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Treatment of petrochemical wastewater by microaerobic hydrolysis and anoxic/oxic processes and analysis of bacterial diversity

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HIGHLIGHTS

- Microaerobic hydrolysis–acidification (MHA) was used as a pretreatment.
- MHA–A/O process was developed to treat actual petrochemical wastewater.
- The total COD removal efficiency was 72–79% and MHA accounted for 33–42%.
- The predominant genera in MHA, anoxic and oxic reactors were determined.

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ABSTRACT

Microaerobic hydrolysis–acidification (MHA)–anoxic–oxic (A/O) processes were developed to treat actual petrochemical wastewater. The results showed that the overall COD removal efficiency was 72–79% at HRT = 20 h, and MHA accounted for 33–42% of COD removal, exhibiting good efficiency of acidogenic fermentation. Ammonium removal was more than 94%. The main pollutants in the influent were identified to be benzene, ketone, alcohols, amine, nitrile and phenols by GC–MS, and the majority of pollutants could be removed by MHA–A/O treatment. *Proteobacteria* was the most dominant bacteria in the system, accounting for more than 55% of the reads. The predominant genera in MHA, anoxic and oxic reactors were *Anaerolineaceae* and *Sulfuritalea*, *Lactococcus* and *Blastocatella*, and *Saprospiraceae* uncultured and *Nitrosomonadaceae*, respectively. This treatment system exhibited good performance in degrading the complex compounds in the petrochemical wastewater.

1. Introduction

A large amount of petrochemical wastewater was generated in the petroleum refining industry and the manufacturing processes of numerous organic chemicals and raw materials, which has become one of the most serious issues. Usually wastewater released from the petrochemical industry contains hazardous chemicals such as petroleum hydrogen, aromatic compounds, phenolic substances and heavy metals, which are highly toxic and biologically recalcitrant (Wang, 2002; Liu et al., 2014).

The treatment processes used for petrochemical wastewater generally include pretreatment to improve the biodegradation and reduce toxicity, followed by biological treatment involving activated sludge process, anoxic–oxic (A/O) process, fluidized bed reactor, membrane bioreactor and biofilm process (Wang et al., 2000; Guo et al., 2009). Among the biological treatment processes available, the A/O process is highly effective in removing organics and nutrients with low operational costs, and has been a promising alternative to conventional activated sludge process (Wang et al., 2002, 2004). The pretreatment processes include several physicochemical methods such as ultrasonic, flocculation, Fenton and ozone oxidation as well as anaerobic hydrolysis–acidification (Lin et al., 2001).

Anaerobic hydrolysis–acidification is the first two stages of anaerobic digester, serving for solubilization of complex macromolecular and particular organic compounds into micromolecular and simple soluble compounds such as volatile fatty acids (VFAs). Recent studies found that the hydrolysis–acidification process could occur under microaerobic conditions by adding a small amount of oxygen (air) into the reactor, which is termed as microaerobic hydrolysis–acidification (MHA) (Lim et al., 2014).

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Studies showed that limited oxygen supply to anaerobic digester did not affect the methane production and organic substances removal (Diaz et al., 2011a). Moreover, Jenicek et al. (2008) found that the application of microaerobic condition was efficient to increase the biodegradation of solid waste. The studies performed by Lim and Wang (2013) showed that microaerobic condition could increase the solubilization and acidification efficiencies, and the conversion rate of other short chain fatty acids to acetate in the anaerobic co-digester of brown water and food waste. This might be due to the enhanced metabolic activities of facultative hydrolytic and acidogenic bacteria under microaerobic conditions. Another reported benefit of microaeration was to accelerate the production of exoenzymes that conducted the degradation of slowly biodegradable organics (Lim and Wang, 2013).

Moreover, it was reported that sulfide oxidizing bacteria, which are responsible for oxidizing sulfide to sulfite with oxygen as electron acceptor, exhibited higher activities in microaerobic conditions than that in anaerobic digester (Jenicek et al., 2011). As a result, the production of hydrogen sulfide (H_2S) content could be decreased effectively. H_2S is a toxic gas with rotten egg odors, is highly soluble and causes corrosion of the equipment. Literature demonstrated that the concentration of H_2S in the biogas was reduced by more than 98% under microaerobic conditions (Diaz et al., 2011b). Up to now, most of studies related microaeration focused on the digester of solid waste, there is a little of information about the application of MHA process on treating industrial wastewater, and even less on petrochemical wastewater. Chen et al. (2011) studied the treatment of pharmaceutical wastewater using combined anaerobic/microaerobic and two-stage aerobic processes. MHA was used to enhance the biodegradability of pharmaceutical wastewater and benefit the subsequent aerobic treatment.

