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Cathodic material effect on electron acceptance towards bioelectricity generation and wastewater treatment

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ABSTRACT

Influence of cathode material on electron accepting conditions during the treatment of recalcitrant pharmaceutical wastewater (PWW) was comparatively evaluated at different organic loads (3, 6, 9 and 15 g/l) in three bioreactors. Two bio-electrochemical treatment systems employed with different electrode materials viz., BET-SS (graphite as anode and stainless steel (SS) as cathode) and BET-G (graphite as both anode and cathode) were evaluated for PWW degradation and bioelectricity generation in comparison to conventional anaerobic treatment (AnT). BET-G exhibited high bioelectrogenic activity than BET-SS, elucidating the impact of varied cathode material. High cathode potential necessary for effective reduction at cathode were observed with graphite-cathode than SS-cathode which are crucial for treatment and power generation. Ohmic losses ascribed to electrode material interference were relatively high in BET-SS in comparison to BET-G. Graphite-cathode exhibited high electron acceptance conditions leading to higher pollutant removal along with organic fraction degradation, bioelectrogenesis and inorganic salts removal, when compared to SS-cathode. Placement of electrode assembly while operating BET with different electrode materials is proved to be significant for treatment and bioelectricity production. Efficient electron accepting conditions and high cathode potential in BET-G proved graphite as promising cathode material over SS for the treatment of PWW.

1. Introduction

Pharmaceutical wastewater (PWW) discharged from bulk drug manufacturing industries is composed of a wide range of complex pollutants, organic compounds and high concentrations of inorganic salts, which cannot be discharged into the environment prior to treatment. However, treatment of PWW is a challenging task. Various conventional methods viz., physical, chemical, biological and advanced membrane based bioreactor treatment have been widely used for the treatment of pharmaceutical wastewaters [1–3]. Biodegradation of recalcitrant PWW using these conventional treatment technologies can occur only up to a certain extent, mandating the need to enhance treatment efficiency [3]. Bio-electrochemical treatment systems (BET) which originated from microbial fuel cells (MFCs) have showed promise in enhancing the treatment efficiency of complex wastewaters viz., diary, distillery, pharmaceutical, petrochemical etc. [4,5]. BET systems find their application in generating bio-electricity with simultaneous treatment of various wastewaters upon utilization of organic fraction [6–13]. BET system is characterized by the presence of electrode assembly comprising of an anode and cathode necessary for carrying out oxidation and reduction reactions. The redox reactions which determine the treatment/energy recovery are dependent on the individual half cell potentials (anode and cathode) [14,15]. These half cell potentials of BET are necessarily dependent on the electrode materials that the anode and cathode are made of. The nature, strength, surface properties, design, conductivity, hardness, anti-corrosive property, biocompatibility with wastewater etc. of the electrode material significantly affects the treatment as well as the power generation capability of a system [16].

Progress has been made in BET on the usage of anode electrode materials (graphite, carbon cloth, carbon felt, stainless steel mesh, brass, nickel, etc.) for the oxidation of the substrate associated with power generation as well as treatment [17–20]. Relatively, less progress has been made on cathode electrode materials viz., graphite, platinum, activated carbon etc. for reduction reactions [21–24]. Though anode tends to form biofilm that degrades the organic fraction, the fate of reducing equivalents subsequently generated via anodic oxidation need to be reduced by cathode [16].

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The fate of reduction reactions depends on the efficiency of cathode material that drives the reducing equivalents from anode to cathode for achieving the reduction of complex pollutants accompanied by power generation in BET systems [25]. The development of biopotential necessary for bio-electrochemical redox reactions in degrading high complex wastes viz., PWW essentially is governed by the combination of anode and cathode material along with the electrodes biocompatibility with wastewater [26,27].

Considering the importance of cathode electrode materials on reduction reactions towards treatment and bioelectricity generation, the present study is designed and executed as follows. Two bio-electrochemical systems employed with similar anode and different cathode electrode material configurations were studied to evaluate the impact of cathode electrode materials on the reduction/degradation of high strength PWW and power generation. Influence of cathode potential and capability of stainless steel and graphite as cathode electrode materials were evaluated in terms of substrate degradation, inorganic total dissolved salts and nutrients removal along with bio-electrogenesis. Variation in treatment efficiency with different electrode configured BET systems was evaluated in comparison to conventional anaerobic treatment (AnT) which lacks the electrode assembly.

2. Materials and methods

2.1. Electrode materials and bioreactor assembly

Two bio-electrocatalyzed systems (BET-G: non-catalyzed graphite as both anode and cathode anode material; BET-SS: graphite as anode and stainless steel (SS) as cathode material) in comparison to a non-electrocatalyzed bioreactor (AnT) were designed and fabricated using perspex material with a total/working volume of 2.6/2.2 L to evaluate the treatment of PWW. Equal dimensions of both anode and cathode (15 × 5 cm; 3 cm thick; 15 × 3 cm) with a surface area of 0.28 cm^2 were taken for both the BET reactors. Copper wires were used to establish contact between electrodes by sealing the contact with 'epoxy' material. Anode was completely submerged in the wastewater, whereas top portion of cathode was exposed to air. Provisions were made in all the reactors for sample port, wire point inputs, inlet, outlet and feed change. Care was taken in the design to maintain anaerobic conditions in the three bioreactors throughout the operation.

