



# Integrating sequencing batch reactor with bio-electrochemical treatment for augmenting remediation efficiency of complex petrochemical wastewater



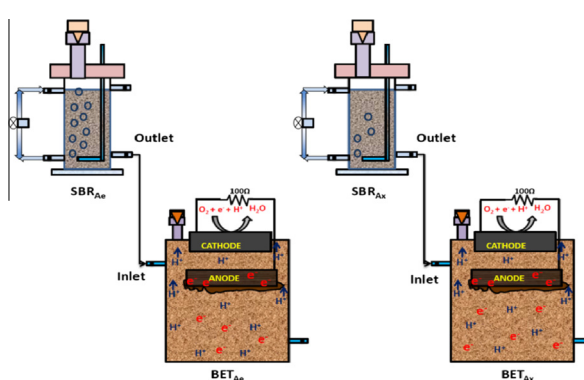
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## HIGHLIGHTS

- Integration strategy of SBR–BET for the remediation of petrochemical wastewater.
- GC–MS/FTIR confirmed the increment of biodegradability in PCW.
- SBR is an effective pre-treatment processes.
- Enhanced bioelectrochemical behavior was observed in BET system.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The present study evaluates the sequential integration of two advanced biological treatment methods viz., sequencing batch reactor (SBR) and bioelectrochemical treatment systems (BET) for the treatment of real-field petrochemical wastewater (PCW). Initially two SBR reactors were operated in aerobic (SBR<sub>Ae</sub>) and anoxic (SBR<sub>Ax</sub>) microenvironments with an organic loading rate (OLR) of 9.68 kg COD/m<sup>3</sup>-day. Relatively, SBR<sub>Ax</sub> showed higher substrate degradation (3.34 kg COD/m<sup>3</sup>-day) compared to SBR<sub>Ae</sub> (2.9 kg COD/m<sup>3</sup>-day). To further improve treatment efficiency, the effluents from SBR process were fed to BET reactors. BET<sub>Ax</sub> depicted higher SDR (1.92 kg COD/m<sup>3</sup>-day) with simultaneous power generation (17.12 mW/m<sup>2</sup>) followed by BET<sub>Ae</sub> (1.80 kg COD/m<sup>3</sup>-day; 14.25 mW/m<sup>2</sup>). Integrating both the processes documented significant improvement in COD removal efficiency due to the flexibility of combining multiple microenvironments sequentially. Results were supported with GC–MS and FTIR, which confirmed the increment in biodegradability of wastewater.

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## 1. Introduction

Industrial wastewaters tend to carry a huge load of organic and inorganic pollutants of which organic pollutants not only appear at high concentrations but also exhibit a wide diversity with respect to their molecular structures (Crowe et al., 2002; Botalova et al., 2009).

More specifically, wastewaters originating from petrochemical industries are characteristically less biodegradable in nature with diverse pollutants containing high concentrations of salt and carbon. Various structural chemicals, viz., polycyclic aromatic, aliphatic hydrocarbons, cyanides, octanols, formaldehyde, phenols, organic acids, sulfides, etc., persisting in petrochemical wastewater (PCW) warrants treatment prior to disposal (Malmasi et al., 2010; Papadimitriou et al., 2009; Verma et al., 2006). Various treatment methods are available for treating PCW viz., physical, biological,

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chemical etc. Physical treatment of PCW can be carried out using advanced membrane bioreactor (MBR), but the process has certain limitations due to its high operational and investment costs (Cheryan and Rajagopalan, 1998). Similarly, biological treatment methods also face significant challenges like, poor availability of hydrocarbons to the microorganisms due to their complex structure and water insoluble nature especially when salinity is higher in wastewaters (O'Neill et al., 2000; Lai et al., 2012; Balapure et al., 2015). Hence, in order to overcome these limitations, conventional wastewater treatment technologies require additional conversion processes to enhance the treatment efficiency.

Sequencing batch reactor (SBR) also known as periodic discontinuous batch reactor (PDBR) facilitates the integration of diverse redox microenvironments in a single reactor, which provides the possibility to achieve enhanced treatment (Wilderer et al., 2001; Buitron et al., 2004; Rao et al., 2005; Hosseini Koupaie et al., 2013; Venkata Mohan et al., 2007a, 2013; Naresh Kumar et al., 2014). Simultaneous provision of feast and famine conditions during SBR cycle operation enforces controlled short-term unsteady state conditions leading to stable steady state conditions in the long run operation. This enhances the robustness of consortia towards the treatment of complex wastewater (Ong et al., 2010; Venkata Mohan et al., 2005, 2007b, 2009b, 2013; Xiao et al., 2014). It also imposes selective pressure that can select a defined population of organisms, which can degrade complex compounds due to its unique flexibility to combine multiple metabolic functions during operation (Buitron et al., 2004; Venkata Mohan et al., 2007c). Bioelectrochemical treatment (BET) system, which is a microbial catalyzed electrochemical system, can facilitate the direct conversion of substrate to electricity through a cascade of redox reactions (Venkata Mohan et al., 2009a; Luo et al., 2009; Huang et al., 2009). It has been reported in literature that BET offers dual benefits of power generation coupled with the improved treatment efficiency, particularly with complex wastewaters (Venkata Mohan et al., 2014; Velvizhi and Venkata Mohan, 2015; Lovley, 2010). BET which facilitates wastewater treatment with simultaneous power generation has similar characteristics of both fuel cell and biological treatment process (Mishra et al., 2001; Huang et al., 2009; Mohana Krishna et al., 2010). Due to its inherent advantage of coupling the diverse processes, BET is emerging as a viable process for treating complex pollutants in various wastewaters viz., pharmaceutical, dairy, textile dye wastewaters, etc., (Venkata Mohan and Chandrasekhar, 2011; Velvizhi and Venkata Mohan, 2011; Vamsi Krishna et al., 2014). Integration of two multiple processes aids in achieving enhanced treatment efficiency, more specifically with complex wastewaters viz., petrochemical wastewater. Hence, by considering the advantage of both the processes discussed above, the present study is designed by integrating the SBR process with BET to achieve enhanced treatment efficiency of complex PCW. Initially, PCW treatment was evaluated by SBR process at two different microenvironments viz., aerobic and anoxic conditions and the resulting effluents of the two SBR outlets were fed into two BET systems to increase the treatment efficiency with simultaneous bioelectricity generation. The process performance of SBR and BET was evaluated with respect to COD and pollutants removal. In addition, the bio-electrochemical parameters viz., bioelectrogenic activity, TDS removal, polarization resistance and anode potential were also assessed for BET systems.

