved at the cathode due to the activity of electroactive microorganisms (Jugnia et al., 2019; Jugnia et al., 2021). Recent bio-geochemical studies have also revealed unexpectedly diverse indigenous microbial communities affecting OSPWs (Foght et al., 2017). Consequently, in this study we focused on reducing impacts of oil extraction on the environment by using the BEAST concept of a flow-through membraneless MEC to achieve simultaneous removal of organics (such as hydrocarbons, naphthenic acids), heavy metals, and metalloids from OSPWs.

As a proof of concept, synthetic water prepared from commercial NA mixtures, the water soluble diesel fraction, metals, and metalloids was used to test the effectiveness of this bioelectrochemical approach as a potential treatment applicable to OSPW. More specifically, the goal of this study was to perform a comprehensive investigation into the effectiveness of this treatment approach through the evaluation of chemical, ecotoxicological, and genomics parameters. Considering the target application for OSPW treatment, the proposed concept is based on a passive flow permeable barrier with an extremely low applied voltage (below the onset of water electrolysis) and, accordingly, low power consumption. The resulting treatment system is expected to feature low treatment costs and operational simplicity.

2. Materials and methods

2.1. Feeding solution preparation

Tank feeding solutions varied depending on the experimental phase. Initially, during the conditioning phase that lasted 20 days, the tanks were fed with 20 L effluent from a laboratory-scale BEAST reactor treating wastewater amended with 50 mL anaerobic sludge (approximately 40 g L^{-1} VSS, Lassonde Inc., Rougemont, QC, Canada). From day 21 to 95, the tanks were fed with a synthetic OSPW solution consisting of (per 6 L): 2.5 L of water-soluble diesel fraction, 2.6 L of tap water, 0.9 L of a salt solution (15 mS cm^{-1}), and 0.216 mL of Naphthenic Acids (Sigma-Aldrich, 98% purity). The water-soluble diesel fraction was prepared by mixing 1 L of standard diesel (from a commercial gas station) with 5 L of tap water on a stir plate at 240 rpm for 24 h. The organic phase was then allowed to separate from the aqueous phase, prior to collecting the aqueous phase used for synthetic OSPW preparation. The 0.9 L of salt solution used to make the synthetic OSPW was prepared in distilled water and consisted of (g L^{-1}): NaHCO 1.607, NH_4HCO 1.071, $CO(NH_2)_2$ 0.857, NaCl 3.214, $CaCl_2 \bullet 2H_2O$ 0.429, KCl 1.607, KH_2PO_4 0.161, K_2HPO_4 0.214; $MgSO_4 \bullet 7H_2O$ 0.321. Finally, from day 96 to 119, tanks were fed the synthetic OSPW described above, with the addition of metals and metalloids to achieve the following concentrations (in mg L^{-1}): As (as AsO_3) 40; Pb (as $Pb(NO_3)_2$) 2; Se (as Na_2SeO_4) 20; and Zn (as $ZnCl_2$) 20. All salts used were laboratory grade.

Table 1
Tanks parameters under study during synthetic OSPW treatment by BES.

Tank ID	Aeration	Applied Voltage
T_1	Yes	Yes
T_2	Yes	No
T_3	No	Yes
T_4	No	No

2.2. Experimental setup, operating conditions and calculations

The OSPW experiments were carried out in four tanks. A schematic of the experimental setup (tanks) denoted T_1 to T_4 used in the study is shown in Fig. 1. As described in Table 1, tank T_1 represented a MEC under microaerobic conditions, while tank T_3 corresponded to an anaerobic MEC. Two control tanks (T_2 and T_4) were also operated to study OSPW treatment under microaerobic and anaerobic conditions, respectively, in the absence of applied voltage. Overall, the four experimental setups were operated for a period of approximately 4 months.

The rectangular-shaped tanks had the following dimensions (cm): length (35), width (5.4), height (13.8) resulting in a total volume of 2.6 L and a working volume of 1.65 L. The tanks were constructed from Plexiglas plates connected with adhesive silicone sealant (SI 595, Loctite Henkel, Mississauga, ON, Canada). Each tank had two electrode compartments (cathode and anode) separated using perforated polypropylene sheets (1/8″ hole diameter) covered with polyester geotextile with an approximate thickness of 2 mm and 1 mm, respectively, attached to the separators to avoid direct electrical contact between compartments. Each electrode compartment had a volume of 670 mL. The tanks were filled with metallurgical coke obtained from Natural Resources Canada (NRCan) that was crushed and sieved (≥ 550 μm). To equilibrate water flow, at both ends of the tanks there were 159 mL influent and effluent compartments. Titanium and stainless steel meshes of approximately 4.5 cm x 12 cm x 1 mm in size were inserted in the middle of anode and cathode compartments, respectively, and served as current collectors. A fixed applied voltage of 1.4 V was maintained in tanks T_1 and T_3 using a Texio PW18–1.8AQ power supply (Kenwood Corp., Tokyo, Japan). Although tanks T_2 and T_4 did not have an applied voltage, they included the same meshes in their respective chambers. Tanks T_1 and T_2 were periodically micro-aerated at a frequency of 10 s per minute (15 L d^{-1} per tank or 7.5 L d^{-1} per electrode chamber). A Masterflex® L/S pump with pump head model 7017–20 and Masterflex Norprene 6404–14 tubing delivered air via aeration stones positioned at the bottom and center of the anodic and cathodic chambers of tanks T_1 and T_2. Tanks T_3 and T_4 were not aerated.

All four tanks were fed with the same influent solution during their conditioning and synthetic OSPW treatment phases so as to obtain a desired hydraulic retention time (HRT). HRT values were calculated based on the total working volume of the tanks (1.65 L), although the total electrode volume was 1.34 L. Feeding solution was introduced to each tank near the bottom, while the resulting treated water was drained out at the upper portion of the tank to promote better mixing. Influent feed (inoculum or synthetic OSPW) was fed to each tank using Masterflex Norprene 6404–14 tubing and a Masterflex® L/S pump with pump head model 7017–20. During the inoculation and conditioning phase, the tanks were operated at a hydraulic retention time of 1.5 days for 20 days. After conditioning, all four tanks were fed the synthetic OSPW at an HRT of 4 d (between days 21 - 27), followed by an HRT of 8 d (between days 22 - 69), and another HRT of 4 d (between days 70 - 119).

