INHIBITION OF HYDROGEN SULFIDE ON UASB TREATING SYNTHETIC WASTEWATER BY SODIUM MOLYBDATE

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Abstract- The effect of hydrogen sulfide (H₂S) inhibition on anaerobic treatment of synthetic wastewater was investigated using a UASB reactor. Sodium molybdate (Na₂MoO₄) was added, in order to inhibit H₂S production. The COD influent was set around 5000 mg/l with HRT (hydraulic retention time) 0.5 day. The COD removal, H₂S concentration, methane yield and sulfate removal were investigated. The experimental results show that H₂S was less than 20 ppm, while the control of UASB reactor was demonstrated in the range of 900-1000, 3500-4200 and 5200-7800 ppm at a COD/SO₄²⁻ ratio of 50, 20 and 15 respectively. However, the COD removal was over than 87.6% and methane yield was 50.5-63.7%. Sulfate removal in control was shown between 71.2-79.3% during reactor with added Na₂MoO₄ was lower than 24.44%.

Keywords- Upflow Anaerobic Sludge Blanket (UASB), Hydrogen sulfide, Sodium molybdate

I. INTRODUCTION

Biogas produced during anaerobic treatment of sulfate containing wastes, such as swine wastewater, invariably contains around 1-3 % (v/v) hydrogen sulfide (H₂S). Being highly corrosive, H₂S reduces the utility of biogas as a fuel for boilers and also makes the generation of electricity from biogas very problematic [1]. Sulfate-reducing bacteria (SRB), anaerobic chemolithotrophic bacteria are characteristically derive energy for growth by coupling electron transport from electron donors to the reduction of sulfate by a process known as dissimilatory sulfate reduction [2]. In anaerobic treatment processes, SRB and MPA (methaneproducing archaea, in many literatures called as methane-producing bacteria) always compete for carbon source [3]. In sulfate-rich wastewater digestion, SRB often outcompete MPA and poisonous sulfide during sulfate reduction. High level of sulfide is toxic to both MPA and SRB. Its accumulation in the digestion reactors usually causes inhibition effects on organics removal and methane production, and can even result in system failure. Moreover, large quantities of sulfide formation can affect biogas quantity and quality. As an alternative to providing an unfavorable environment for SRB growth, researchers have investigated SRB suppression through chemical contact. Chemical inhibitors of SRB activity have been reviewed and summarized by Saleh et al [4], Including antibiotics, detergents, dyes, mercurials, metal ions, complexes, nitrocompounds, phenolic substances, sulfate analogues, sulfoamides, and other miscellaneous substrates. The most common chemical inhibitor of SRB has been molybdate (MoO₄²⁻) in the form of sodium molybdate (Na₂MoO₄). Molybdate enters cells via a sulfatetransport system and interferes with the formation of adenosine phosphosulfate (APS), leading to deprivation of reduced sulfur compounds for growth. It forms adenosine phospho-molybdate in the cell [5]. Upflow Anaerobic Sludge Blanket (UASB) reactors are widely applied especially in high strength organic wastewater treatment. The low operational cost, low sludge production and biogas (mthane) production of this reactor make it very attractive. It is reported that over 3000 large-scale systems based on this technology are operating around the world [6]. These studies demonstrated successful inhibition of hydrogen sulfide in UASB reactor. The dose of Na₂MoO₄ and COD/SO₄²⁻ ratio applied varied over a very range.

II. MATERIALS AND METHODS

A. Experimental set-up

The UASB reactor used in this study made of clear acrylic glass with a cylindrical double wall. A working volume of 10 L and an internal diameter of 0.1 m. On top of the reactor was a gas–liquid–solid separator with an internal diameter of 150 mm and a height of 295 mm. The temperature in the reactor was controlled with water recirculation using a heated water bath. The operational temperature was kept constant at 35 ± 1 °C. The produced biogas was connected to a wet gas flow meter via a simple liquid displacement unit. (as shown in Fig. 1) Two UASB
reactors were used in this experiment. The first UASB reactor (reactor I) was set as control and the second reactor (reactor II) was tested by adding Na$_2$MoO$_4$. The both of reactors were inoculated with 3 L granular sludge from a full-scale UASB reactor treating brewing wastewater. The initial sludge concentration of the reactor was 94 g VSS/L. The upflow velocity of UASB was about 1.0 m/h. The OLR was set at 10 g COD/L d with a HRT of 12 h under start-up condition, until more than 80% of soluble COD (SCOD) were removed after 45 days operation.

