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Anoxic bio-electrochemical system for treatment of complex chemical wastewater with simultaneous bioelectricity generation

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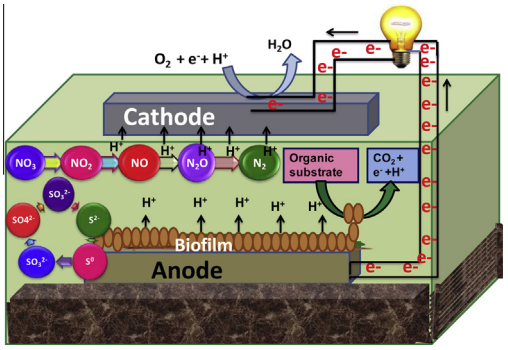
HIGHLIGHTS

- Novel anoxic BET system was developed in the absence of membrane.
- Effective multiple pollutant removal was observed in anoxic BET.
- In comparison with anoxic treatment, BET reported higher toxicity reduction.
- Anoxic BET showed higher bio-electrochemical behaviour than anoxic treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Bioelectrochemical treatment system (BET) with anoxic anodic microenvironment was studied with chemical wastewater (CW) in comparison with anoxic treatment (AxT, sequencing batch reactor (SBR)) with same parent anaerobic consortia. BET system documented relatively higher treatment efficiency at higher organic load (5.0 kg COD/m^3) accounting for COD removal efficiency of (90%) along with nitrate (48%), phosphate (51%), sulphates (68%), colour (63%) and turbidity (90%) removal, compared to AxT operation (COD, 47%; nitrate, 36%; phosphate, 32%; sulphate, 35%; colour, 45% and turbidity, 54%). The self-induced bio-potential developed due to the electrode assembly in BET resulted in effective treatment with simultaneous bioelectricity generation (631 mA/m^2). AxT operation showed persistent reduction behaviour, while simultaneous redox behaviour was observed with BET indicating balanced electron transfer. BET operation illustrated higher wastewater toxicity reduction compared to the AxT system which documents the variation in bio-electrocatalytic behaviour of same consortia under different microenvironment.

1. Introduction

The function of microorganisms depends on the microenvironment in which they reside. In anaerobic treatment processes, the electrons and protons generated through substrate metabolism get reduced in the presence of terminal electron acceptors viz., nitrates, nitrites, phosphates sulphates, etc. by forming methane, carbon dioxide, hydrogen, hydrogen sulphide, ammonia, etc. (Pham et al., 2006). On the contrary, if electrode-membrane assembly is provided in a microbial fuel cell (MFC) under anaerobic condition, the electrons and protons get discharged to solid external electrode with the help of mediators and membrane-bound organelles. This creates an *in situ* bio-potential which can be used to harvest bioelectricity (Logan et al., 2006; Venkata Mohan et al., 2009). MFC is a biologically catalyzed bio-electrochemical system which facilitates direct conversion of chemical energy to electrical energy through a cascade of redox reactions (Venkata Mohan et al., 2013a). Bioelectrochemical treatment (BET) is a hybrid system

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which couples biological and electrochemical processes in a defined fuel cell type setup. Due to its inherent advantage of coupling the diverse processes, BET is emerging as a able process for treating complex pollutants in wastewaters (Rabaey et al., 2006a,b; Virdis et al., 2008; Mu et al., 2009; Dutta et al., 2009; Clauwaert et al., 2007; Venkata Mohan et al., 2009; 2010; Logan, 2010). BET which facilitates wastewater treatment with simultaneous power generation has similar characteristics of both fuel cell and biological treatment process.

Conventional wastewater treatment technologies require additional conversion processes to harness various forms of energy from wastewater. While in case of BET, the electrical energy can be directly retrieved without any further process conversion and treating wastewater is not energy consuming instead, it offers an added advantage of energy generation (Venkata Mohan et al., 2010; Ledezma et al., 2013; Mohanakrishna et al., 2010; Velvizhi and Venkata Mohan, 2013). Typically, BET consists of an anode and cathode chamber separated by a proton exchange membrane (PEM) in a dual assembly configuration whereas in a single assembly configuration the anode and cathode are sandwiched with PEM in a single compartment. The presence of membrane might limit the applicability of BET in full scale operation due its economic concerns (Liu and Logan, 2004; Jang et al., 2004; Ghangrekar and Shinde, 2007; Zhang et al., 2011; Zhu et al., 2011). In the present study, a bioelectrochemical treatment (BET) system without membrane was designed and operated under anoxic condition with chemical wastewater (CW). Chemical wastewaters are relatively complex due to the presence of soluble organic materials, inorganic chemicals, priority pollutants, heavy metals, toxic organics, refractory substances, volatile matter, colour, etc., (Venkata Mohan et al., 2001). Anoxic microenvironment facilitates the flexibility of operating the system with wastewater hence the anodic microenvironment was maintained under microaerophilic conditions. Anoxic microenvironment in anodic chamber of single chambered MFC showed relatively good bio-electrogenic activity compared to anaerobic operation (Venkata Mohan et al., 2008a). Anoxic treatment system (AxT), more precisely a sequencing batch reactor (SBR) was operated simultaneously without an electrode assembly. This helps in understanding the functional role of electrodes as electron acceptor in the treatment process. Both the systems were inoculated with same parent anaerobic consortia to study the relative influence of microenvironment. The performance of BET system was evaluated at four substrate loads of CW and the process was monitored based on substrate degradation and multi-pollutant removal viz., nitrates, phosphates sulphates, colour and turbidity.

