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Evaluating sulfuric acid reduction, substitution, and recovery to improve environmental performance and biogas productivity in rubber latex industry

Sumate Chaiprapat[a,*], *Sunsanee Wongchana*[b], *Surapich Loykulnant*[c], *Chaveewan Kongkaew*[c], *Boonya Charnnok*[b]

[a] *Energy Technology Research Center, Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Hat Yai Campus, Hat Yai, Songkhla 90110, Thailand*
[b] *Faculty of Environmental Management, Prince of Songkla University, Hat Yai Campus, Hat Yai, Songkhla 90110, Thailand*
[c] *National Metal and Materials Technology Center, 114 Paholyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand*

ABSTRACT

Sulfuric acid is heavily used in concentrated rubber latex factories to coagulate rubber particles in skim latex. The resulting sulfate-rich wastewater creates the onset of toxic H_2S gas production in the wastewater holding ponds, causing severe corrosion to materials and community disturbance when dispersed to ambient air. This work identified and evaluated measures to reduce H_2S production by minimizing sulfate concentration in the wastewater. Sulfuric acid use could be cut down by pre-removal of ammonia in the skim latex as well as a stricter manipulation of acid dosing. In search of a more benign chemical, a heat sensitive polymer was identified and tested as sulfuric acid substitute. The use of hydroxypropyl methylcellulose polymer (HPMC) changed wastewater characteristics and was found to increase biogas production approximately by 2.4 times in batch assay at the initial pH 7.0 and methane yield by 2.7 times in continuous digester operation at HRT 7 days. Finally, a resource recovery option was evaluated. The remaining H_2S in the produced biogas was oxidized in the biotrickling filter to sulfuric acid that has a potential to partially supplement the fresh acid. This work demonstrated an integrated approach in waste management to improve environmental performance, safety and energy recovery in the concentrated latex industry.

Keywords: Polymer; Sulfuric acid; Biogas; Rubber latex; Biotrickling filter; H_2S

1. Introduction

Rubber is an important economic crop of many countries in tropical region, such as Malaysia, Indonesia, Vietnam, Thailand, Bangladesh, Cameroon, Turkey and India. Thailand has been the world leader in natural rubber production as its planting area currently covers over 22,400 km^2 and is still expanding. In 2012, the export value amounted for 336,287 million baht (approximately 10,508 million US dollars) from over 3.6 million tons of various rubber products (Office of Agricultural Economics, 2013). The majority of fresh field latex, a milky liquid tapped from rubber trees, is processed into blocked rubber, smoked sheet rubber, and concentrated rubber latex by each respective kind of factories. Concentrated

* Corresponding author at: Department of Civil Engineering, Faculty of Engineering, Hat Yai Campus, Hat Yai, Prince of Songkla University, Songkhla 90110, Thailand. Tel.: +66 815403037; fax: +66 74 459396.
E-mail address: sumate.ch@psu.ac.th (S. Chaiprapat).

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rubber latex industry is a notable source of air and water pollution by its rotten egg smell and high nitrogen effluent. In Thailand alone, there are 64 of such factories concentrating in southern and eastern regions of the country (Department of Industrial Works, 2013). The wastewater from concentrated rubber latex factories contains both organic constituents from the natural latex itself and inorganics such as ammonia and sulfate which are added during the manufacturing process.

In concentrated latex production, ammonia is added to the arriving field latex for preservation, while various chemicals are added for latex conditioning. This pretreated latex then goes through rubber centrifugation to remove liquid in order to concentrate the latex from 30 to 60% in dry rubber content (DRC). The rejected liquid from centrifugation still containing 4–8% DRC, called skim latex, is doped with sulfuric acid to coagulate these rubber particles and make a by-product called skim rubber. The coagulated rubber is further processed by crushing, cutting, and drying before packaging as skim rubber block. This type of rubber is a byproduct of lower quality but it still generates a sizable income for these factories. Wastewater from rubber skimming process is highly acidic, pH 2.0–4.5, high in COD and sulfate, 32,560 and 5411 mg/L, respectively (Jakaew, 2003).