2.2. Pharmaceutical wastewater

Real field pharmaceutical wastewater (PWW) was acquired from pharmaceutical industry to evaluate its remediation during the bio-electrochemical treatment process in comparison to the anaerobic treatment. PWW obtained was characterized that consists of pH (6.34), ORP (38 mV), total chemical oxygen demand (COD-15120 mg/l), total dissolved solids (TDS- 5098 mg/l), Colour (1255 Hazen units), nitrates (3.47 mg/l), sulphates (19.62 mg/l), phosphates (314 mg/l), VFA (1917 mg/l) and suspended solids (335 mg/l).

2.3. Biocatalyst

An indigenous anaerobic consortium acquired from a full scale anaerobic reactor treating composite chemical wastewater was used as biocatalyst. The inoculum was washed thrice with buffer to eliminate the interfering particles and the resulting bacterial consortia was enriched in synthetic wastewater (SWW) [Glucose-3.0 g/l, NH_4Cl-0.50 g/l, KH_2PO_4-0.25 g/l,K_2HPO_4-0.25 g/l, $MgCl_2$-0.30 g/l, $CoCl_2$-25 mg/l, $ZnCl_2$- 11.50 mg/l, $CuCl_2$-10.50 mg/l, $CaCl_2$-5 mg/l, $MnCl_2$-15 mg/l,$NiSO_4$-16 mg/l, $FeCl_3$-25 mg/l]. All the three reactors viz., BET-G, BET-SS and AnT were inoculated with the same biocatalyst to comparatively evaluate the reactors performance under variable operating conditions.

2.4. Experimental methodology

Treatment of PWW was comparatively evaluated in BET-SS, BET-G and AnT. Initially, all the three reactors were operated with SWW under anaerobic microenvironment for acclimatization of bacteria to wastewater environment. After attaining stable COD removal (glucose as substrate), reactors were fed with PWW to evaluate the treatment efficiency. Reactors were operated under varying organic loadings viz., OL1, 3 g/l; OL2, 6 g/l; OL3, 9 g/l; OL4, 15 g/l and the required OL of PWW was adjusted by diluting the crude effluent with tap water. All the reactors were operated in batch mode with a hydraulic retention time (HRT) of 48 h (one cycle length), consisting of 15 min of FILL, 47 h of REACT, 30 min of SETTLE and 15 min of DECANT phases. Wastewater during REACT phase was circulated in a closed loop to achieve homogeneous distribution of the substrate and consortia along the reactor depth using peristaltic pump at a flow rate of 100 ml/min. Settled biomass (10%) was retained after every feeding cycle. The influent pH of the wastewater was adjusted to 7 using either orthophosphoric acid (88%) or 1 M NaOH. After feeding the wastewater, head-space of the reactor was sparged with oxygen free nitrogen gas for 2 min to ensure that complete anaerobic microenvironment was maintained.

2.5. Process monitoring

The influence of cathodic material on treatment of PWW in both the BET reactors in comparison with AnT system was evaluated by monitoring chemical oxygen demand (COD) (closed-reflux method), TDS, sulphates, nitrates, phosphates, pH and VFA according to standard methods [28]. Decrement in bioelectrogenic activity and COD removal are considered as indicators to feed change. BET-G and BET-SS systems were monitored for bioelectricity and voltage generation. Potential difference (V) and current (I) (100 Ω) measurements were recorded by a digital multimeter. Polarization, anode and cathode potential measurements were carried out at wide range of resistances viz., 30 kΩ to 100 Ω. Current and power densities were derived from polarization profiles for both the systems to evaluate the efficiency of reactors as fuel cells. Cyclic voltammetry (CV) was used to study the bioelectrochemical behaviour of biocatalyst in both systems during stabilized phase of operation using potentiostat-galvanostat system (Autolab-PGSTAT12, Ecochemie). Voltammograms were recorded by applying a potential ramp (+0.50 to −0.50 V) at a scan rate of 30 mV/s to study the electron transfer mechanism of the biocatalyst. All the assays were performed in BET considering anode as working electrode and cathode as counter electrode against reference electrode (Ag−AgCl(S)) while in the AnT systems, two graphite electrodes (as both anode and cathode) along with Ag−AgCl electrode (reference) were placed, only during bioelectrochemical analysis.

3. Results and discussion

3.1. Bio-electrochemical performance

3.1.1. Bioelectricity generation

BET-SS, BET-G and AnT were operated with real field PWW at varying organic loadings (OL) viz., OL1: 3 g/l, OL2: 6 g/l, OL3: 9 g/l and OL4: 15 g/l COD. Influence of cathode electrode material on both power generation as well as treatment efficiency was comparatively evaluated in both BET reactors. Significant variation