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An alternative anaerobic treatment process for treatment of heavy oil refinery wastewater containing polar organics

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ABSTRACT

Heavy oil is an important part of energy sources, but the refining wastewater is difficult to treat by the conventional anaerobic process, which has low efficiency and poor ability to resist impact load. In this study, an up-flow anaerobic sludge bed (UASB) reactor was applied to treat heavy oil refinery wastewater containing large amounts of polar organics. Through a progressive increase of hydraulic conditions, the average removal efficiencies of COD and total oil reached 70% and 72%, respectively, at an organic loading rate (OLR) of 3.44 kg COD/m^3 d. GC–MS analysis revealed that more biodegradable organic acids and alcohols were generated and macromolecular polar organics were degraded into small molecular intermediates after UASB treatment. The morphology observation of the sludge demonstrated that granular sludge with an average particle size of 1 mm was formed. Moreover, the predominant species and microbial community shift could reflect the performance of the reactor. The long-term operation of UASB exhibited excellent polar organic removal efficiency. The study demonstrated the potential of UASB as an alternative for high-efficiency anaerobic treatment of heavy oil refinery wastewater.

1. Introduction

With the increase in energy demand, the world oil consumption increased from 88.3 million barrels per day in 2010 to 91.2 million barrels per day in 2013 [1]. Driven by petroleum and chemical product consumption of emerging markets, such as China and India, the global oil requirement is projected to rise by 20–25% over the next decade [2]. Heavy oil, as an important part of the energy supply, is being increasingly exploited. Accordingly, huge amounts of heavy oil refinery wastewater are generated from crude oil processing. Compared with light oil refinery wastewater, heavy oil refinery wastewater contains more polar organics and complicated dissolved recalcitrant compounds, such as naphthenic acid, heterocyclic compounds, surfactants and heavy mineral oil [3]. Most of those contaminants are toxic and macromolecular, which causes poor biodegradability and low solubility of the wastewater [4]. Furthermore, heavy oil refinery wastewater strongly fluctuates in terms of quantity and quality, increasing the difficulty of biological treatment. Currently, most heavy oil refinery wastewater is treated by conventional anaerobic-aerobic treatment processes. In an anaerobic unit, only an organic loading rate (OLR) of 0.3–0.6 kg COD/m^3 d was obtained [5]. It is possible that the poor ability of sludge sedimentation leads to microbe washout and poor resistance to toxic compounds, causing biological inhibition.

In recent years, researchers have attempted to develop some innovative pretreatment methods to remove biorefractories and improve biodegradability, such as electrolysis [6], ozonation [7] and the electron-beam method [8]. Although these methods are well established in lab-scale experiments, it is necessary to have a rapid application of low cost and mature technology in the treatment of heavy oil refinery wastewater. Highly-efficient anaerobic biological technology has been widely applied, because it has minimal operational cost, small occupation, strong resistance to impact load and excellent organic removal efficiency [9]. Because of the simple design, easy construction and maintenance, UASB bioreactors, as one of the most popular highly-efficient anaerobic wastewater treatment systems, have been used throughout the world since the 1980s [10]. It has proven effective for the treatment of medium- and high-strength wastewater, such as printing and dyeing wastewater [11], slaughter wastewater [12], paper-making wastewater [13], brewery wastewater [14] and food processing wastewater [15]. In

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these wastewater treatment systems, UASB was utilized as an effective anaerobic treatment unit replacing the conventional anaerobic digestion tank. High-density biomass with high activity and excellent settling properties satisfy greater efficiency and better effluent quality. Recently, interest in utilizing UASB reactors for the treatment of petrochemical wastewater has grown [16]. For example, Gasim et al. [17] reported a UASB reactor was successfully operated to treat petroleum refinery wastewater. Additionally, Nasirpour et al. [18] examined the treatment of petroleum refinery effluents in a combined UASB and an aerobic packed-bed biofilm reactor. However, these reports are mostly limited to petroleum refinery wastewater treatment. There are few applications of UASB to heavy oil refinery wastewater. Such wastewater is enriched with dissolved recalcitrant organic compounds and higher levels of sulfur, metals and salts [3]. In case of overloading, a serious influence on biochemical systems can occur [19]. Until now, there are no references of whether UASB proceeds smoothly during the long-term operation of heavy oil refinery wastewater. Further investigation in assessing the continuous stability of UASB is still urgently required to drive industrial application.

Therefore, in this study, a lab-scale UASB reactor was constructed. The objective of the research is to investigate an alternative anaerobic treatment process for the treatment of heavy oil refinery wastewater that contains polar organics. By choosing this strategy, the problems of low OLR and poor biodegradability encountered in current anaerobic units can be overcome.

2. Materials and methods

2.1. Heavy oil refinery wastewater and seed sludge

Heavy oil refinery wastewater was collected in a sour water stripping unit from the Liaohe Petrochemical Branch Company (Liaoning province, China), which is a main heavy oil refinery in China, with a capacity of over 3 Mt/a. The characteristics of the wastewater are shown in Table S-1 (Supplementary material).