Improper management of this wastewater has long caused water and air pollution to nearby communities (Agamuthu, 1999; Boonreongkaow, 2002; Bunyakan et al., 2004). The treatments widely used are simple wastewater holding ponds in series or aerated lagoon followed by holding ponds; both are open systems. These systems generate a malodorous off-gas comprising hydrogen sulfide (H_2S) from an anaerobic decomposition of sulfate in the wastewater. H_2S production was carried out by the sulfate reducing bacteria, which could proliferate in the wastewater containing sulfate (SO_4^{2-}) and other sulfur compounds under anaerobic condition. At concentration 200 ppmv, H_2S poses severe toxic effects to humans after a 1-min exposure period (Verschueren, 1983). Respiratory and central nervous system paralysis will result when exposed to H_2S concentrations above 500 ppmv (Shy, 1978), while it is acutely lethal above 800 ppmv. The H_2S produced is also toxic to the microorganism communities inside the biogas system. H_2S concentration in the biogas produced from concentrated latex factory wastewater could get to as high as 12,000 ppmv (Chaiprapat et al., 2011) while many biogas engine (electric generator) manufacturers require the H_2S content to be as low as 100 ppm to prevent damage from corrosion to metal parts in contact.

Although aerobic wastewater treatment, such as activated sludge and aerated lagoons, could be carried out, the high energy cost for air delivery systems has always discouraged the continual operation. In many cases, the systems were left un-aerated and turned to be anaerobic ponds which again cause H_2S emission. Enclosed system such as anaerobic digester is an attractive choice because it not only prevents smell emission but also generates methane gas that can be used as an alternative fuel, and requires low energy to operate (Speece, 2008; Deublein and Steinhauser, 2008; Khanal, 2008). In Thailand, past failures and instability in full-scale operation of anaerobic digesters in the concentrated latex industry combined with the low biogas yield have been a huge disincentive for this technology. With increasingly expensive fossil fuels, biogas technology has again started to catch attention. Still, a big caution of the wastewater anaerobic treatability and high H_2S in the biogas remains. Attempts to reduce the use of sulfuric acid and identification of a suitable chemical to replace sulfuric acid and its consequential effects should be studied.

Methods for getting rid of the H_2S in the biogas could follow the waste management hierarchy that includes prevention, reuse/recovery, and treatment, in order. The options at higher hierarchal orders are more preferable (Bishop, 2000), which in the case of concentrated latex industry, sulfuric acid use must be reduced. When the preventive measure is applied, the sulfur loading to the anaerobic treatment system is cut back. Our approach was to introduce a heat sensitive polymer as the acid substitute. The effects on wastewater characteristics as well as subsequent biogas production and its quality were evaluated. Moreover, the economic feasibility of sulfuric acid recovery from H_2S contaminated biogas was presented. The developments and attempts to tackle H_2S problem in this study will play a part in helping the concentrated rubber latex industry improve its environmental performance and enabling the potential application of its biogas technology.

2. Materials and methods

2.1. *Factory surveys and identification of potential measures*

In order to determine the opportunities for effective management of the wastewater, a group of 10 concentrated latex factories was selected for survey and data collection. The survey was performed during January to May 2011 to gain the information of production process and resource use. Direct and indirect measurements of water, chemical, and energy uses were performed in addition to the factories' data. Supplementary re-visits were conducted for the selected factories to identify and confirm possible measures for practical waste management. This latter survey emphasized on the prospects of reducing H_2S in the biogas by means of preventing sulfur compounds to get into the wastewater.

2.2. *Development and testing of the heat sensitive polymer (HPMC) for sulfuric acid substitution*

While different measures were evaluated, the first focal part of this work was dedicated to the experiments on the development of a polymeric compound as a substitute for sulfuric acid (H_2SO_4) in the rubber skimming (or coagulating) process. It would later on lead to its effects on the wastewater treatability by anaerobic system.

Many polymeric compounds were screened in order to induce effective separation of rubber particles from the rubber skim wastewater. The hydroxypropyl methylcellulose polymer (HPMC) was selected and tested according to Loykulnant and Kongkaew (2006). To determine an optimal dose, HPMC was dissolved in deionized water (50 mL) to prepare a polymer solution at various concentrations. The rubber skim latex (200 g), a rejected liquid from centrifuging the fresh latex (marked A (Ⓐ) in Fig. 1), was then mixed with the prepared HPMC solutions to obtain the final concentrations of 0.1–0.8% (w/w), and the mixture was constantly stirred for 1 h to ensure thorough mixing. The mixture was then allowed to stand at room temperature in a separating funnel. The rubber particles then formed a cream phase layer which was clearly separated from the liquid serum phase. It should be noted that serum is typically referred to the liquid part in natural rubber latex. A concentration of the rubber in the cream phase (W_1)

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