

Research Article

Effect of Influent HRT on Pretreatment of Sulfate-Laden Food Wastewater for Desulfurization-Denitrification Process

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Abstract: In order to treat wastewater rich in sulfate and organic carbon, an anaerobic attached-growth bioreactor was set up. It was the pretreatment of mixotrophic desulfurization-denitrification process and the effect of influent HRT was considered. The HRT was decreased from 128 to 6.2 h, while the sulfate removal rate, the organic carbon removal rate and sulfide generating rate were analyzed, respectively. The results showed that the suitable HRT in sulfate reduction stage for the pretreatment of desulfurization-denitrification process was 7.7 to 10.2 h.

Keywords: Attached-growth, desulfurization, organic carbon, SRB, sulfate-laden food wastewater

INTRODUCTION

Much wastewater containing high concentration of sulfate and organic carbon could be discharged by many agricultural and food industrial production processes, such as fish aquaculture wastewater (Zhu *et al.*, 2012). From 70s of 20th century, the single-phase anaerobic process has been used for sulfate-laden wastewater treatment (Postgate, 1984; Tony and David, 2003). However, in this process the anaerobic digestion would easily be inhibited by sulfate reduction. Also, hydrogen sulfide gas generated from the process would bring secondary pollution to the environment (Ziomer and Shrouf, 2000), inhibit the Sulfate Reduction Bacteria (SRB) (Blanca *et al.*, 2009; Martijn *et al.*, 2009) and increase the difficulty for the methane recovery (Roel *et al.*, 2009; Samantha *et al.*, 2004). Therefore, two-phase anaerobic digestion process and some physical-chemical process (Wei *et al.*, 2007), such as air stripping, chemical precipitation and electrodialysis were explored for the sulfate removal (Li *et al.*, 2012; Tait *et al.*, 2009). But these processes had some disadvantages: high investing and operating costs, repairing difficulty, generating much chemical sludge and non-thorough prevention of sulfurous compounds pollution.

This research introduced mixotrophic desulfurization-denitrification process to the treatment of sulfate-laden wastewater and adopted anaerobic attached-growth bioreactor for the pretreatment. The sulfate would be reduced to sulfide ion rather than

hydrogen sulfide gas by SRB, while the sulfate removal rate was maintained high. In the subsequent treatment, sulfide ion would be converted to sulfur by mixotrophic desulfurization-denitrification process. Furthermore, the sulfur could be recycled. In order to seek the proper Hydraulic Retention Time (HRT) range for the pretreatment of desulfurization-denitrification process, the removal of sulfate and organic carbon and the generation of sulfide were observed under different influent HRT values.

MATERIALS AND METHODS

Attached growth bioreactor and sludge inoculation:

The anaerobic attached-growth bioreactor of 5.1 L in column shape was used and illustrated in Fig. 1. One peristaltic pump was used to feed artificial wastewater from the bottom of reactor into system and the other peristaltic pump was used to circulate sludge and water to achieve uniform mixing. The up-flow velocity was 0.4 m/h. On the reactor top, a three-phase separator was used to separate biogas, sludge and outflow water. Biogas was collected by water sealing tank. In order to increase the biomass inside reactor, raschig rings with inner diameter of 10 mm were applied as attached-growth media. The Oxidation-Reduction Potential (ORP) detector and pH detector were inserted into bioreactor to test ORP and pH. Constant temperature of 35±0.2°C inside the reactor was realized via temperature sensor connected with temperature controller (MWZK-02, China) and heating threads

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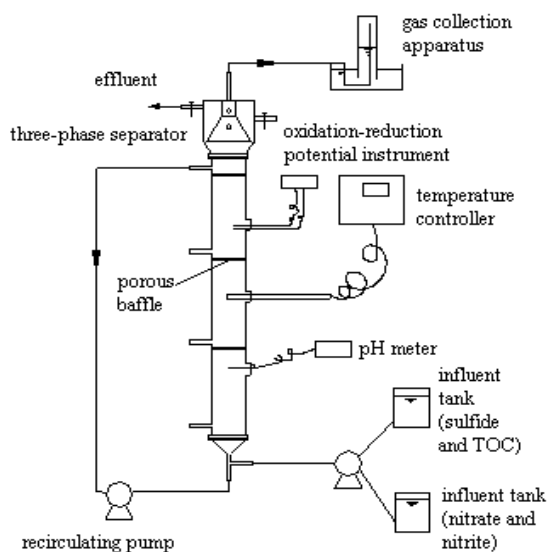


