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Pathways of 3-biofules (hydrogen, ethanol and methane) production from petrochemical industry wastewater via anaerobic packed bed baffled reactor inoculated with mixed culture bacteria

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ABSTRACT

Simultaneous production of 3-biofuels (hydrogen, ethanol and methane) as by-products of the biodegradation of petrochemical wastewater containing MEG via anaerobic packed bed baffled reactor (AnPBBR), was extensively investigated. A four-chambered reactor supported by polyurethane sheets, was operated at a constant hydraulic retention time (HRT) of 36 h and different organic loading rates (OLRs) of 0.67, 1, 2 and 4 gCOD/L/d. The maximum specific H_2 and CH_4 production rates of 438.07 ± 43.02 and 237.80 ± 21.67 ml/L/d were respectively achieved at OLR of 4 gCOD/L/d. The residual bio-ethanol significantly increased from 57.15 ± 2.31 to 240.19 ± 34.69 mg/L at increasing the OLR from 0.67 to 4 gCOD/L/d, respectively. The maximum MEG biodegradability of 98% was attained at the lowest OLR. Compartment-wise profiles revealed that the maximum H_2 and ethanol production were achieved at HRT of 9 h (1st compartment), while the CH_4 production was peaked at HRTs of 27 and 36 h (last two compartments). Kinetic studies using Stover–Kincannon and completely stirred tank reactor (CSTR) in series models were successfully applied to the AnPBBR overall and compartment-to-compartment performance, respectively. The economic evaluation strongly revealed the potentials of using AnPBBR for simultaneous treatment and bio-energy production from petrochemical wastewater as compared to the classical anaerobic baffled reactor (ABR). Microbial analysis using Illumina MiSeq sequencing showed a diversity of bacterial community in AnPBBR. *Proteobacteria* (36.62%), *Firmicutes* (20.85%) and *Bacteroidetes* (3.44%) were the most dominant phyla.

1. Introduction

The global industrial development, during last decades, caused depletion of fossil fuel reserves, which states essential concerns regarding sustainability [1]. Anaerobic digestion has been well considered as a promising solution for biofuels (hydrogen, ethanol and methane) production from degradation of wastewater containing biodegradable organics [2,3]. Regarding the industrial effluents, one of the basic compounds in the petrochemical industries is ethylene with global demand about 115 million tons per year. Among the ethylene derivatives, mono-ethylene glycol (MEG) has the highest demand, which is forecast to be increased from 18.93 million tons in 2009 to 34.09 million tons in 2020 [4]. MEG is the main ingredient in the production of polyester fibers and film, polyethylene terephthalate (PET) resins, engine coolants and deicing fluids for airplanes and runway deicers [5]. Furthermore, MEG is widely used as antifreeze, as well as a dewatering agent in the natural gas industry, also with respect to the industry to generate MEG. Huge amounts of industrial wastewater containing MEG (500–7000 m^3/d) are generated in Egypt, which negatively affect on the environment and undoubtedly contaminate the surface water streams. Hence, an affordable and sustainable solution for valorization of the petrochemical wastewater is urgently required.

Nano-filtration, vacuum membrane distillation and photocatalytic and direct oxidation have been investigated for the treatment of MEG contaminated wastewaters [6–8]. However, these technologies still face economic and environmental drawbacks for the treatment of huge flow rates of industrial wastewater. Concerning the biological treatment strategies, the anaerobic processes have several advantages over the aerobic systems, such as

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the low capital and operating cost, low excess sludge production, design simplicity, easy operation, application of high organic loading rates and bio-energy production in the form of hydrogen, ethanol and methane [9–11]. Formerly, Marin et al. [12] found that the anaerobic baffled reactor (ABR) achieved a COD removal efficiency of 75% while treating aircraft de-icing fluid (ADF) wastewater containing MEG at 33 °C. A higher COD removal of 85–98% was registered at an OLR exceeding 10 gCOD/L/d in an up-flow anaerobic sludge blanket (UASB) reactor [13]. Komisar et al. [14] used a pilot-scale anaerobic fluidized bed reactor for treatment of ADF wastewater based on propylene glycol and 95% COD removal efficiency was attained at 33 °C. Meanwhile, the anaerobic degradation of petrochemical wastewater containing MEG for biofuels production at ambient temperature has not yet been investigated; whereas, it would reduce significantly the costs incurred during mesophilic and thermophilic operations [15,16]. This is of special concern since Egypt is a subtropical country with an average low-to-high ambient temperature of (9.5–17 °C) to (23–32 °C) during winter and summertime, respectively on the northern coast. Moreover, the weather changes very much farther in the interior and south where average temperatures easily soar over 40 °C during summer time.