B. Synthetics wastewater
The synthetic wastewater was made in laboratory. This wastewater contained about 5,000 mg/L sucrose, NaHCO$_3$ dosage was controlled at 2500 mg/L. Sulfate was added into wastewater in the form of Na$_2$SO$_4$. Compositions of the buffer and trace elements used were as follows (in mg/L): 100 (NH$_2$)$_2$CO, 108 KH$_2$PO$_4$, 40 CaCl$_2$.2H$_2$O, 40 FeCl$_2$.7H$_2$O, 40 MgSO$_4$.7H$_2$O, 10 KI,10 CoCl$_2$.6H$_2$O and 0.5 each of H$_2$BO$_3$, ZnCl$_2$, CuCl$_2$.4H$_2$O, MnCl$_2$.4H$_2$O, AlCl$_3$.6H$_2$O, and NiCl$_2$.6H$_2$O.

C. Analytical methods
The chemical oxygen demand (COD), sulfate, dissolved sulfide, alkalinity and volatile fatty acids (VFA) were routinely determined during the operation using standard analytical procedures published by the American Public Health Association [7]. Oxidation-reduction potential (ORP) and pH were measured with Multi-parameter benchtop meters (WTW, GmbH). Total suspended solids (TSS) was measured with IQ Sensor net system (WTW, GmbH). The methane content was monitored by gas chromatography (SHIMADZU GC-2010A) equipped with a flame ionization detector (FID). H$_2$S in the biogas was measured with RAE Systems Colorimetric Gas Detection Tubes (LP-1200 Hand Pump).

D. Activity test procedure
Table I summarizes the operating conditions applied to the UASB in different experimental periods (I–III) over a period of 30 days. After start-up condition, 1.0 mM Na$_2$MoO$_4$ was added into influent wastewater tank. The concentration was changed to 1.5 and 2.0 mM respectively. The COD/SO$_4$$^{2-}$ ratio was increased stepwise from 50 to 15 via adding Na$_2$SO$_4$ in order to test the COD/SO$_4$$^{2-}$ effect on the performance of the reactor.

Table I
Operational conditions of the UASB reactor.

III. RESULTS AND DISCUSSION
A. Effect of sodium molybate and COD/SO$_4$$^{2-}$ ratio on hydrogen sulfide concentration

<table>
<thead>
<tr>
<th>Period</th>
<th>Days</th>
<th>COD/SO$_4$$^{2-}$</th>
<th>Na$_2$MoO$_4$ Added (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1-10</td>
<td>50</td>
<td>1.0</td>
</tr>
<tr>
<td>II</td>
<td>11-20</td>
<td>20</td>
<td>1.5</td>
</tr>
<tr>
<td>III</td>
<td>21-30</td>
<td>15</td>
<td>2.0</td>
</tr>
</tbody>
</table>

The inhibition of hydrogen sulfide (H$_2$S) by adding sodium molybdate on the UASB was tested in experimental periods (I–III). Fig. I(a) was shown H$_2$S concentration, on reactor I there are maintained in the
range of 900-1000, 3500-4200 and 5200-7800 ppm when increase COD/\(\text{SO}_4^{2-}\) ratio 50, 20 and 15 respectively. On reactor II, \(\text{H}_2\text{S}\) concentration was maintained that not over than 20 ppm with all experiment.

B. COD removal and methane yield

As shown in Figs. II(b) with the influent COD kept around 5000 mg/L. COD removal rate was steadily maintained in the range of 87.6-92.7% and 88.3-91.5% on reactor I and reactor II respectively. Methane yield as shown in Figs. II(d) was maintained in the range of 50.5-63.7% on the both of reactor. However methane yield on reactor I was decrease below 56.32% when COD/\(\text{SO}_4^{2-}\) ratio increase to 15. On the other hand, methane yield in reactor II was shown in the range of 55.2-62.2%.

C. Sulfate removal

The experimental results on sulfate removal are shown in Fig. II (c). On reactor I, the range of sulfate removal was maintained between 71.2-79.3% during reactor II was lower than 24.44% in all periods. This results demonstrated that 1.0, 1.5 and 2.0 mM \(\text{Na}_2\text{MoO}_4\) can inhibit SRB for sulfate reduction on COD/\(\text{SO}_4^{2-}\) ratio 50, 20 and 10 respectively.

CONCLUSIONS

In this study, Two UASB reactor was operated under a continuous mode achieved about 5000 mg/l COD with the HRT of 0.5 day in treating synthetics wastewater. The experiment periods was varied COD/\(\text{SO}_4^{2-}\) ratio at 50, 20 and 10 respectively. For reactor II \(\text{Na}_2\text{MoO}_4\) was added 1.0, 1.5 and 2.0 mM by stepwise. The result was shown that \(\text{H}_2\text{S}\) was immediately decrease lower than 20 ppm at all periods. The COD removal and methane yield, respectively, maintained above 87.6% and 55.2%.

REFERENCES