Fig. 1: Schematic diagram and instructions of anaerobic attached-growth bioreactor

Table 1: Variation of influent substrates in bioreactor

Operation time (day)	HRT (h)	Sulfate loading rate (mg S/L·day)	TOC loading rate (mg C/L·day)
20	128.00	50	225
30	72.70	88	395
40	51.20	125	561
20	13.76	465	2089
20	10.19	628	2820
30	7.70	829	3727
30	6.20	1030	4627

bonded around reactor. The bioreactor was inoculated with 1.5 L of the sludge collected from a Continuous Stirred Tank Reactor (CSTR) used to treat municipal wastewater, giving the biomass concentration of 15.19 MLVSSg/L.

Design of experiment and substrates: Artificial wastewater containing sodium sulfate, magnesium sulfate, potassium sulfate (Na_2SO_4 : $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$: $\text{K}_2\text{SO}_4 = 1.5:1.7:1$) and glucose (TOC: $\text{SO}_4^{2-} = 1.5:1$) as sulfate and organic carbon sources, sodium bicarbonate as inorganic carbon source, ammonium chloride and potassium dihydrogen phosphate (C:N:P = 150:5:1) as nitrogen and phosphorus sources for bacteria growth was used as the feed to bioreactor. During start-up, the bioreactor was fed semi-continuously for 150 days. The wastewater of 1.5 L was fed to the bioreactor every 12 h. When removal rates of sulfate and TOC reached 80%, the bioreactor was started to operate under continuous feeding conditions. The loading rates of substrates with different HRTs were shown in Table 1.

Analytical methods: To measure sulfate, liquid samples were filtrated with a 0.45 μm filter and injected into an ion chromatography (DIONEX ICS 3000, USA) equipped with an inhibitory type conductivity detector and an Ionpac column (AG4A AS4A-SC, 4 mm). The

flow rate of carrier liquid was 1.0 mL/min. The sulfide was measured by methylene blue spectrophotometry with the spectrophotometer (UV-2550, Japan) (APHA, 1994). Measurements for TOC and IC (inorganic carbon) were taken by the TOC analyzing instrument (TOC-VCPH, Japan). MLVSS were analyzed according to the standard methods 11. ORP and PH were measured by pH meter models (pHs-3c, China).

RESULTS AND DISCUSSION

Degradation of sulfate and generation of sulfide: With the stable influent sulfate concentration, HRT was decreased stepwise to increase the sulfate volumetric loading rate. The degradation of sulfate and generation of sulfide were illustrated in Fig. 2 and 3.

The sulfide generating rate represented the level of sulfide dissolving in wastewater, which was defined as sulfide concentration $\times 100\%$ / (influent sulfate concentration - effluent sulfate concentration). The sulfate removal rate and sulfide generating rate increased gradually and could reach 97.79 and 58.82%, respectively, at HRT of 128~7.7 h. The reason for this phenomenon was discussed below. With HRT decreasing, the chances for SRB to contact with sulfate increased. Therefore, the activity of SRB increased gradually, leading to the sulfate removal rate and sulfide generating rate rise. Figure 4 showed the variation of pH and ORP. At the initial stage of the bioreactor operation, the pH was maintained at 7.5 and this high pH value was easy for sulfide to dissolve in wastewater. Otherwise, the sulfide would convert to hydrogen sulfide gas and escaped from the bioreactor (Cai *et al.*, 2001). Then the sulfide ion concentration increased with HRT rising. It was reported that high concentration of sulfide has negative effect on SRB (Zhang and Liu, 2007). Although the sulfide concentration increased gradually, it was still low and would not influence the sulfate reduction at initial stage of this research. When HRT decreased from 7.7 to 6.2 h, sulfate removal rate and sulfide generating rate decreased. That was because the degradation activity of SRB reached saturation when the sulfate loading rate reached certain degree and relative quantity of removed sulfate declined gradually.