Seed sludge was obtained from a hydrolysis acidification tank of the refinery wastewater treatment plant of the Liaohe Petrochemical Company (Liaoning province, China). It showed good settleability and a dark brown color, with 17.23 g/L of mixed liquor suspended solids (MLSS) and 8.74 g/L of mixed liquor volatile suspended solids (MLVSS), respectively.

2.2. UASB configuration

The laboratory-scale UASB bioreactor consisted of a 5 mm-thick Plexiglas plate, a total volume of 4.45 L, with effective volume of 3.38 L, an internal diameter of 7 cm and a height of 55 cm. The reactor was composed of a three-phase separator with a volume of 0.27 L to separate gas, water and sludge. The UASB reactor configuration is illustrated in Fig. 1. The technological process can be found in the supplementary material section. The UASB reactor ran for 285 days, and the steady state performance was studied under four influent flows (1.81 L/d, 2.72 L/d 3.63 L/d and 4.54 L/d) and the corresponding HRTs (45 h, 30 h, 22 h and 18 h). The pH, biogas production and composition, VFA, ORP, COD and oil concentration were determined during the experiment. Samples were analyzed in duplicate and average values were reported.

2.3. Anaerobic biodegradability evaluation experiment

A batch-scale experiment was conducted to evaluate the biodegradability of the heavy oil refinery wastewater. Detailed information can be found in the supplementary material section.

According to stoichiometric calculation, methane conversion (M%), acidification rate (A%), biodegradable COD (COD_{BD}) and biodegradability (BD%) were obtained by the following equations [20]:

$$\text{Methaneconversion(M\%)} = \frac{COD_{CH_4}}{COD_0} \times 100 \quad (1)$$

$$\text{Acidifiationrate(A\%)} = \frac{COD_{acid}}{COD_0} \times 100\% \quad (2)$$

$$\text{Biodegradability(BD\%)} = \frac{COD_{BD}}{COD_0} \times 100\% = E\% + VFA\% \quad (3)$$

in which COD_0 = initial COD, COD_{CH4} = conversion of CH_4 to COD, 1 g COD is equal to 350 mL CH_4 under the standard condition, COD_{acid} = acidified COD = $COD_{CH4} + COD_{vfa}$, COD_{vfa} = conversion of VFA to COD, 1 g VFA in terms of acetic acid is equal to 1.067 mg COD, E% = the removal rate of COD, and VFA% = $\frac{COD_{vfa}}{COD_0} \times 100\%$.

2.4. Microbial structure analysis

2.4.1. DNA extraction, PCR amplification and high-throughput sequencing

The bacterial communities in seed and acclimated sludge were investigated by Illumina high-throughput sequencing. DNA was extracted from sludge samples with a PowerSoil DNA Isolation kit (Mobio Laboratories Inc., Carlsbad, CA, USA) following the manufacturer's protocol. The homogenization step was performed at 5000 rpm for 20 s using Precellys® 24 (Bertin Technologies, France). The extracted DNA was stored at −20 °C prior to further analyses. The V3 and V4 regions of the 16S rDNA gene were selected for PCR. The primers are 340F (5′-TCCTACGGGAGGCAGCAGT-3′) and 805R (5′-GGACTACCAGGGTATCTA ATCCTGTT-3′) [21]. All PCR reactions were conducted in 50 μL reactions with 38.8 μL of ddH_2O, 5 μL of 10× Buffer A (KAPA BIOSYSTEM, UAS), 1 μL 10 mM dNTPs, 2 μL reverse primers, 0.2 μL of KAPA Taq DNA Polymerase (KAPA BIOSYSTEM, UAS) and 1 μL template DNA. PCR amplification was performed as follows: 95 °C for 3 min, followed by 30 cycles of denaturation at 95 °C for 30 s, annealing at 50 °C for 30 s, elongation at 72 °C for 60 s and final extension at 72 °C for 7 min. After PCR amplification, 5 μL PCR products were mixed with the same volume of 1X loading buffer (containing SYBR green) and electrophoresis was conducted on 1.5% agarose gel to detect positive amplified bands. Samples with the bright main strip between 400 and 450 bp were chosen for further analyses. Then, PCR products were purified with a gel extraction kit (MinElute Gel Extraction Kit, QIAGEN, Germany). Amplicons from different sludge samples were sent out for pyrosequencing on the Illumina MiSeq platform at SinoGenoMax Co., Ltd (Beijing, China).

2.4.2. Pyrosequencing data analysis for microbial communities

For quality control, the reads that contained one or more ambiguous bases ("*N*") were first removed. Illumina sequencing generated a pair of reads from the two ends (paired-end reads) for one DNA fragment. Paired-end reads from the original DNA fragments were merged by software (SOAPdenovo) to avoid overlaps. Then, the tag sequences were sorted into different individual files according to the barcodes of all samples. Sequence data were processed by read trimming and identification of V3–V4 sequences, followed by filtering and assigning the operational taxonomic units (OTUs). OTUs were identified with a cutoff of 97 % identity. The reads from filtered OTUs are processed using the Quantitative Insights into Microbial Ecology (QIIME) program to construct a representative sequence for each OUT. Representative sequences from each OUT were selected to annotate taxonomic information.