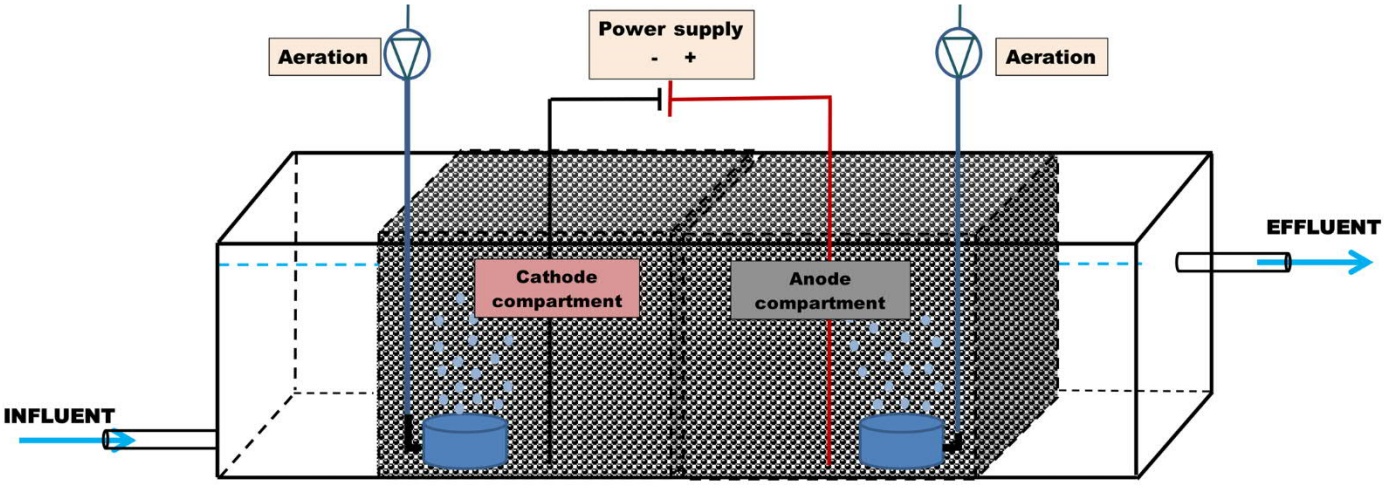

Fig. 1. Schematic designs of the tanks used in treating synthetic OSPW.

Tanks were operated at a room temperature of 21–23 °C. During the second phase, the performance of each of the different tanks was assessed through physico-chemical, eco-toxicological, and biomolecular analyses carried out as described below.

Coulombic efficiency (CE) was calculated as the ratio of total electrons recovered during one day of the experiment to the theoretical amount (Tartakovsky and Guiot 2006):

$$CE = \frac{I \cdot t}{F \cdot n \cdot w/M} 100\% \quad (1)$$

where I is the current (A); t is the time interval (86,400 s); F is the Faraday constant (96,485 C/mol); n is the is the number of moles of electrons produced per mol of substrate (mol/mol); w is the daily amount of removed CODs, and M is the COD molecular weight (g). An average molecular weight of 178.6 g was assumed based on average diesel $C_{12.9}H_{23.9}$ (Soares 2015). Accordingly, $n = 24$ was used for the calculations.

2.3. Measurements, sample collection and analysis

2.3.1. Physical and chemical analyses

The performance of each tank was monitored by periodically analyzing samples collected from the influent and effluent streams. Flow rates were measured by collecting the effluent from each tank for over 24 h. Samples for chemical oxygen demand (COD) and metals were filtered prior to preservation and/or analysis. COD was analyzed using a PeCOD analyzer (Mantech Inc., Guelph, ON). Dissolved metals were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) as outlined in method MA. 200 – Mét. 1.2 by the centre d'expertise en analyze environmentale du Quebec. Petroleum hydrocarbons were analyzed using gas chromatography with a flame ionization detector (GC/FID) following the modified version of Ontario's Ministry of Environment petroleum hydrocarbon method E3421." https://files.ontario.ca/protocol_for_analytical_methods_used_in_the_assessment_of_properties_under_part_xv.1_of_the_environmental_protection_act.pdf .

Naphthenic acid (NA) concentrations were analyzed using a Bruker MicroTOF-Q Mass Spectrometer coupled with an Agilent HPLC system using electrospray ionization in negative ion mode. For this analysis, 950uL of each sample was spiked with 50uL of a 1 mg L^{-1} Decanoic acid-d3 internal standard. A 50uL aliquot of this mixture was then injected into a PerkinElmer Brownlee™ SPP C8 (2.1 mm x 100 mm, 2.7 µm) column at 30 °C. The gradient method at a flow rate of 0.3 mL/min was 45% mobile phase B held isocratically for 2 min, followed by the linear gradients from 45% to 67% B in 1 min and 67% to 100% B in 7 min and held at 100% B for 5 min. The mobile phase A and B composition was 90%/10% water/methanol with 10 mM ammonium acetate and 100% methanol with 10 mM ammonium acetate, respectively. The MicroTOF-Q was scanned over a mass range of 100–650 m/z. The ESI source temperature and drying gas flow rate was 200 °C and 8 L min^{-1}, respectively. A commercial standard mixture of naphthenic acid (Sigma-Aldrich 70,340–250 mL) was diluted to a concentration of 50 ppm, spiked with the same concentration of Decanoic acid-d3 internal standard and analyzed using the method described above. One wash injection with 50uL of 0.02% NH_4OH and Isopropanol (1:1 v/v) followed by one equilibrium injection with 50 ppm Decanoic acid-d3 internal standard blank was performed after each sample injection to ensure the removal of any possible carryover and ensure column equilibration before the injection of the next sample. This method was used to determine the characteristic retention time of individual NAs and to determine the presence and total amount of NAs in samples using extracted ion chromatography (EIC) with Bruker Compass TargetAnalysis software. The total amount of NAs in each sample was calculated based on the response relative to the 50 ppm standard mixture of NAs.

2.3.2. Aquatic toxicity testing and data analysis

Dose response curves for Microtox and algal toxicity tests were carried out on tank influent and effluent samples collected at the end of the experiment. The Microtox toxicity assay was carried out as described by Environment Canada (1992). The light intensity of the luminescent bacteria *Vibrio fischeri* was spectrophotometrically measured before and after 15 min exposure to the collected water sample. The Microtox apparatus (model 500, Modernwater, New Castle, USA) had an integrated spectrophotometer which measured light intensity at a wavelength of 490 nm. The decrease in light intensity relative to negative controls following exposure to samples indicates potential toxic effects. Microtox data was expressed as the average percentage of light emission inhibition compared with the negative control. Tests were done in triplicate with 2% NaCl in water used as a negative control. *Vibrio fischeri* had optimal bioluminescence at pH values between 6.0 and 8.0. The pH of water samples was adjusted to 6–7, if pH was below 6, and to 7–8 when it was higher than 8 using 1 N of HCl and NaOH solutions, respectively.

