Bioresource Technology 221 (2016) 70–77

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Electro-biocatalytic treatment of petroleum refinery wastewater using microbial fuel cell (MFC) in continuous mode operation

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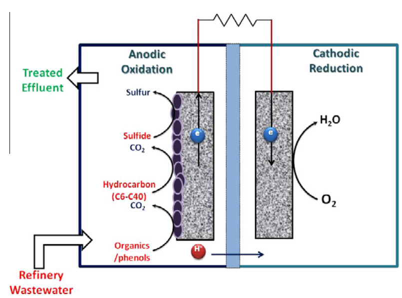
HIGHLIGHTS

- Contaminants present in refinery wastewater treated in continuous mode MFC operation.
- Continuous mode operation showed higher performance (225 ± 1.4 mW/m^2) over batch mode.
- GC chromatogram showed significant removal of hydrocarbon content of C6 to C40.
- Phenol and sulfide removal was also significant in continuous mode operation.
- Projected power yields showed the possibility of process up-scaling.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 August 2016
Received in revised form 5 September 2016
Accepted 7 September 2016
Available online 13 September 2016

Keywords:
Bioelectrochemical system (BES)
Organic load
Phenol degradation
Sulfide removal
Oil degradation
Hydrocarbon treatment

ABSTRACT

Refinery wastewater (RW) treatment in microbial fuel cell (MFC) was studied in batch mode operation followed by continuous mode operation with 8 h and 16 h hydraulic retention time (HRT). The MFC performance was evaluated in terms of power density, organics removal, specific contaminants (oil & grease, phenol and sulfide) removal and energy conversion efficiency with respect to operation mode. Higher power density of 225 ± 1.4 mW/m^2 was observed during continuous mode operation with 16 h HRT along with a substrate degradation of 84.4 ± 0.8% including the 95 ± 0.6 of oil content. The columbic efficiency during this operation was about 2 ± 0.8% and the projected power yield was 340 ± 20 kW h/kg COD_R/day. Batch mode operation also showed good substrate degradation (81 ± 1.8%) but took longer HRT which resulted in significantly low substrate degradation rate (0.036 ± 0.002 kg COD_R/m^3-day) over continuous mode operation (1.05 ± 0.01 kg COD_R/m^3-day). Overall, current study depicted the possibility of utilizing RW as substrate in MFC for power generation along with its treatment.

1. Introduction

Oil refinery is an essential and central part of the downstream petroleum industry, where crude oil is refined into more useful products such as naphtha, gasoline, diesel fuel, asphalt base, heating oil, kerosene and liquefied petroleum gas, etc. (Gary et al., 2007). Refinery operations are quite complex in nature, require large volumes of water, and the composition of refinery wastewaters can vary substantially (Benyahia et al., 2005). Refinery wastewater (RW) contains organic pollutants, like hydrocarbons along with inorganic constituents, like sulfides, ammonia, nitrates, heavy metals, etc., which are less biodegradable and sometimes toxic to microbes (Chen et al., 2008). The conventional treatment methods are highly energy intensive and also not effective in meeting the stringent environmental norms. On the other hand, the

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http://dx.doi.org/10.1016/j.biortech.2016.09.034
0960-8524/

recent trend in waste disposal has taken a paradigm shift towards direct valorisation to valuable materials and energy, as a result of economic concerns and the increasing concern about low availability of raw materials. High energy consumption by the conventional treatment methodologies also drive the demand for alternative and effective systems that can fulfil the energy gap, by its ability to produce clean and sustainable energy/fuels with simultaneous assimilation of wastewater (Ren et al., 2013; Zhang et al., 2014). Biohydrogen production (Venkata Mohan et al., 2010), biomethanation (Sun et al., 2015), etc., from waste organics has garnered significance across the globe in this direction. However, there is a large gap in the net energy balance for these processes also due to the greater energy consumption compared to that produced. Also, the conversion efficiencies are on lower side resulting in left over metabolites like, VFAs and alcohols, having high energy values along with the incomplete treatment (ElMekawy et al., 2014b). Further research for the development of processes towards effective utilization of wastewater to generate sustainable energy has gained attention across the globe.

In microbial fuel cell (MFC), the chemical energy of substrates can be transformed into electrical energy by the metabolic activity of microorganisms (Logan et al., 2006; Srikanth et al., 2011). Coupling of anodic microbial oxidation with abiotic/biotic reduction at two distinct electrodes separated by an ion permeable membrane will drive the electron flow into circuit against the potential gradient (Srikanth and Mohan, 2012a). MFC application for wastewater treatment is preferred due to its efficiency of waste remediation compared to conventional treatment processes associated with the energy extraction (Mohan and Chandrasekhar, 2011; Velvizhi and Mohan, 2011). A wide range of wastewaters have been utilized as anodic fuels in MFC for the power generation as well as their valorization (ElMekawy et al., 2014a; Pant et al., 2010). But, very few studies were reported so far on the treatment of RW (Guo et al., 2016, 2014; Majumder et al., 2014; Ren et al., 2013; Zhang et al., 2014), petroleum sludge (Chandrasekhar and Venkata Mohan, 2012; Mohan and Chandrasekhar, 2011), oil-contaminated soil (Li et al., 2015; Lu et al., 2014; Wang et al., 2012), etc., using MFC. However, most of these studies were reported as proof of concepts or focused on the treatment efficiencies of organics. Detailed and long-term studies in continuous mode operations for the treatment of both organic and inorganic constituents of wastewater are lacking.

