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Improving hydrolysis acidification by limited aeration in the pretreatment of petrochemical wastewater

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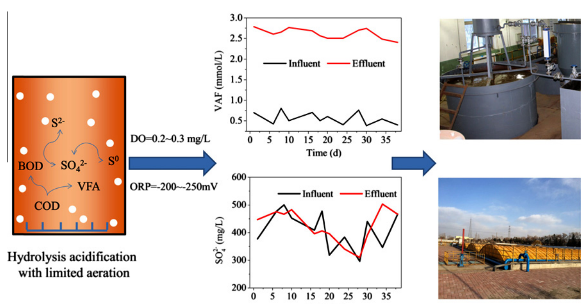
HIGHLIGHTS

- The optimized DO of limited aeration was 0.2–0.3 mg/L.
- The biodegradability, toxicity and treatability improved obviously.
- SO_4^{2-} reduction can be inhibited by limited aeration hydrolysis acidification.
- SRB was inhibited by limited aeration hydrolysis acidification.

GRAPHICAL ABSTRACT



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ABSTRACT

Petrochemical wastewater was pretreated by hydrolysis acidification to improve the biodegradation and treatability on limited aeration conditions. The results showed limited aeration with DO from 0.2 to 0.3 mg/L (average ORP was −210 mV) was the best condition. The BOD_5/COD of influent was 0.23, and it increased to 0.43 on this condition. Limited aeration can obviously reduce the reduction of SO_4^{2-}, reducing the generation of toxic gas H_2S, and almost no H_2S can be detected in the off-gas. The sulfate reducing bacteria (SRB) diversity and abundance on limited aeration condition was obviously inhibited. Limited aeration condition was benefit for the removal of benzene ring organics, such as benzene, toluene, ethylbenzene and xylenes (BTEX), improving the toxicity and treatability of the wastewater. Based on the experiment results, an anaerobic hydrolysis acidification tank (100,000 m^3) has been transformed into limited aeration hydrolysis acidification tank and it runs well.

1. Introduction

The petrochemical wastewater is characteristics with high pollutants concentration and salinity, a certain degree of toxicity, low biodegradability and large fluctuations in water quality and quantity. In China, the current annual discharge of industrial wastewater is more than 2.1×10^{10} t, and the percentage of discharged petrochemical wastewater is about 3–4%. However, the percentage of the volatile phenols discharged by petrochemical wastewater is over 35% (Wu et al., 2015). Many technologies, such as biological processes, advanced oxidation, membrane and adsorption methods, can be used in petrochemical wastewater treatment (Lei et al., 2010). Normally, the cost of physical and chemical technologies is relatively high; therefore, the biological wastewater treatment technology is the most promising treatment

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process for petrochemical wastewater treatment because of its affordable cost and high efficiency.

Pretreatment of petrochemical wastewater is often needed due to its low biodegradability and high toxicity. Pretreatment can improve the biodegradability of the wastewater (typically measured with BOD_5/COD), making it suitable for the subsequent biological treatment. In practice, hydrolysis acidification process is often used as a pretreatment process in refractory biodegradable wastewater treatment (Lei et al., 2010). The role of hydrolysis acidification is to change the refractory complex macromolecules, such as aromatic hydrocarbons or heterocyclic substances, into small molecules, such as small molecule organic acids and alcohol. However, the composition of petrochemical wastewater is very complex. The hydrolysis process conditions influence the molecular weight and structure of organics in the effluent, which in turn affects the toxicity of the wastewater (Shi et al., 2011). This may affect the performance of subsequent aerobic biological treatment process. It is known that the hydrolysis of organic-complex wastewater is a limiting stage of the degradation process. In addition to the COD removal and BOD variation, the variation of molecular weight, removal of toxic organic pollutants, reduction of toxicity and biodegradability of wastewater, are also needed to investigate.

The content of sulfate is relatively high in the petrochemical wastewater (Zhang et al., 2013a). The sulfate can be reduced on the hydrolysis acidification condition due to the presence of SRB (Zhang et al., 2013a). Some relatively easily degraded carbon, such as volatile fatty acids (VFA) can be consumed during the process, weakening the role of hydrolysis acidification (Xu et al., 2014). In addition, sulfide from the sulfate reduction also causes toxic effect on microbial metabolism and the emission of hydrogen sulfide is dangerous to the wastewater treatment plant (WWTP) operatives (Zhang et al., 2011; Xu et al., 2012). Therefore, the inhibition of sulfate reduction is very important in the hydrolysis acidification process in the pretreatment of petrochemical wastewater.