The freshwater green algae *Pseudokirchneriella subcapita* was used to study chronic toxicity according to procedures described by Environment Canada (2007). Algae were exposed separately to different concentrations of influent and effluent samples in a 96-well microplate under continuous lighting (4500 ± 500 lux) at 24 ± 1 °C for 3 days. At the end of the exposure time, the number of algae cells was counted using a Coulter Z2 cell counter (Beckman Coulter) and the percentage of cell growth in the test sample was compared to the negative control (water).

For each toxicity assay, the data was plotted as concentration-response curves and best curve-fitting was selected using TOXCALC v

5.0 software (Tidepool scientific, CA). The toxicity endpoints were expressed as concentrations causing 20% or 50% inhibition of the control (IC20 or IC50). The differences between various treatment groups were identified using the Fisher least significant difference or Bonferroni adjusted t-tests. A significance level of $p \leq 0.05$ was accepted for all statistical tests. Based on these results, the lowest effect concentration (LOEC) and the no effect concentration (NOEC) were determined only for tests with completed dose-response curves.

2.3.3. Biomolecular analyses

At the beginning and end of the test, corresponding to day 130 of tank operation, electrode material (metallurgical coke) samples were collected from the anode and cathode compartments of all four tanks (T_1, T_2, T_3 and T_4) for biomolecular analyses.

High-throughput 16S rRNA gene amplicon sequencing was carried out to determine microbial community composition and relative abundance in each of the metallurgical coke samples tested in triplicate. Only certified RNase and DNase-free plasticware and water were used during the course of the nucleic acid extraction and sequencing library preparation. Genomic DNA was extracted from a 0.5 g (wet weight) metallurgical coke sample using the DNeasy PowerSoil Kit (Qiagen, Toronto, Canada) following manufacturer's protocols. DNA sequencing libraries were then prepared for sequencing on the Illumina MiSeq^{TM} platform using Illumina's 16S Metagenomic Sequencing Library preparation protocol and the universal 16S rRNA primers 515F and 926R as recommended by the Joint Genome Institute (JGI). Raw reads were analyzed through the NRC's internal rRNA short amplicon analysis pipeline as previously described (Tremblay et al., 2015). Briefly, reads were filtered, assembled with their overlapping paired-end and clustered at 97% identity. Taxonomy was then assigned to each cluster based on the Greengenes taxonomy (Greengenes v13_5) and OTU tables were generated, filtered to exclude eukaryotes and chloroplasts and normalized as described in McMurdie and Holmes (2014). These normalized OTU tables were used for computing alpha and beta diversity metrics and to generate taxonomic graphs using the RStudio Shiny package.

3. Results and discussion

Several previous studies demonstrated successful COD removal in membraneless flow-through MECs (Hussain et al., 2017; Tartakovsky et al., 2018). However, these experiments were carried out using municipal wastewater with COD levels ranging from 300 to 500 mg L^{-1} (low to medium strength wastewater). Depending on the wastewater strength in these experiments, an acceptable treatment efficiency (e.g. biological oxygen demand, BOD_5, below 25 mg L^{-1}) was obtained at HRTs of 2 – 3 days. While OSPW contains relatively low levels of organic materials, typically around 200 mg L^{-1} COD, the presence of hydrocarbons, NAs, and metals significantly limit OSPW biodegradability. It was therefore decided to evaluate OSPW bio-treatability under bioelectrochemical conditions at sufficiently longer retention times, e.g. at an HRT of either 4 days or 8 days.

While microbial fuel cells (MFCs) require oxygen to be present in the cathode compartment (Tartakovsky and Guiot 2006), MECs are typically operated under strictly anaerobic conditions at the cathode (Rousseau et al., 2020). Furthermore, electroactive microorganisms at the anode typically require anaerobic conditions. To enable electron flow to the anaerobic cathode, a power supply is used, while ensuring that the applied voltage is below the water electrolysis threshold (Escapa et al., 2016). Nevertheless, in several studies anodophilic electroactive microorganisms were shown to be able to tolerate the presence of oxygen (Rosenbaum et al., 2010). NAs have been shown to be biodegraded under anaerobic conditions, however the biodegradation process may be slow, at a scale of several months, while aerobic degradation of NAs is a faster process (Headley and McMartin 2004; Clothier and Gieg 2016). For this reason, OSPW treatment in an anaerobic MEC was compared to that of a MEC operated under microaerobic conditions imposed by providing low air flow rate intermittent aeration to both the anode and cathode compartments.

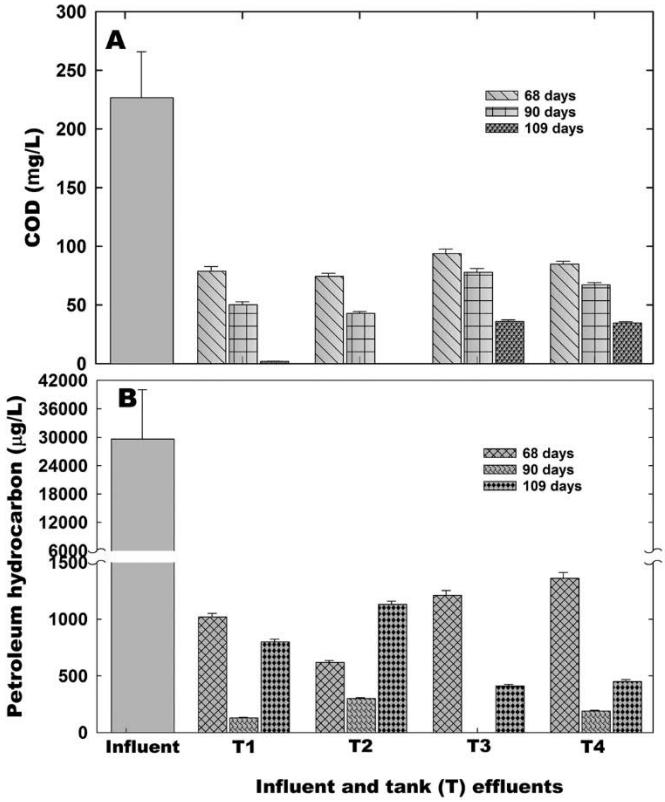

Fig. 2. Changes in (A) COD concentrations and (B) petroleum hydrocarbon concentrations between the influent and effluent of the tanks. Error bars show standard deviation calculated using all influent COD measurements obtained throughout the study period (Influent COD) and standard deviation of the analytical method (effluent COD).