In this study, MHA and A/O processes were developed to treat the real petrochemical wastewater from a large petrochemical company in northeast China. Experiments were conducted to: (1) evaluate the performance of the system in removing organics, nitrogen and phosphorus compounds; (2) analyze the composition of organics in influent and effluent; (3) identify the bacterial community of the sludge in each tank. Knowledge of the microbial community structure is helpful for a better control of the biological processes. With this information it was aimed to deepen our understanding about MHA and provide a new choice for industrial wastewater treatment.

2. Methods

2.1. Experimental set-up

The experimental set-up was built in an Integrated Petrochemical Wastewater Treatment Plant (IPWWTP) in northeast China. It consisted of a MHA reactor, an A/O reactor and a settling tank, with an effective volume of 33 L, 43 L and 28 L, respectively (Fig. 1). The MHA reactor was divided into four compartments. Air was supplied into the bottom of the first three compartments through aquarium-type diffuser with a flow rate of 0.3 L/h. The sludge from the fourth chamber was recycled into the first chamber. The A/O reactor consisted of an anoxic and two oxic compartments, with a volume ratio of 1:2:2. Dissolved oxygen (DO) concentration in the oxic tanks was maintained at 4–6 mg/L by adjusting the input aeration flowrate (Wang and Yang, 2004). An electric agitator was equipped in the anoxic tank to provide a mixture of sludge and wastewater. Sludge from the settling tank was recycled into the anoxic tank with a ratio of 100%.

2.2. Wastewater and characteristics

The wastewater used in this study was the influent of IPWWTP, which consists of petrochemical industry wastewater and domestic wastewater with a ratio of 3:1. The industrial wastewater came from more than 70 sources involving fertilizer plant, oil refinery plant, resin factory, acrylonitrile butadiene styrene (ABS) plants, etc. It was pre-treated in the plants and effluent was discharged into the IPWWTP. The domestic wastewater is the used water from houses, commercial and schools in the area around IPWWTP.

The experiment was divided into two working periods. The reactor was operated by feeding the influent of IPWWTP in the first period and industrial wastewater alone in the second period. Table 1 presents the characteristics of wastewater. The concentrations of COD and sulfate (SO_4^{2-}) in the influent fluctuated significantly. The volatile phenolic compounds (VPCs) and benzene compounds (BCs) were mainly from the industrial wastewater. There is not great difference in total nitrogen (TN) and total phosphorus (TP) concentration for the wastewater at two phases.

2.3. Start-up and operation of MHA–A/O reactor

The MHA–A/O reactor was started up by seeding the recycled sludge taken from the recirculation line of the IPWWTP at an initial hydraulic retention time (HRT) of 48 h. The HRT was decreased gradually by using the COD removal (15–30% for MHA and 65–70% for A/O reactors) as a reference parameter until stable operational conditions were achieved. After a month, the system was started-up successfully and operated for nearly a half of year, from Aug 2014 to Jan 2015, at HRT of 20 h (12 h and 8 h in the MHA and A/O reactor, respectively). The sludge retention time was set at 30 d. The loading rate of the MHA and A/O reactor ranged 0.2–0.7 and 0.1–0.4 g COD/L d, respectively. The temperature of the system ranged 22–28 °C.

During steady-state operation, the performance of the system was evaluated by measuring the following parameters in influent and effluent periodically: COD, TN, ammonium (NH_4-N), nitrate (NO_3-N), nitrite (NO_2-N), TP, UV_{254}, VFA, SO_4^{2-} and sulfide (S^{2-}). All the samples were settled and filtered using 0.45 μm syringe filters before analysis. The distribution of COD and NH_4-N at each tank of the reactors, BOD_5, total suspended solids (TSS) and volatile

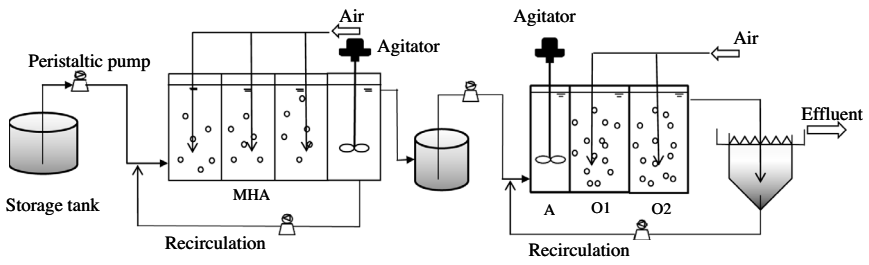

Fig. 1. Schematic diagram of the experimental set-up.