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Hythane ($H_2 + CH_4$) production from petrochemical wastewater containing mono-ethylene glycol via stepped anaerobic baffled reactor

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ABSTRACT

Hythane ($H_2 + CH_4$) production from petrochemical wastewater containing mono-ethylene glycol (MEG) via a novel stepped anaerobic baffled (SAB) reactor was investigated. The reactor was continuously operated for five months at constant hydraulic retention time (HRT) of 72 h and different organic loading rates (OLRs) of 0.33, 0.67 and 1.67 gCOD l^{-1} d^{-1}. The maximum H_2 yield of 359.01 ± 33.46 ml H_2 $gCOD^{-1}_{removed}$ and H_2 production rate of 5.12 ± 0.48 l d^{-1} were obtained at OLR of 1.67 gCOD l^{-1} d^{-1}. Nevertheless, the maximum methane yield of 159.11 ± 14.72 ml CH_4 $gCOD^{-1}_{removed}$ and methane production rate of 2.48 ± 0.22 l d^{-1} were recorded at OLR of 0.67 gCOD l^{-1} d^{-1}. The maximum CH_4 and H_2 content of 52.08 and 49.84% were achieved at OLR of 0.33 and 1.67 gCOD l^{-1} d^{-1}, respectively. Compartment-wise hythane profiles were assessed to optimize the production rate. Microbial community analysis was conducted and showed the dominant bacteria of *Proteobacteria* (44.3%), *Firmicutes* (28.9%), *Chloroflexi* (8.9%), *Actinobacteria* (5.7%), and *Bacteroidetes* (5.6%).

1. Introduction

Waste-to-energy concept has become a vital key as sustainable energy source, where biodegradable organic wastes are converted by microorganisms to bio-energy forms (hydrogen and/or methane) (Dincer, 2007; Ratanatamskul et al., 2015). In this context, as recently reported (EIA, 2015), Egypt is the largest consumer of oil and natural gas in Africa, with only 4% of the total energy consumption from renewable resources (mainly hydroelectric). No considerable records for producing energy using biomass were reported in Egypt. Moreover, Egypt is now among the top ten countries that subsidizes fossil fuels for the local customers, that makes the problem increasing with a direct effect on the national income. Meanwhile, it was found that one of the most environmental problems in Egypt is the discharging of petrochemical industry wastewater into Mediterranean Sea and/or sewer network. It has become substantial to eliminate dangerous pollutants away from these effluents using cost effective and sustainable processes. Many of these end-pipe industries' effluents are rich with mono-ethylene glycol (MEG), which has serious effects on environment and human health such as brain, nervous system, joints and eye damages (Leth and Gregersen, 2005). Mostly, the polyester industries have a special interest because of the use of MEG as raw material; moreover, this petrochemical industry has a great portion of the global exports in Egypt (more than 70% of the production).

Several treatment methods such as photo-catalytic and direct oxidation, nano-filtration, vacuum membrane distillation and aerobic biological treatment, have been investigated for the degradation of the petrochemical wastewater containing MEG (Zerva et al., 2003; Mohammadi and Akbarabadi, 2005; Orecki et al., 2006; Kim and Hoffmann, 2008). Hassani et al. (2013) found that the COD removal of 95.1 and 60.7% were achieved at influent MEG concentrations of 1000 and 3000 mgCOD l^{-1}, respectively; using moving bed biofilm reactor (MBBR). The sequencing batch reactor (SBR) was investigated by Shakerkhatibi et al. (2013) using MEG-based synthetic wastewater, resulting in COD removal efficiency between 83.5 and 79.5%, when MEG initial concentrations were varied from 500 to 3000 mgCOD l^{-1}. These aerobic technologies

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still face serious economic problems such as; intensive energy consumption and operational problems with high excess sludge production. Therefore, alternative low cost technologies for bio-energy production and treatment of petrochemical wastewaters have become essential for low income countries like Egypt.

The anaerobic fermentation processes of industrial wastewater are globally preferred nowadays. It has several advantages such as; design simplicity, easy operation, low level of excess sludge, sufficient efficiency, useful by-products and low capital, operation and maintenance costs (Hassan and Dahlan, 2014). Moreover, various anaerobic technologies have been studied for the treatment of medium and high strength industrial effluents (Ghaniyari-Benis et al., 2010; Li et al., 2015). Recently, researchers concentrated on improving the production of bio-hydrogen/methane from the anaerobic digestion, especially due to the rising in energy demand and rapid exhaustion of non-renewable fossil fuel (Tawfik and Salem, 2014; Elsamadony et al., 2015b). Marin et al. (2010) found that 75% COD removal and an average methane production of 0.3 l CH_4 $gCOD^{-1}_{removed}$ were achieved from the anaerobic degradation of the diluted aircraft de-icing fluid (ADF) containing MEG at 33 °C. A pilot-scale anaerobic fluidized bed reactor was successfully used for treatment of propylene glycol (PG) based deicing wastewaters (95% COD removal efficiency) (Komisar et al., 1998). Treatment of ADF wastewater (with initial COD of 5, 10 and 20 g l^{-1}) using up-flow anaerobic sludge blanket (UASB), was investigated by Darlington and Kennedy (1998). The COD removal efficiencies were varied from 85 to 98% at OLR not exceeding 10 gCOD l^{-1} d^{-1}.