3.1. Hydrocarbon and chemical oxygen demand removal

Petroleum hydrocarbon (PHC) removal was assessed by comparing the influent and effluent COD values of the tanks in addition to detailed chemical analysis of hydrocarbon concentrations. COD measurements throughout the experiment are presented in Fig. 2A. On average, COD concentrations in the influent were greater than 200 mg L^{-1}, contrasting with effluent concentrations of the different tanks which were relatively low, fluctuating between 0 and 94 mg L^{-1}. The influent COD values remained relatively constant throughout the test (coefficient of variation <15%). Meanwhile, COD removal efficiencies differed between the tanks, as can be seen from the effluent COD concentrations shown in Fig. 2A. Best COD removal was observed in tanks T_1 and T_2, improving from 55 to 99% and from 67 to 100% for tanks T_1 and T_2, respectively. COD removal in tanks T_3 and T_4 was less efficient, although it improved over time from 35 to 87% for T_3 and 53 to 87% for T_4. Overall, improved removal of COD over time in all tanks was indicative of microbial communities' adaptation to OSPW degradation. Removal tended to be lower in tanks without aeration compared to tanks with aeration, for which COD concentrations reached zero by the end of the study. The determination of COD based on photoelectrochemical oxidative degradation (PeCOD) relies on the measurement of currents from electrochemical reactions, which strongly depend on the presence of individual compounds in the case of organic matter oxidation (Geerdink et al., 2017). It is probable that not all organic matter present in the effluent water samples was measurable. This, in addition to the different conditions prevailing in each of the tanks under study,

may explain why the variation of COD and PHC concentrations in the influent and effluent from the tanks did not exhibit the same trend at all times, as described below.

Unlike COD, a high degree of PHC removal was already observed during the first sampling campaign (Fig. 2B). The PHC removal efficiency obtained for all tanks and samples analyzed was 93.6 ± 8.1%. PHC removal efficiency obtained during the first sampling campaign, when the HRT was at 8 days, averaged 83 ± 5%. This removal increased during the second and third sampling campaigns, averaging 98.8 ± 0.8%, despite the fact that the HRT was decreased to 4 days. Overall, these results suggest that PHC removal was successfully achieved within the different tanks, and the increasing removal efficiencies observed between the first and subsequent sampling campaigns is an indication of microbial communities adapting to PHC degradation in all tanks. The increased presence of diesel-degrading bacteria can be hypothesized. Biodegradation of PHCs by microorganisms is well known (Boonchan et al., 2000; Hendrickx et al., 2006; Varjani and Upasani 2012; Wilkes et al., 2016) and bacteria are reported as the main degraders of petroleum pollutants in the environment (Atlas 1981; Varjani and Upasani 2012; Abbasian et al., 2015; Meckenstock et al., 2016) consuming PHCs for their energetic and carbon needs for growth and reproduction.

PHC removal trends in all tanks were relatively similar for any given sampling campaign (Fig. 2B). For example, during the first sampling campaign when the flow rate was at 0.25 L d^{-1}, PHC removal was relatively high and fluctuated between 78 and 90% (Mean ± SD = 83.3 ± 5.1%) with the highest values associated with aerated tanks (Fig. 2B). With the second sampling campaign conducted after the flow rate was increased to 0.5 L d^{-1}, removal efficiencies increased for all the different tanks reaching 99 to 100% (M ± SD = 99.0 ± 0.6%) with the highest values observed in tanks with applied voltage (Fig. 2B). These removal efficiencies remained relatively stable at 98.3 ± 0.8% with only minor variations between tanks during the third sampling campaign. Removal of petroleum oil pollutants using indigenous microorganisms is a slow process and the most widely used approach to speed up the degradation process consists of stimulating the growth of indigenous oil degraders by adjusting environmental factors (Widdel and Rabus 2001; Abbasian et al., 2015; Smith et al., 2015; Meckenstock et al., 2016; Engelhardt et al., 2018; Liu et al., 2019; Jugnia et al., 2020). Mohanakrishna et al. (2020) recently reported a correlation between increased electrochemical activity and total petroleum hydrocarbon degradation following the addition of acetate and sewage. In the present study, providing oxygen did not appear to significantly affect PHC degradation, an observation in line with many previous studies that demonstrated PHC biodegradation under both aerobic and anaerobic conditions (Salminen et al., 2004; Truskewycz et al., 2019). A more pronounced difference could be expected at shorter HRTs. In most cases, the bioelectrochemical treatment of diesel-contaminated waters coupled with aerobic and anaerobic biodegradation ended up being the most optimal condition tested. This condition is also likely to be the most efficient in treating other co-contaminants such as NAs, metals, and metalloids which are typically present in OSPW.

3.2. Naphthenic acid removal

Similar to results obtained for PHCs, NA removal was observed in all tanks. Tanks with aeration (T_1 and T_2) exhibited the best performance with an overall mean removal efficiency approaching 74.6 ± 10.5% versus 50.8 ± 25.8% for tanks without aeration (T_3 and T_4, Fig. 3A). This is in agreement with a study by Lai et al. (1996), which reported that lower dissolved oxygen concentration resulted in a decreased rate of surrogate NA degradation. Our results are also in line with experimental evidence to date indicating that NA degradation is a predominantly aerobic process (Del Rio et al. 2006); although anaerobic degradation of this chemical has also been reported (Clothier and Gieg 2016). During

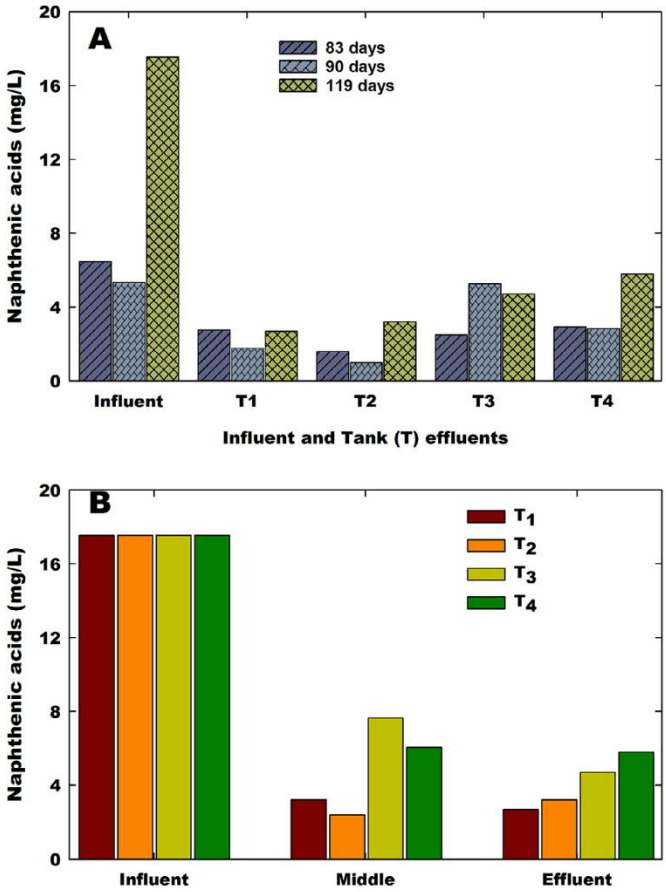

Fig. 3. Changes in naphthenic acids concentrations between A - the influent and effluent of the tanks and B – between different compartments of each tank (end of the study).

the first two sampling campaigns, NA removal efficiency was highest in tank T_2 (with aeration but no applied voltage), followed by T_1 (with aeration and applied voltage) and thereafter T_3 and T_4. However, in the samples collected one month later, T_1 exhibited the best removal efficiency followed by T_2, T_3 and T_4 (Fig. 3A).