2. Methods

2.1. BET construction

The anoxic-BET system was fabricated using perspex material [27 × 18.6 × 12.5 cm (L/B ratio = 1.5)] with a total designed volume of 6 l and working volume of 2.5 l (Fig. 1). The reactor was designed such that more than 50% of the reactor volume was packed with different layers of gravel bed. Coarse and medium gravels were packed at height of 2.0 cm and fine gravel was packed to 1.2 cm height. The top layer of fine gravel was covered by sand (0.3 cm) with an effective size (D_{10}) of 0.35–0.55 mm and uniformity coefficient (D_{60}/D_{10}) of 1.2–1.8. Non-catalyzed graphite electrodes (7 × 3.5 cm; 0.6 cm thick; 61.6 cm^2 surface area) were arranged as anode on the top layer of the gravel bed and similar-sized electrode (cathode) was placed at a distance of 4.2 cm from the anode. The top portion of cathode was exposed to open-air while its bottom portion was submerged in the wastewater (anolyte). Anoxic treatment system (AxT) was fabricated using perspex material similar to BET without electrode assembly. To evaluate the influence on bio-electrogenesis on wastewater treatment.

2.2. Anaerobic consortia

Prior to start-up both the systems under study were inoculated with same parent consortia to study the relative influence of reactor microenvironment on process variation. The consortia were collected from a local municipal wastewater treatment plant. The parent biomass was washed twice with phosphate buffer saline (PBS) and re-suspended in DSW (chemical oxygen demand (COD) of 3 g/l) overnight at 28 °C. The overnight grown culture was inoculated to the respective bioreactors by re-suspending through feed (VSS, 4870 mg/l).

2.3. Experimental details

Both BET and AxT systems were initially operated with designed synthetic wastewater (DSW) at OL of 1.2 kg COD/m^3 for 10 cycles (5 days per cycle). Subsequent to stabilized performance, the feed was replaced with real field chemical wastewater (CW) [pH, 7.45 ± 5; colour, 1200 ± 10 HU; turbidity, 235 ± 5 NTU; chemical oxygen demand (COD), 12,000 ± 10 mg/l; biochemical oxygen demand (BOD_3), 4000 ± 10 mg/l; phosphates (as PO_4^{3-}), 230 ± 8 mg/l and nitrates (as NO_3^{2-}) 400 ± 7 mg/l]. Performance of both the systems was evaluated at four incremental organic loads (OL) of CW at respective hydraulic retention time (HRT) (OL1, 1.25 kg COD/m^3, 10 days; OL2, 2.5 kg COD/m^3, 16 days; OL3, 3.75 kg COD/m^3, 22 days and OL4, 5.00 kg COD/m^3 and 28 days). Systems were operated with each OL's for three cycles. The required OL of CW was adjusted by diluting with tap water prior to feeding. Before feeding, the pH of feed was adjusted to 7 using concentrated orthophosphoric acid (88%).

2.4. Analysis

The performance of BET system was assessed by monitoring chemical oxygen demand (COD; 5220-C), colour (2120-B), sulphates (4500-E), nitrates (4500-B), phosphates (4500-D), pH (4500-H^+B) and turbidity (2130-B) as per the procedures outlined in the Standard Methods (APHA, 1998). Coulombic efficiency (CE) was calculated based on relation CE = CP/CT × 100%, where CP is the theoretical coulombs calculated by integrating the current as CP = $\int Idt$ and CT was calculated as CT = $FbV\Delta COD/M$, where F, b, V, ΔCOD and M are Faraday's constant (96,485 C/mol of electrons), number of moles of electrons produced per mol of substrate (b = 4), liquid volume (l), COD concentration difference (g/l) and molecular weight of the substrate (M = 32) respectively (Kaewkannetra et al., 2011; Oh et al., 2004; Moon et al., 2006).

Voltage and current were measured using a digital multi-meter at 100 Ω resistance. Anode potential was measured with reference to Ag/AgCl using working electrode as anode at varying resistor (30–0.05 kΩ). Cyclic voltammetry (CV) was used to study the bioelectrochemical behaviour of the biocatalyst during the stabilized phase of operation using a potentiostat–galvanostat system via applying a potential ramp (+0.5 to −0.5 V) (Autolab-PGSTAT12, Ecochemie). All the assays performed in the BET were done considering the anode (graphite) as working electrode and cathode (graphite) as counter electrode against reference electrode (Ag/AgCl). In AxT system, two graphite electrodes (anode and cathode) along with Ag/AgCl electrode (reference) were placed only during the electrochemical analysis.

2.5. Toxicity

Toxicity tests were performed for inlet and outlet samples for both BET and AxT systems using Zebra fish (*Brachydanio rerio*) as