The anaerobic metabolism of MEG follows the path of producing sequentially ethanol, hydrogen, and methane as the final by-product [17]. So far, 3-biofuels (hydrogen, ethanol and methane) production from petrochemical industry wastewater containing MEG was not extensively investigated, especially using a developed anaerobic packed bed baffled reactor (AnPBBR). These beneficial by-products increased the interest to separate and optimize their related phases to achieve the desired incentive for the manufacturers to apply such technology for simultaneous wastewater treatment and bio-energy production. Furthermore, the bio-ethanol generation pathways from disaccharides, from starches, and from lignocellulosic biomass have been well investigated [18,19]; whereas, its pathway through the anaerobic decomposition of MEG contaminated wastewaters, should be examined. From this perspective, the ABR as a series of UASB reactors was recommended. Various packing materials such as glass, peat, powdered minerals, natural zeolite and expanded clay, polystyrene sheets, recycled polyethylene, fibrous carriers and porous ceramic material have been examined in the anaerobic systems [20–23]. Among the aforementioned carrier materials, the polyurethane foam (PU) showed high applicability because of its high surface area, low cost, low toxicity, reuse possibility, flexibility for scaling up and good mechanical resistance [24,25]. To the best of our knowledge, polyurethane foam (PU) foam has been successfully investigated for treatment of a wide range of industrial effluents in anaerobic systems [24,26]. However, using PU as packing bed media, in the ABR configuration has not been yet studied, particularly for simultaneous treatment and bio-energy production from the petrochemical wastewaters.

Therefore, the main objectives of this study are to: (1) assess the performance of anaerobic packed bed baffled reactor (AnPBBR) for conversion of petrochemical wastewater containing MEG into affordable 3-bio (hydrogen, ethanol and methane) at different OLRs, at ambient temperature, with emphasis on the metabolite products, (2) investigate the pathway of the 3-bio (hydrogen, ethanol and methane) production through the AnPBBR compartments, (3) determine the appropriate kinetic coefficients to fit the AnPBBR outputs for both the overall and compartment-to-compartment performance, (4) identify the adapted microbial community responsible for the degradation of MEG and (5) highlight the economic benefits of using AnPBBR compared to the classical ABR treating petrochemical wastewater.

2. Materials and methods

2.1. Seed sludge and feed composition

The anaerobic packed bed baffled reactor (AnPBBR) was inoculated with mixed culture bacteria harvested from the thickener of sewage treatment plant situated in Al-Agamy, Alexandria, Egypt. The sludge was initially screened (<2 mm, sieve) in order to remove the large particles and debris. The pH, total solids (TS) and volatile solids (VS) of the sludge were 7.09 ± 0.17, 32.98 ± 0.93 g/L and 22.35 ± 0.66 g/L, respectively. The AnPBBR was inoculated uniformly with mixed culture bacteria with VS concentration up to 15.48 g/L. Among the petrochemical industries, the polyethylene terephthalate (PET) polyester, ethylene glycol/oxide industries and the coolant liquid discharges showed that MEG was the sole contaminant, with trace amounts of aldehydes (<0.5%) [27–30]. In accordance, these effluents were characterized as odorless and colorless liquid with a COD range from 500 to 30,000 mg/L; negligible amounts of suspended solids and less than 1–2 mg/L of TKN, NH_4-N and PO_4-P. As a result, synthetic wastewater, maintaining different OLRs based on MEG contamination, was efficiently proposed in this study in order to assess the AnPBBR performance under a controlled environment. Moreover, several studies to deal with such effluents were conducted using synthetic wastewaters supplemented with different MEG concentrations [29,31–33]. Hence, the reactor was continuously fed with synthetic petrochemical wastewater containing different concentrations of MEG ($C_2H_6O_2$). Nutrients addition, using ammonium chloride (NH_4CL) and potassium dihydrogen phosphate (KH_2PO_4), was adjusted to obtain a COD/N/P ratio of 400/7/1 [34,35]. The synthetic feed was prepared and diluted with tap water every 2 days from a preserved stock solution. The buffer and trace elements concentrations that supplemented to the feed were as follow (mg/L) [36]: $NaHCO_3$, 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.

2.2. Reactor configuration, operation and packing media

Fig. 1 shows a schematic diagram of the anaerobic packed bed baffled reactor (AnPBBR) used in this investigation. The working volume of the reactor was 15 L and consisted of four identical compartments (1st, 2nd, 3rd and 4th compartment). The compartments of the reactor were separated using intermediate baffles to increase the contact time between the anaerobic bacterial community and the substrate. The total dimensions of the reactor were 55 cm in length, 14.2 cm in width, and 27 cm in height. The working dimensions for each compartment are 13 × 13 × 22.5 cm. The AnPBBR was manufactured from Perspex material and was continuously supplied with synthetic petrochemical wastewater using a peristaltic pump (Masterflex – USA, Cole-Parmer Instrument Company). Polyurethane (PU) foam sheets were used as packing bed media in the reactor. The PU sheets were distributed uniformly in each compartment of the reactor and their dimensions and characteristics are shown in Table 1. The reactor was operated at organic loading rates (OLRs) of 0.67, 1, 2 and 4 gCOD/L/d by increasing the MEG concentrations (1000, 1500, 3000 and 6000 mgCOD/L, respectively). A HRT of 36 h, (9 h for each compartment) and flow rate of 10 L/d were kept constant, and the ambient temperature was varied from 15 to 30 °C.

2.3. Analytical methods

The influent and treated effluents were sampled two times a week for analysis of chemical oxygen demand (COD), total volatile