There are many ways to inhibit the reduction of sulfate on the reducing conditions, such as ferric iron dosing (Zhang et al., 2009) or nitrate dosing (Chen et al., 2009). Aeration can also inhibit the growth of SRB (Xu et al., 2012). Xu et al. (2012) reported that the activities of SRB were inhibited when the DO was over 0.3 mg/L in a micro-aerobic sulfur recovery reactor. The sulfate reduction decreased obviously in this DO level. The DO level is a promising controlling factor for the sulfate reduction and low DO benefit the fermentative strains. However, the excessive oxygen supply can also affect the hydrolysis acidification process, and it can also stimulate the reduction of biodegradable COD by heterotrophic bacteria oxidation process. The control range of DO is the key to the hydrolysis acidification of petrochemical wastewater. The relationship of SRB and sulfate reduction, and the microbial populations and functional genes distribution in a sulfate removal bioreactor, have been investigated in detail (Xu et al., 2014). However, the aim of limited aeration in their study is to improve the S^0 production through the coupling of sulfate reduction and sulfide oxidation. When the wastewater is the toxic petrochemical wastewater, the effect of limited aeration on hydrolysis acidification performance, concerning the VFA production, sulfate reduction, organic molecular weight variation, toxic organic pollutants removal and toxicity variation, were not clear. The bioreactor performance and the microbial population variation are closely related (Xu et al., 2014). It is necessary to investigate the microbial population variation on different conditions in limited aeration hydrolysis acidification process.

In this study, a continuous operated reactor was run under different DOs. As a comparison, another reactor with the same size was operated on anaerobic condition. The COD removal, VFA production and SO_4^{2-} variation were investigated. In addition, the microbial community structure, organics removal, toxicity and biodegradability variations were also studied.

2. Methods

2.1. Reactor and operation

In this study, two reactors were operated in parallel. The size of two reactors is the same, with the inner diameter of 200 mm and the height of 450 mm. The schematic diagram is shown in Fig. 1. One reactor was operated on limited aeration condition (Reactor A) with different DO, and the wastewater and activated sludge were mixed by aeration and stirred mixer. The other was operated on anaerobic condition (Reactor B), with wastewater and activated sludge mixed by slowly operated stirred mixer. Each reactor was equipped with a settling tank used for wastewater and activated sludge separation, as well as sludge recycle. The influent of the Reactor A and B was the same with the flowrate of 0.875 L/h, resulting in the hydraulic retention time (HRT) of 16 h. The average mixed liquid suspended solids (MLSS) in Reactor A and B was 6–8 g/L. Both reactors were equipped with DO, ORP and pH meters. The whole operating period was about 135 d. There was no change in the operating parameters in Reactor B. The average ORP of Reactor B was −350 mV. However, in the operation of Reactor A, the whole time was divided into 4 periods (I, II, III and IV), with the average DO of about 0.1–0.2 (I), 0.2–0.3 (II), 0.3–0.4 (III) and 0.4–0.5 mg/L (IV), respectively (Supplementary data, Fig. S1). The average ORP of Period I, Period II, Period III and Period IV were −270, −210, −164 and −99 mV, respectively (Supplementary data, Fig. S2).

2.2. Wastewater

The wastewater used in this study was the influent of a centralized petrochemical WWTP with hydrolysis acidification-anoxic/oxic as the core process. The wastewater treated by this petrochemical WWTP is the mixed wastewater discharged from a petrochemical industrial park containing more than 50 sets of petrochemical production plants, including typical petroleum refining plants, basic petrochemical raw materials (intermediates) production plants and petrochemical synthetic material plants. The main qualities of the wastewater were: COD 320–500 mg/L, BOD_5 50–170 mg/L, NH_4^+—N 15–25 mg/L, NO_3^-—N 2.5–12.1 mg/L, PO_4^{3-}—P 2.0–7.0 mg/L, SO_4^{2-} 296–570 mg/L, and pH 6.5–8.7.

2.3. Water quality analysis

COD, BOD_5 were measured according to the Standard Methods (APHA, 2005). DO and ORP were determined by a portable meter (WTW 340i, Germany). VFA was measured by titration method using Delta 320-s pH meter (Mettler-Toledo Group, Greifensee, Switzerland) (Feitkenhauer et al., 2002). Sulfate was determined by ion chromatography using a conductivity detector (Dionex ICS-1000, Japan). Total sulfide in the wastewater was analyzed by the potentiometric titration method (Mettler-Toledo Group, Greifensee, Switzerland). H_2S in the off-gas was measured by gas chromatography (Agilent 6890, USA) according to the Standard Methods (APHA, 2005).

2.4. Microbial community structure analysis

The activated sludge samples were taken on day 50 from Reactor A (DO = 0.2–0.3 mg/L) and B. Total DNA extraction