A more detailed analysis of NA concentrations in electrode compartments indicated a progressive decrease in NA concentrations in each compartment (Fig. 3B). It can be hypothesized that over time, there was a buildup of microorganisms involved in NA removal, particularly in tank T_1 (MEC with micro-aeration applied). Evidently, a combination of electroactive microorganisms and aerobic NA degraders increased the removal efficiency in this tank relative to other tanks. Interestingly, when comparing results of NA distribution between influent and effluent from the different tanks (Fig. 4), it can be seen that some of the NAs present in the influent of tank T_1 decreased in concentration (i.e. NAs C11, C12, C13, C14) or had completely disappeared in the effluent (NAs C17, C20, C21, C24). In tank T_3 (anaerobic MEC) the concentrations of some of the NAs degraded in T_1 remained almost unchanged (C11, C12, C13, C14, Fig. 4). Overall, more compounds with higher carbon numbers were completely degraded in T_1. In a study that aimed to treat OSPW using a membrane bioreactor with a submerged flat-sheet ceramic microfiltration membrane, Xue et al. (2016) reported bioconversion of NAs with higher carbon numbers into NAs with lower carbon numbers that were more bio-persistent with the possibility that a longer HRT may be needed to achieve complete NA removal.

Several characteristics of NAs impact their biodegradability. These include the degree of branching, spatial arrangement of branching, periodicity and environmental factors such as oxygen availability, nitrogen

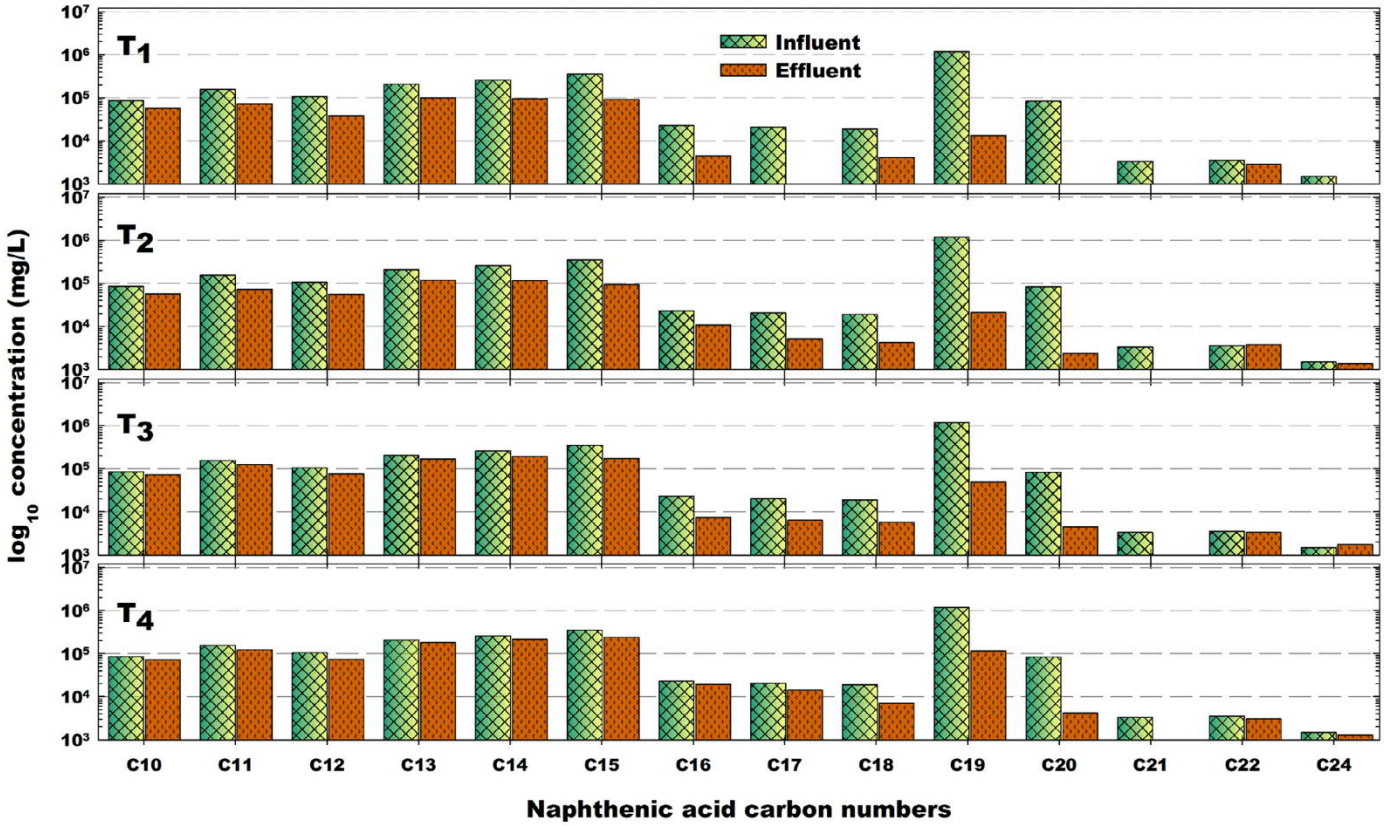

Fig. 4. Concentrations of individual naphthenic acids (logarithmic scale) in the influent and effluent streams of all tanks (day 109).

and phosphorus limitation as well as microbial community composition. NAs are known as the primary compounds responsible for the toxicity of OSPW (Mikula et al., 1996; Quagraine et al., 2005) and the effective removal of NAs in real oil-containing wastewaters, like OSPWs, has been the subject of an increasing number of recent studies (Kannel and Gan 2012; Wang and Ren 2014; Brown and Ulrich 2015). To the best of our knowledge, this study represents the first attempt to use a micro-aerated MEC for treating NA contaminated water, using commercial (synthetic) NAs as a surrogate for assessing NA removal from OSPW. Overall, experimental results suggest that this bioelectrochemical approach can be used for cost-efficient treatment of NA - contaminated water. Considering that this proof of concept was obtained using synthetic NAs, additional efforts are needed to confirm the NA degradation performance with real OSPWs, understand the factors influencing the removal efficiency, and optimize the process. Main expected differences between the synthetic NAs used in this study and NA-like compounds founds in real OSPWs might be related to the more simplistic composition of synthetic NAs. Accordingly, synthetic NAs are expected to be somewhat easier to biodegrade and real OSPW toxicity is expected to be higher compared to synthetic NAs. Nevertheless, this demonstration is an important first step in developing a novel MEC-based technology for OSPW treatment.