As shown in Fig. 4, the pH and ORP were the important indicative parameters to indicate the running status of bioreactor. Although much sulfide had certain buffer action on pH variation, the pH in this reactor still decreased from 7.7 to 6.2, because sulfate reduction and degradation of organic carbon produced much hydrogen ion with decreasing HRT. Some sulfide ion converted to hydrogen sulfide gas and led to sulfide concentration decreasing. But sulfide was still higher than 150 mg S/L and had inhibition on SRB. That was another reason for

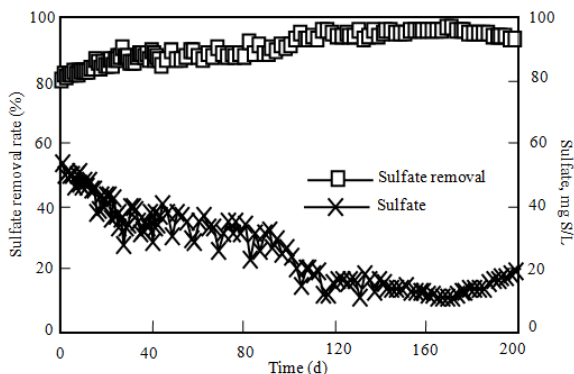


Fig. 2: Removal rate and concentration of sulfate

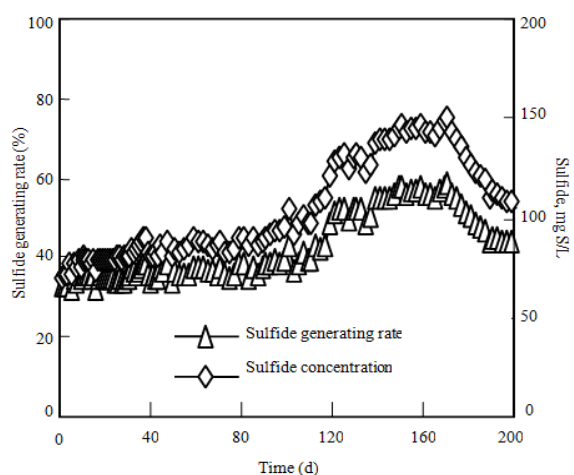


Fig. 3: Generating rate and concentration of sulfide

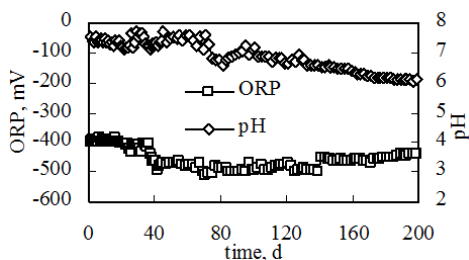


Fig. 4: Variation of pH and ORP in the bioreactor

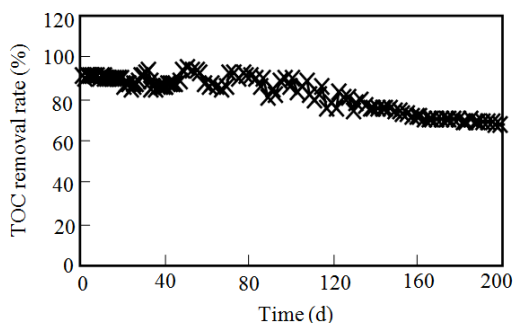


Fig. 5: Removal rate of TOC

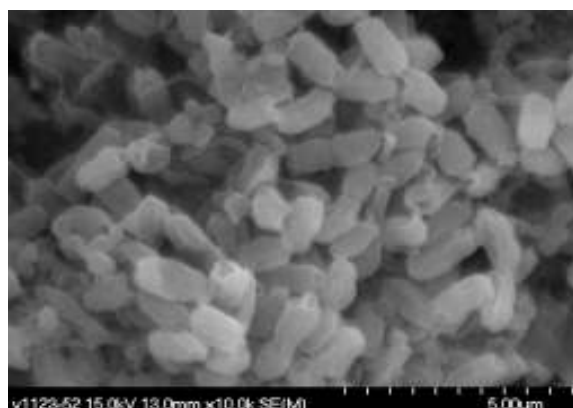
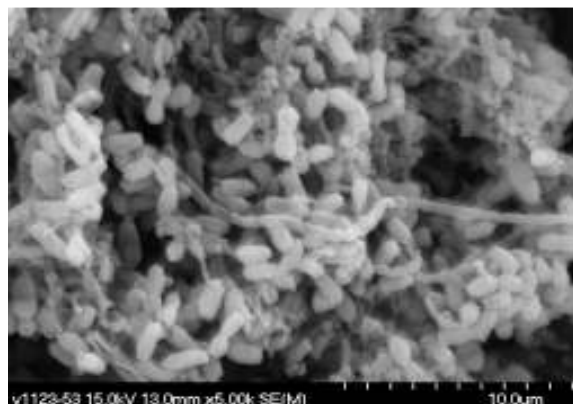


Fig. 6: Scanning electron microscopic images of microorganisms attached on media in the bioreactor

sulfate decreasing. Some researchers reported that ORP must be maintained below -320 mV in order to keep sulfate removal above 80%. ORP could indicate the concentrations of reducing substances in wastewater and its variation had correlation with sulfide concentration variation. Therefore, the ORP increased after initial decreasing and was in the range of -500~-360 mV in this research. This range was lower than the one reported in traditional sulfate reduction process (-320~-360 mV) but was beneficial to the subsequent process.

Degradation of TOC: The variation of TOC in bioreactor was illustrated in Fig. 5. The microorganisms enriched in rings were shown in Fig. 6. With HRT declining from 128 to 7.7 h, the TOC removal rate decreased from 91.1 to 74.8%. With sulfate volumetric loading rate increasing, the sulfate degradation by SRB increased. Then the SRB activity increased and would win the competition for substrates with the Methane Production Bacteria (MPB). SRB used organic carbon as electron donors for sulfate reduction, but the utilization of organic carbon was still lower than MPB. Therefore, the absolute amount of removed TOC declined as shown in Fig. 5. Also the TOC volumetric loading rate increased with HRT declining and the