In this context, detailed study was performed for about 100 days of MFC operation including the batch and continuous mode operations, which showed potential for the application of BES in refineries for treating the RW in sustainable way. Present paper reports the successful operation of single chamber MFC in continuous mode with 8 h and 16 h retention time for the treatment of hydrocarbons as well as sulfides and phenols along with the power generation. Comparative evaluation of the results with the existing literature was also presented.

2. Materials and methods

2.1. Biocatalyst and characteristics of RW

Pre-enriched electrogenic mixed culture from corroded metal surfaces predominating with iron reducing bacteria, sulfur reducing bacteria, sulfur oxidizing bacteria and acid producing bacteria, was used as inoculums. RW was collected from effluent treatment plant of an operating oil refinery of Indian Oil Corporation. The RW was characterized (pH, 8.07; Phenol, 60 ppm; Sulfides, 94 ppm; Oil and Grease (O&G) content, 720 ppm and COD, 1040 ppm) after collection and was stored at 4 °C till use.

2.2. MFC construction

Single chamber (horizontal cylinder) mediator-less MFC was fabricated using Perspex glass (total/working volume, 0.25/0.20 L). Carbon cloth with carbon coating (0.5 mg/cm^2) was used as anode and carbon cloth with platinum coating (0.5 mg/cm^2) was used as cathode. Anode was completely immersed in the substrate, while the bottom portion of cathode was in contact with substrate and top portion was exposed to air (open-air cathode). Proton exchange membrane (Nafion117, Sigma-Aldrich) was sandwiched between the electrodes. The membrane electrode assembly was fixed in a groove like arrangement so that the electrolyte will be in contact with one side of the cathode. Stainless steel wires were used as current collectors for both the electrodes. Leak proof sealing was employed to maintain anaerobic microenvironment in the anode compartment.

2.3. MFC start-up and operation

The anodic compartment was inoculated with enriched mixed culture along with RW and operated at ambient temperature (29 ± 2 °C). The organic loading rate (OLR) varied based on the retention time of batch and continuous mode operations (Table 1). Prior to feeding, pH of the wastewater was adjusted to 7 ± 1 using concentrated orthophosphoric acid (88%)/0.1 N NaOH. Anode and cathode were connected externally through an external resistance of 460 Ω, except when stated otherwise. Initially, MFC was operated in batch mode with a hydraulic retention time (HRT) of 7 days and once the performance was stabilized with respect to power generation and COD (chemical oxygen demand) removal, the HRT was extended to ~15 days. Later the MFC operation was changed into continuous mode with 8 h HRT and further the HRT was increased to 16 h to improve the treatment efficiency.

Before every feeding event in batch operation, the inoculum was allowed to settle down (30 min) and the exhausted feed (180 ml) was decanted (15 min) under anaerobic conditions. The inoculum settled at the bottom (20 ml by volume) was used for subsequent operations. Feeding, decanting, and recirculation operations were performed by peristaltic pumps. Anodic content (anolyte) was continuously recirculated (0.2 L/h) in the direction of flow to avoid the formation of concentration gradient during batch operation. Anode chamber was sparged with oxygen free N_2 gas for 2 min to maintain anaerobic microenvironment after every feeding and sampling event. During continuous mode operation, constant N_2 gas supply was maintained into the reactor along with feed through a T-joint at the inlet. Constant voltage output and treat-

Table 1
Consolidated data pertaining to the MFC operation in batch and continuous mode (8 h HRT and 16 h HRT) operations.

	Batch mode	Continuous mode (8 h HRT)	Continuous mode (16 h HRT)
Cell voltage across 460 Ω resistance (mV)	318	328	648
Power density (mW/m^2)	54.11	55.48	225 ± 1.4
ξ_{COD} (%)	82.88	42.12	84.4 ± 0.8
ξ_{Oil} (%)	73.5 ± 1	52 ± 1	95 ± 0.6
ξ_{Phenol} (%)	85 ± 1.5	52.3 ± 1	80 ± 1.8
$\xi_{Sulfide}$ (%)	76 ± 0.6	61.5 ± 1.25	79.5 ± 1.2
OLR (g COD/m^3-day)	0.049	2.496	1.248
SDR (kg COD$_R$/m^3-day)	0.036 ± 0.002	1.04 ± 0.01	1.05 ± 0.01
Columbic efficiency (%)	10.5 ± 2.5	2 ± 0.8	2 ± 0.8
Projected power yield (kW h/kg COD$_R$/day)	12.5 ± 1	135 ± 10	340 ± 20