A comparison of electrical currents in tanks T_1 and T_3 (micro-aerated and anaerobic MECs, respectively), suggested a link between the observed current and the degree of NA removal. Indeed, the highest current (3.3 ± 0.5 mA) was observed in T_1, where the highest COD and NA removal was also observed. Under steady state conditions, the observed current in the anaerobic MEC (tank T_3) was considerably lower, remaining at 2.3 ± 0.5 mA. This difference may be related to the limited availability of organic materials in all tanks. PHCs and especially NAs have low biodegradability, as well as relatively low solubility in water. Also, electroactive microorganisms are not known to be capable of direct biodegradation of either NAs or PHCs. It can be hypothesized that biodegradation was achieved by a microbial consortium of PHC and NA degraders, which provided biodegradation intermediates for metabolic activity of the electroactive bacteria. It can also be suggested that degradation of PHC and the commercial NAs used proceeded at a higher rate under microaerobic conditions, as can be seen from the higher current observed in T_1. Notably, initial tests under abiotic conditions, and in the absence of any carbon source, showed a current of 0.3 - 0.5 mA in both tanks, which was used as a background value for Coulombic efficiency (CE) calculations. Thus, the increase in current when the OSPW was supplied to tanks is likely attributable to the metabolic activity of electroactive microorganisms.

CE was calculated by comparing electrical current with the amount of CODs removed in each tank (Eq (1)). CE estimations of 21% and 16% were obtained for tanks T_1 and T_3 respectively. These estimations, once again, suggested higher electrochemical performance of the micro-aerated MEC, likely due to the improved bioavailability of diesel compounds under microaerobic conditions. Importantly, tank T_2 was also operated under microaerobic conditions. However, it showed lower removal efficiency as compared to T_1, emphasizing the important contribution of electroactive microorganisms to the overall removal of PHCs and NAs.

3.3. Metal removal

Results from samples collected and analyzed for metals (Cu and Zn) and metalloids (As and Se) indicated that metals were more efficiently removed than metalloids (Fig. 5). The removal efficiency for Cu was 53 ± 21% and Zn removal efficiency was 40 ± 19%. In general, the highest removal efficiencies were associated with tanks T_1 and/or T_3 (with applied voltage) and the lowest ones to tanks T_2 and/or T_4 (without applied voltage). In the absence of applied voltage, metal removal probably occurred due to the activity of sulfate reducing bacteria (SRB) as demonstrated elsewhere (Jugnia et al., 2019). On the other hand, in tanks with applied voltage (bioelectrochemical systems) metal removal

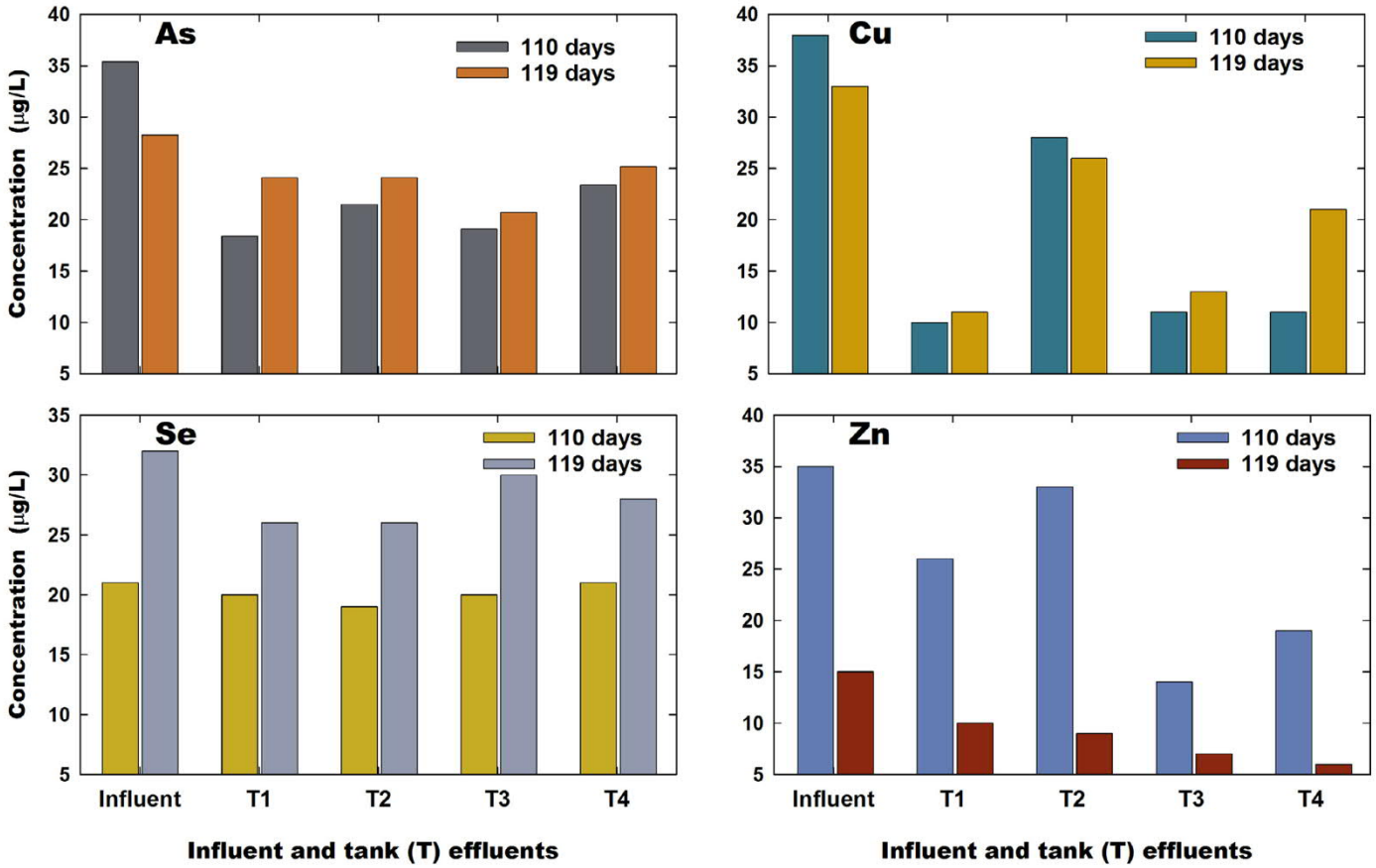

Fig. 5. Changes in concentrations of metalloids and metals concentrations between the influent and effluent streams of the different tanks.

was accomplished by a combination of SRB-related and electroactive activities associated with redox reactions known to immobilize metals (Wang and Ren 2014; Nancharaiah et al., 2016; Ezziat et al., 2019), provided that organic materials were continuously supplied to the anode in order to provide a source of electrons. In a recent study, metal removal was demonstrated in a MEC with peat moss as the carbon source (Jugnia et al., 2019). Another recent study demonstrated selenate and selenite removal in a MEC and reported a decrease in removal efficiency under carbon source limiting conditions (Jugnia et al., 2021). In this study, the observed Se and As removal efficiencies were relatively low in comparison to the studies mentioned above, ranging from 11 to 48% for As and 0 to 18% for Se. It can be hypothesized that the low biological and bioelectrochemical removal of these metalloids was associated with insufficient carbon source availability. Thus, the removal efficiency could potentially be increased by supplying readily biodegradable organics.

