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## Biological Hydrogen Sulfide and Sulfate Removal from Rubber Smoked Sheet Wastewater for Enhanced Biogas Production

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### Abstract

The sulfate-rich wastewater from rubber smoked sheet industry could generate hydrogen sulfide (H<sub>2</sub>S) under anaerobic condition, which created bad smell to the community and might cause toxicity and damage to the environment. The H<sub>2</sub>S can be removed from the biogas by sulfur-oxidizing bacteria (SOB) with the ability to convert H<sub>2</sub>S to sulfate. Sulfate-reducing bacteria (SRB) could remove sulfate in wastewater before anaerobic treatment for biogas production. The microbial sludge from wastewater and anaerobic digestion system was collected and test for sulfate and H<sub>2</sub>S removal efficiency. Anaerobic microbial sludge has a high ability to produce methane from gelatin with a specific methane production rate of 92.4 ml CH<sub>4</sub> gVSS<sup>-1</sup> day<sup>-1</sup>. Anaerobic microbial sludge has lower methane production when gelatin and sulfate used as a substrate with a specific methane production rate of 81.4 ml CH<sub>4</sub> gVSS<sup>-1</sup> day<sup>-1</sup>. The biomethane potential, hydrogen sulfide removal and sulfate removal in anaerobic digestion system by addition of enriched cultures of SOB and SRB were investigated. The methane yield of SRB consortium was 60.1 ml CH<sub>4</sub>/gCOD with 20% sulfate reduction from wastewater and no sulfide reduction. The methane yield of SOB consortium was 41.9 ml CH<sub>4</sub>/gCOD with no sulfate and sulfide reduction from wastewater. The addition of SRB consortium could increase methane production by reducing sulfate concentration in wastewater consequently to a reduced concentration of H<sub>2</sub>S in biogas.

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## 1. Introduction

Rubber smoked sheet wastewater containing high sulfate and the sulfate could converse to hydrogen sulfide ( $H_2S$ ) under anaerobic condition by sulfate-reducing bacteria. Hydrogen sulfide created a bad smell (rotten egg odor) to public health. If people received a high concentration of  $H_2S$ , it affects the respiratory system. Biogas production from sulfate-rich wastewaters resulted in high hydrogen sulfide concentration in biogas. It may cause serious problems in the application of biogas because the  $H_2S$  concentration in the gas phase higher than 1000 ppmv could not direct combustion. The limitation of  $H_2S$  for internal combustion engine fuel is 100 ppmv and much lower 16 ppmv is set for compressed natural gas for transportation fuel [1]. Moreover, sulfide in the liquid phase (dissolved sulfide) generated during the anaerobic treatment of sulfate-rich wastewater also imposes toxicity to methanogens [2]. Treatment technologies to remove the high concentrations of  $H_2S$  in the gas phase are physical (adsorption, absorption, and dilution), chemical (chemical absorption, neutralization, and combustion) and biological (activated sludge and biofilter) methods [3].  $H_2S$  in Biogas is difficult to remove because of methanogenic archaea and sulfate-reducing bacteria growth in the same condition. Under anaerobic environment with the presence of chemical oxygen demand (COD), the sulfate-reducing bacteria (SRB) can convert sulfate in wastewaters to sulfide. Biological conversion of sulfide to elemental sulfur or sulfate using sulfide-oxidizing bacteria (SOB) is a capable process to remove  $H_2S$  from biogas [4, 5]. In natural, the SRB and SOB can coexist in hydrothermal vents, microbial mats, marine sediments and wastewater biofilms as a response of high organic input and low dissolved oxygen (DO) concentration [6]. Therefore, the combination of the SRB and SOB for remove sulfide and sulfate in biogas reactor is of practical interest.

The aim of this study was to gain more insight into the syntrophic interactions between the different bacterial trophic groups in biogas process. For this purpose, activity tests in the presence of various substrates were carried out to fully elucidate the outcome of competition between the sulfate reducers and the other anaerobic consortia in high sulfate wastewater. The biomethane production, hydrogen sulfide removal and sulfate removal in anaerobic digestion of rubber smoked sheet wastewater by adding enriched cultures of SRB and SOB were investigated.

## 2. Methodology

### 2.1. Sampling and Inoculum

The rubber smoked sheet wastewater was collected from Yangkaw cooperative rubber sheet plant. The chemical and physical compositions of wastewater were analyzed according to standard water and wastewater examination methods [7]. The sludge inoculum was collected from biogas plant of the Yangkaw cooperative rubber sheet plant. Wastewater adjusting the initial pH in the range of 7-7.5 by ash and  $NaHCO_3$  was used as the substrate for seed sludge. Prior to use, the sludge inoculums were incubated for 1-2 weeks to activate microorganism activities. The sulfate-reducing bacteria also enriched from anaerobic sludge collected from the Yangkaw cooperative rubber sheet plant. It was kept at a temperature of 4°C during transport to the laboratory. Postgate medium C was used for enrichment and cultured sulfate-reducing bacteria [8]. Postgate medium C 1 L contained of 6.0 ml Lactic acid, 4.5 g  $Na_2SO_4$ , 1.0 g  $NH_4Cl$ , 1.0 g Yeast extract, 0.5 g  $KH_2PO_4$ , 0.3 g Sodium citrate· $2H_2O$ , 0.06 g  $CaCl_2 \cdot 6H_2O$ , 0.06 g  $MgSO_4 \cdot 7H_2O$ , 0.004 g  $FeSO_4 \cdot 7H_2O$  and pH adjusted at  $7.0 \pm 2$ . The sulfide-oxidizing bacteria were enriched from biofilter sludge collecting from Pitak palm oil CO., LTD. Thiosulfate mineral medium was used for enrichment and culturing sulfide-oxidizing bacteria [9]. Thiosulfate mineral medium 1 L contained of 5.1 g  $Na_2S_2O_3$ , 2.0 g  $K_2HPO_4$ , 2.0 g  $KH_2PO_4$ , 0.4 g  $NH_4Cl$ , 0.2 g  $MgCl_2 \cdot 7H_2O$ , 0.01 g  $FeSO_4 \cdot 7H_2O$  and pH adjusted at  $7.0 \pm 2$ .

### 2.2. Specific methanogenic activity

A specific methanogenic activity (SMA) test was used to determine for microbial activity in anaerobic digestion [10]. SMA tests were carried out in the presence and absence of sulfate ( $NaSO_4$  30 mM). The substrates tested including acetic, avicel, glucose and gelatin and combinations at the concentrations of 4 g/L COD. SMA was carried out in test vials (60 ml) with anaerobic sludge and incubated under mesophilic condition (35 °C) for a period of 7 days. All tests were performed in the presence and absence the addition of sulfate into the medium. The biogas

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