## 2. Methods

### 2.1. Petrochemical wastewater (PCW)

Real field petrochemical wastewater (PCW) was used in the present study. The effluent has high concentration of carbon load

(23,232 mg COD/l) and salt concentration (16,730 mg TDS/l) with low biodegradable nature (BOD<sub>5</sub>/COD: 0.36) [pH 12.4; nitrates 98 mg/l; phosphates 369 mg/l; sulfates 15.5 mg/l, TSS 23.5 mg/l]. Prior to usage, the effluent was stored at 4 °C. Before feeding, the pH of PCW was adjusted to 7.0 ± 0.2 using 0.1 N HCl.

### 2.2. Bioreactors

Two sequencing (periodic discontinuous) batch reactors (SBR/PDBR) were designed with a total volume of 1.1 l and interchangeable water volume of 0.99 l (diameter, 7.5 cm; length, 22.5 cm). SBR-aerobic reactor (SBR<sub>Ae</sub>) was operated by sparging air through pump. Single chambered BET systems were also fabricated with perspex material with a total/working volume of 1.2/1.0 l with a dimension of 14 × 11 × 4 cm (Venkata Mohan et al., 2013). BET was operated without membrane using non-catalyzed graphite plate as cathode (280 cm<sup>2</sup>) and stainless steel mesh as anode (280 cm<sup>2</sup>) with a distance of 3.5 cm. The anode was completely submerged in the anolyte and cathode was partially submerged (bottom portion) and top portion was exposed to atmospheric air. Proper provisions were made in design for feeding, decanting, recirculation and air supply operations.

### 2.3. Biocatalyst

The aerobic consortium procured from a full scale effluent treatment plant (ETP) was used as parent inoculum for both the bioreactors (SBR<sub>Ae</sub>/SBR<sub>Ax</sub>). In the case of bioelectrochemical treatment (BET) process, anaerobic consortium procured from a full scale anaerobic effluent treatment plant was used as parent inoculum. Prior to inoculation, the parent biomass was washed (5000 rpm, 20 °C) twice with phosphate buffer (50 mM) followed by enrichment in designed synthetic wastewater (DSW) [glucose: 3 g/l; NH<sub>4</sub>Cl: 0.50 g/l, KH<sub>2</sub>PO<sub>4</sub>: 0.25 g/l, K<sub>2</sub>HPO<sub>4</sub>: 0.25 g/l, MgCl<sub>2</sub>:0.30 g/l, CoCl<sub>2</sub>:25 mg/l, ZnCl<sub>2</sub>:11.50 mg/l, CuCl<sub>2</sub>:1: 0.50 mg/l, CaCl<sub>2</sub>:5 mg/l, MnCl<sub>2</sub>:15 mg/l, NiSO<sub>4</sub>:16 mg/l, FeCl<sub>3</sub>:25 mg/l] at required microenvironments.

### 2.4. Experimental design and operation

Experiments were designed by integrating SBR with BET to enhance the remediation of PCW. SBR operation was carried out in two different microenvironments, viz., aerobic (SBR<sub>Ae</sub>) and anoxic (SBR<sub>Ax</sub>) with an organic loading rate of 9.6 kg COD/m<sup>3</sup>-day with sequential operation comprised of 15 min of filling phase (FILL), 2820 min of react phase and recirculation (REACT) phase, 30 min of settling phase (SETTLE) and 15 min of decant phase (DECANT). During REACT phase of SBR<sub>Ae</sub> operation DO concentration was maintained (4 ± 1.5 mg/l) by sparging air. In SBR<sub>Ax</sub> air was sparged for 10 min for every 4 h of cycle period during REACT phase, by maintaining DO within 0.75 ± 0.25 mg/l (Venkata Mohan et al., 2013). The outlet of SBR reactors were subsequently fed into the two BET systems viz., BET<sub>Ae</sub> and BET<sub>Ax</sub>, with the respective OLR of 6.33 ± 0.56 kg COD/m<sup>3</sup>-day and 5.81 ± 0.47 kg COD/m<sup>3</sup>-day. Bioreactors were operated in suspended growth configuration with a cycle period (retention time) of 48 h at ambient room temperature.

### 2.5. Analysis

The process performance of all the bioreactors (SBR/BET) was assayed by evaluating the chemical oxygen demand (COD; 5220-C; closed-reflux (titrimetric) method), pH (4500-H+B) and TDS (2540 C) according to standard methods (APHA, 1998). Voltage and current were measured using a digital multimeter. Anode potential was measured with reference to Ag/AgCl (S) employing

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