3.4. Ecotoxicity

In vitro toxicity tests are a common approach for evaluating toxicity. These tests are effective screening tools to quickly evaluate the effectiveness of water treatment techniques using species with different endpoints reported as bioluminescence (Microtox® assay with the marine bacterium *Vibrio fischeri*), mortality (e.g. freshwater amphipod of *Hyalella azteca*), viability (e.g. freshwater mussel larvae *Lampsilis cardium* (Bartlett et al., 2017)) or cell growth (e.g. microalgae *Pseudokirchneriella subcapitata* (Debenest et al., 2012)). The Microtox assay is a widely used screening and monitoring tool that is simple and reproducible (Brown and Ulrich, 2015; Clemente and Fedorak, 2005). A study by Bartlett et al. (2017) reported that microbial populations indigenous to oil sands mining area were more sensitive to both commercial NAs and NAs from OSPW than *V. fischeri*, suggesting that even low toxicity reported using *V. fischeri* could be lethal to these species. On the other hand, Frank et al. (2010) hypothesized that the principal mode of action for acute toxicity attributed to commercial NAs and NAs from OSPW is membrane disruption (narcosis), a phenomenon characterizing the endpoint of the Microtox® assay that is assessed via bioluminescence measurements. Previous studies questioned the fact that *V. fischeri*, a marine microorganism, could be used to predict effects on freshwater species (Frank et al., 2010; Martin et al., 2010), since *V. fischeri* was the least sensitive organism and *H. azteca* the most sensitive organism when evaluating toxicity of aquatic species for both commercial NAs and OSPW NAs (Bartlett et al., 2017). Therefore, the toxicity results presented for commercial NAs in this study should be interpreted with caution, e.g., qualitatively, since commercial NA mixtures have been shown to differ from OSPW NAs in chemical composition (Marentette et al., 2015).

Toxicity is commonly evaluated based on IC50 or IC20 values corresponding to concentrations causing 20% or 50% inhibition of a specific biological or biochemical function. IC50 (5%) and IC20 (57%) values (v/v) were obtained for untreated synthetic contaminated water in the Microtox and algal growth assays, respectively (Fig. 6). Toxic effects were reduced after treatment as illustrated by increased IC50 (12% – 73%) for the Microtox assay and IC20 (85% –100%) for algal growth when using effluents from the different tanks under study (Fig. 6). Interestingly, the highest values (lowest toxicity) of IC50 for the Microtox assay and IC20 for algal growth were both reported for tank T_1 (aerated MEC) where the removal efficiency of NAs was also the highest. This suggested that residual commercial NAs contributed to the higher level of toxicity observed for effluent samples collected from other tanks. The observed decrease of synthetic water acute toxicity might be due to the altered structure and composition of NAs and/or their biodegradation. It should be mentioned that commercial naphthenic acid mixtures are typ-

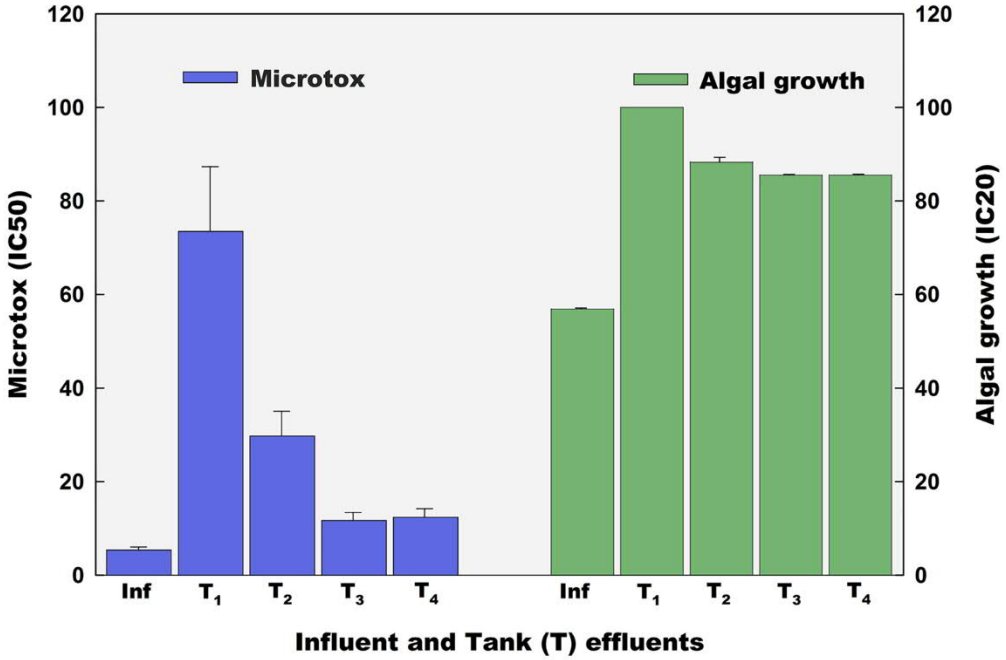

Fig. 6. Changes in acute toxicity of the influent and effluent water samples from the different tanks. Error bars show standard deviation of the measurements.