accumulation of TOC appeared, which led to TOC removal rate declining. When HRT decreased to 6.2, the sulfide accumulated in bioreactor began to inhibit both SRB and MPB. Then TOC removal rate continued to decrease to 67.9%.

Because the sulfate reduction was the pretreatment of mixotrophic desulfurization-denitrification process, its effluent would be fed into the subsequent bioreactor. The desulfurization-denitrification process required pH range of 6.5~7, low TOC and high sulfide. Then this pretreatment operation should be considered to reach such conditions. As high TOC would inhibit the mixotrophic denitrification microorganisms, ORP in this sulfate reduction process should be controlled in range of 7.7-10.2 h to reach sulfate removal of 95% and TOC removal of 80%. At this time, the effluent sulfide concentration was 150 mg S/L, which was higher than the one in traditional sulfate reduction process and was beneficial to be used as electron donors in subsequent treatment. Furthermore, the effluent pH of 6.6 was beneficial to the subsequent treatment.

After the bioreactor run steadily, some raschig rings were carried out for the microorganism morphological characteristics by the electron microscope scanning, as shown in Fig. 6.

The rings supplied solid support and shelter for SRB from being washed away by wastewater. It was beneficial to the selective enrichment and dominant growth of SRB. The short bacilli predominated in the ring, which was consistent with a number of research reports (Wan *et al.*, 2004).

CONCLUSION

The effect of HRT value on the pretreatment for desulfurization-denitrification process was revealed in this study. Main conclusions could be drawn as follows.

Firstly, With HRT declining from 128 to 6.2 h stepwise, the sulfate removal rate and sulfide generating rate decreased after the initial increase.

Secondly, when HRT was 7.7~10.2 h, the removals of contaminants were the best and sulfate removal, TOC removal and sulfide generating rate reached 95.79, 80 and 58.82%, respectively. Then the suitable HRT range for the pretreatment of desulfurization-denitrification was 7.7~10.2 h.

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