Hythane production, consisting of bio-hydrogen and bio-methane, via two fermentation stages connected in series, is a potential high-value solution for the valorization of industrial effluents (Liu et al., 2013). Stepped anaerobic baffled (SAB) reactor has been used in this investigation for hythane ($H_2 + CH_4$) production from petrochemical wastewater containing mono-ethylene glycol. The reactor is similar to the classical anaerobic baffled reactor (ABR); however, each compartment in SAB system has different volume to eliminate the shock loads effects and perform a uniform OLR distribution along the reactor length. The reactor combines the benefits of using up-flow anaerobic sludge blanket (UASB) reactor, and anaerobic baffled reactor (ABR) while minimizing their limitations. Each compartment of the reactor represented as one UASB reactor where the sludge accumulates gradually in the reactor, creating different solids residence times (SRTs) and sufficient contact time between the substrate and the anaerobic consortium bacteria. The separation of different anaerobic consortia, producing bio-ethanol, hydrogen and methane, can be developed in the reactor. However, the type of bio-energy production is mainly affected by operational conditions i.e. OLR, HRT, temperature, etc. The aims of this study are to (1) assess the efficiency of stepped anaerobic baffled (SAB) reactor for bio-hythane ($H_2 + CH_4$) production from petrochemical wastewater industry containing MEG, (2) investigate the effect of organic loading rate (OLR) on the bio-hythane production, (3) determine a reliable kinetic model to describe the SAB reactor performance, and (4) identify the microbial community responsible for bio-hythane production.

2. Materials and methods

2.1. Seed sludge and synthetic wastewater

Mixed culture bacteria, which were used as inoculum in this study, were collected from the sludge gravity thickener of a domestic wastewater treatment plant located in Alexandria, Egypt. The harvested sludge was allowed to be settled for 24 h, and then the supernatant was removed. The inoculum sludge was daily supplemented with wastewater and kept under anaerobic conditions for two weeks. The average pH, total solids (TS) and volatile solids (VS) of the sludge were 7.2, 41.8 g l^{-1} and 24.6 g l^{-1}, respectively. The SAB reactor was inoculated with 16 l of sludge which represented 50% of the total reactor volume. The reactor was continuously fed with synthetic petrochemical wastewater containing mono-ethylene glycol ($C_2H_6O_2$). Ammonium chloride (NH_4CL) as nitrogen source and potassium dihydrogen phosphate (KH_2PO_4) as phosphorus source, were regularly added as nutrients to meet COD:N:P ratio of 400:7:1 (Wahab et al., 2014). The synthetic wastewater was prepared every 2 days using tap water. The feed was supplemented with the following buffer and trace elements (mg l^{-1}): $NaHCO_3$, 326; $CoC1_2 \cdot 6H_2O$, 1.2; $FeC1_3$, 5.0; $CuSO_4 \cdot 5H_2O$, 5.0; $MgSO_4 \cdot 7H_2O$, 39.0; $MnSO_4 \cdot 4H_2O$, 13.9; $CaCl_2 \cdot 2H_2O$, 36.8; $ZnC1_2$, 5.0 (Gopala Krishna et al., 2008).

2.2. Experimental setup and operational conditions

Fig. 1 shows a schematic diagram of the stepped anaerobic baffled (SAB) reactor used in this study. The working volume of the reactor was 32 l, consisting of five graded compartments ended with settler for excess sludge removal. The reactor compartments were separated using intermediate baffles to increase the contact time between the bacterial community and the substrate. Interestingly, the stepped configuration, as depicted in Fig. 1, was investigated by a total of 33% reduction in volume between the first and last compartment, to eliminate the variation of both internal OLRs and food-to-microorganisms ratios (F/M) along the SAB reactor length. The reactor total dimensions were 83.5 cm in length, 15.6 cm in width, and 44 cm in height. The reactor was manufactured from Perspex material and was continuously fed with wastewater using peristaltic pump (Masterflex – USA, Cole–Parmer Instrument Company). The reactor was operated at constant flow rate of 10.5 l d^{-1} and HRT of 72 h at ambient temperature (21 ± 6 °C). The OLR was increased from 0.33 to 0.67 and then to 1.67 gCOD l^{-1} d^{-1} (Table 1). Furthermore, Table 1 shows the SAB compartments' dimensions, volumes and HRTs in addition to the initial F/M ratios.

2.3. Analytical methods

Samples from the influent and the treated effluent were collected three times a week for analysis of chemical oxygen demand (COD), ammonium nitrogen (NH_4–N), total volatile fatty acids (TVFAs). All analyses were carried out according to the APHA (APHA, 2005). Analysis of ethanol (EtOH) and VFAs in terms of acetate (HAc), butyrate (HBu) and propionate (HPr) were performed by high performance liquid chromatography (LC-10AD, Shimadzu, Japan). The temperature of the column oven was 40 °C. A mobile phase of 4 mM H_2SO_4 was considered with flow rate of 0.5 ml min^{-1} for 22 min followed by 0.4 ml min^{-1} for 8 min. During the study period; the produced gas was measured using wet gas meter. The gas compositions (H_2, CH_4 and CO_2) were analyzed by a gas chromatography (GC, Agilent 4890D) with a thermal conductivity detector (TCD) and a 2.0 m stainless column packed with Porapak TDS201 (60/80 mesh). The used carrier gas was Helium, with flow rate of 25 ml min^{-1}. The HPLC and GC analysis procedures were conducted as described earlier by Nasr et al. (2014b) and Elsamadony et al. (2015a). In addition, physico–chemical parameters were also analyzed for each compartment of the reactor at each operational condition's steady state. All measurements were performed in triplicates and average values were presented. Analysis of both liquid and gas samples was recorded (mean ± standard deviation) during steady state operation. In addition, statistical analysis using paired student's t-test was conducted to check the differences significance at a *P*-value less than 0.05 level.