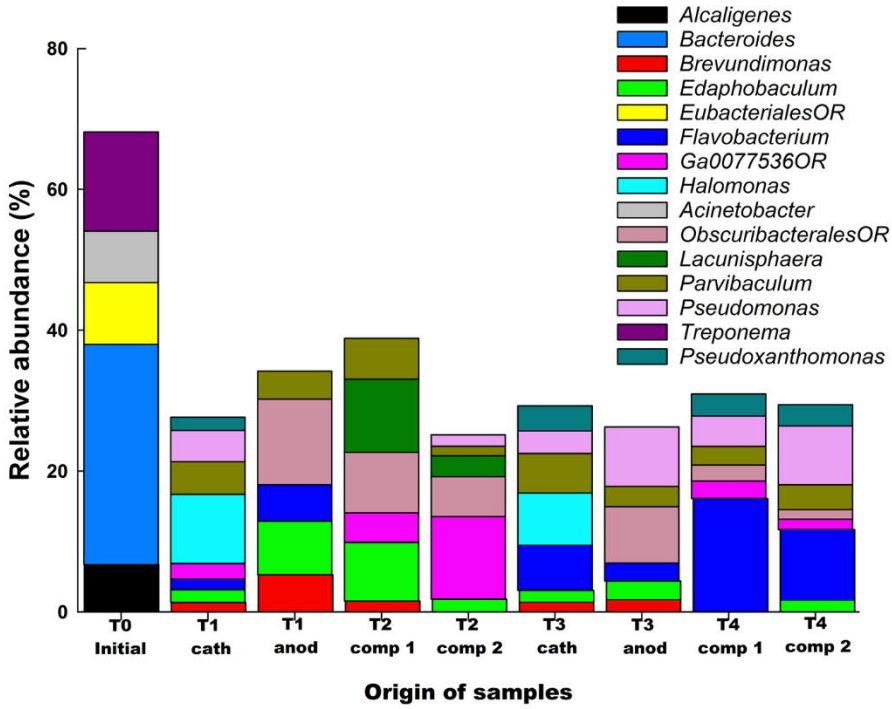

Fig. 7. Relative abundance (percent per reads of total reads) for the 15 most abundant OTUs identified via high-throughput 16S genes amplicon sequence.

ically comprised of smaller and structurally simpler compounds that are more biodegradable (Brown and Ulrich 2015) compared to NAs found in OSPWs. OSPW NAs could be more toxic (Clemente et al., 2004) and their acute toxicity may decrease following degradation (Marentette et al., 2015).

3.5. Microbial population analysis

Next-Generation Sequencing (NGS) of the 16S rRNA gene was used to assess the impact of MEC operating conditions on microbial community relative abundance and structure during the course of the experiment. Results representing the relative abundance of operational taxonomic units (OTUs) in averaged triplicate samples are illustrated in Fig. 7. Only the 15 most abundant taxa or OTUs are discussed.

The main OTUs in the initial samples (T_0), Bacteroides, Eubacteriales, *Acinetobacter* and *Treponema*, were completely absent in all samples collected at the end of the study. This is an indication that strong selection occurred within bacterial communities following the different treatment conditions applied. MECs with applied voltage (T_1 and T_3) exhibited variable proportions of similar OTUs, irrespective of the oxygenation regime, contrasting with tanks without voltage (T_2 and T_4), which contained variable proportions of different OTUs. This suggests that applied voltage contributed to limit bacterial diversity beyond tank oxygenation. Microbial communities in tanks were dominated by Bacteriodetes (*Flavobacterium* and *Edaphobaculum*), Gammaproteobac-

teria (*Pseudomonas, Halomonas* and Ga0077536), Alphaproteobacteria (*Parvibaculum*) and Obscuribacterales, a heterotroph closely related to Cyanobacteria. Dominant Betaproteobacteria and Gammaproteobacteria present in oil sands tailing ponds have been previously reported as degraders of NAs and aromatic hydrocarbons (Yergeau et al., 2012). Moreover, except for *Edaphobaculum* and Ga0077536, these bacteria have all been linked to the biodegradation of various aromatic and recalcitrant hydrocarbons including NAs and aromatic hydrocarbons (Röling et al., 2002; Bell et al., 2013; Frankel et al., 2016; Xue et al., 2017). Other bacterial genera associated with metal transformations, nutrient cycling and the degradation of NAs and hydrocarbons, such as *Brevundimonas* and *Pseudoxanthomonas,* were also found to be present in samples.

More specifically, members of the *Halomonas* genus were found exclusively at the cathode of MECs with applied voltage (T_1 and T_3), somewhat replacing Obscuribacterales that were found at the anode of these tanks in addition to tank T_2 with oxygenation. *Halomonas* are aerobic or facultative anaerobic heterotrophs (Mnif et al., 2011) and have been described with PAH-degrading qualities. *Halomonas* were found at all cathodes of microbial fuel cells in a recent study by Rago et al. (2017). Members of Obscuribacterales have broader metabolic capabilities and are also capable of aerobic respiration under both high and low oxygen conditions (Soo et al., 2014; Fischer et al., 2016) and were highly abundant in aerated tanks (T_1 and T_2) along with *Edaphobaculum, Lacunisphaera, Parvibaculum* and Ga0077536. Members of the *Parvibaculum* genus have been reported to contain numerous genes putatively involved in the metabolism of aromatics, alkanes, toxic and refractory organic compounds (Wang et al., 2020) consistent with the synthetic OSPW used. Furthermore, *Flavobacterium* and *Pseudomonas* appeared as the predominant OTUs in non-oxygenated tanks (T_3 and T_4).

Despite differences in microbial community composition and relative abundance, MEC tank T_1 exhibited the highest rate (55%) of NA removal. Microorganisms capable of effective NA degradation include members of the Proteobacteria, particularly *Pseudomonas spp* that were present in Tank 1 but not as abundantly as in other tanks, namely T_3 and T_4. However, according to Skeels and Whitby (2019), NA molecular structure and composition, as well as environmental factors such as the presence of specific electron acceptors, trace metals and competition for substrates from non-NA-degrading microbes, are important drivers shaping NA-degrading microbial communities. It can therefore be hypothesized that tank T_1 represented the system with the most optimal conditions leading to significant removal of pollutants from the synthetic OSPW under treatment thereby reducing its toxicity.

Overall, these results illustrate the complex nature of NA biodegradation and suggest that the biodegradation of NAs with differing molecular structures may be performed by different microbial species, either independently or synergistically. Further studies are needed to determine the factors influencing microbial degradation of NAs and other co-contaminants such as metals in OSPW.

Conclusion

Overall, our results suggest that a MEC with micro-aerated electrode compartments could be successfully used for OSPW treatment. This approach enables a combination of metabolic activities of several microbial trophic groups including aerobic, anaerobic, and electroactive microorganisms. As a result, removal of complex organic compounds, such as NAs, PHC, metals, and metalloids is facilitated. The simplicity of the proposed approach and low energy consumption associated with MEC operation at an applied voltage below the onset of water electrolysis enables cost-efficient process scale-up, e.g. using a permeable biobarrier approach. Considering that NAs from OSPW differ from commercially available NAs, which were used in this study (Marentette et al., 2015), it should be emphasized that further experimental work is needed to evaluate MEC performance for treating real OSPW, gain a better understanding of the biodegradation process, and optimize operating parameters such as applied voltage, micro-aeration rate and hydraulic retention time.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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