Sulfate removal using rubber wood ash to enhance biogas production from sulfate-rich wastewater generated from a concentrated latex factory

Marisa Raketh, Rattana Jariyaboon, Prawit Kongjan, Eric Trably, Alissara Reungsang, Burachat Sripitak, Saowapa Chotisuwan

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2 **rich wastewater generated from a concentrated latex factory**

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ABSTRACT

Skim latex serum (SLS) is high-strength wastewater generated from latex processing. Anaerobic treatment of SLS can be enhanced by reducing the sulfate content, which is an inhibitor in the biogas production system. This study investigates the effect of mixing time and rubber wood ash (RWA) loading on sulfate removal from SLS. The optimum sulfate removal efficiency of 42% was achieved when 10 g/L of RWA was loaded for 10 min. The biogas production efficiency from both desulfated and raw SLS was investigated. The highest 306.36 mL-CH_4/g-COD of methane production yield was achieved from desulfated SLS using RWA loading of 10 g/L (DSLS10), which is 16% higher than the yield generated using raw SLS as a substrate. Moreover, hydrogen sulfide content in the biogas produced by desulfated SLS was two times lower than raw SLS. The results indicate removing sulfate from SLS using RWA before feeding to the anaerobic digestion enhanced biogas production yield and quality.

1. Introduction

Thailand is a leading producer and exporter of natural rubber in several primary products, including concentrated latex, block rubber, and ribbed smoked sheet rubber [1]. The demand for latex in domestic and foreign markets has increased significantly in the concentrated rubber latex industry, which produces concentrated latex as raw material for other downstream industries such as rubber gloves, medical, surgical items, boots, and balloons.

Disc bowl centrifuge is used to produce 60% dry rubber content (DRC) concentrated latex from field latex, which originally contains approximately 30% DRC. The remaining liquid from centrifugation is called 'skim latex', which still contains 4–8% DRC. Skim latex is doped with sulfuric acid to coagulate the remaining rubber particles to produce rubber sheets or rubber blocks [2]. Wastewater from the rubber skimming process, which is non – rubber, is called skim latex serum (SLS). SLS contains high chemical oxygen demand (COD) (35.29 - 43.11 g/L), high sulfate (4,933-7,500 mg/L), and low pH (5.0 – 6.0) [3]. Due to high sulfate content, the factory is facing a serious odor problem with the nearby community. Hence, treating this wastewater to meet the environmental standard is crucial; otherwise, it may result in water, air, and soil pollution.

The anaerobic digestion process is an attractive choice to treat SLS. Some latex factories have replaced the old wastewater treatment method with the anaerobic process. Due to high sulfate content, there is a need to dilute the wastewater before feeding it to the anaerobic digester. Under anaerobic conditions, sulfate-reducing bacteria (SRB) use sulfate as a terminal electron acceptor to suppress organic compounds [4], [5]. The sulfate-reducing bacteria (SRB) are not only competing with methane-producing

73   bacteria (MPB) to use organic substances resulting in lower methane production yield

74   [6]. However, they also produce H_2S, which inhibits methane-producing bacteria

75   (MPB), slowing or stopping methane production [7]. Microorganism inside the biogas

76   system was found inhibited at sulfate concentration higher than 500 mg/L [8].

77   Therefore, sulfate in SLS has to be removed to enhance biogas production yield and

78   lower its sulfate content. Moreover, very high H_2S content (1-3%) is found in the biogas

79   generated from rich sulfate SLS [9].

80   Several methods can be used to remove sulfates from wastewater, such as ion

81   exchange, membrane filtration, biological treatment, chemical precipitation, and

82   adsorption. Ion exchange and membrane filtration are not suitable for removing sulfate

83   from SLS because SLS has high suspended solids, resulting in fouling problems. Also,

84   biological treatment is not suitable for treating SLS because the high sulfate level can

85   inhibit the microorganism [10]. On the other hand, sulfate precipitation with metallic

86   ions and adsorption on metal oxide surface are interesting methods because the sulfate

87   product can be easily separated from the solution.

88   Rubber wood residue is widely utilized as wood fuel in several industries in

89   Southern Thailand. These industries include biomass power plants, smoked rubber,

90   rubber glove, and seafood processing. 2.5-3.0% by weight of rubber wood ash (RWA)

91   is generated from the combustion [11]. RWA is an industrial waste, which needs to be

92   adequately treated because the ash might contain heavy metal and its leachate is

93   alkaline. Intong (2008) has studied sulfate reduction in latex processing wastewater

94   using precipitation with fly ash, lime, and ash from rubber wood. As mentioned above,

95   the study found that sulfate reduction efficiency is 2.4%, 3.21%, and 5.32%,

96   respectively, at the initial sulfate concentration of 8,364 mg/L [12].

97   However, the sulfate remaining in wastewater generated from a concentrated

98 latex factory remained high, while the biogas produced from the wastewater after

99 blending with the ashes have not been investigated. Moreover, using RWA can reduce

100 the sulfate, while the alkaline property of RWA can increase the pH of SLS to attain the

101 desired value for further biogas production. To the best of our knowledge, no study has

102 been carried out on sulfate reduction in SLS using RWA and biogas production potential

103 using desulfated SLS. Hence, this research aims to investigate (i) the suitable RWA on

104 sulfate removal from SLS and (ii) the enhancement of biogas production of the

105 desulfated SLS using anaerobic digestion in batch mode.

106

107 **2. Materials and methods**

108 2.1. Materials

109   Fresh raw SLS was collected from skim latex serum coagulation baths of Top

110 Glove Technology Co., Ltd., Songkhla, Thailand. The SLS collected was stored at 4°C

111 until use to minimize self-biodegradation and acidification (the maximum storage was 1

112 month). RWA was collected from the high-pressure steam boiler of Top Glove Medical

113 (Thailand) Co., Ltd. Songkhla, Thailand. The RWA collected was stored in a

114 temperature room until use. Mesophilic methane inoculum was obtained from the

115 biogas plant of Phasaeng Green Power Co., Ltd., Surat Thani Province, Thailand, while

116 palm oil mill effluent was used as a substrate.

117

118 2.2. Removal of sulfate from SLS

119   The effect of sulfate removal from SLS was studied at different RWA initial

120 loadings of 5, 10, 15, 20, and 30 g/L (DSLS5, DSLS10, DSLS15, DSLS20, and

121 DSLS30). A certain amount of RWA was added to 1 L SLS before stirring continuously

122 with a magnetic bar at a speed of 150 rpm. The influence of mixing time (5, 10, 15, 20,

123 or 30 min) was studied at all RWA loading. After the stirring was stopped at the set

124 time, the ash residue was immediately separated from mixed solutions using a paper

125 filtration (glass microfiber filters). The characteristics of solutions before and after

126 adding RWA were analyzed in terms of pH, sulfate, alkalinity, and element composition

127 were investigated by inductively coupled plasma optical emission spectrometry (ICP-

128 OES). The dried residue was weighed and then the percentage of dissolved RWA was

129 calculated. Raw RWA and the residue RWA from SLS was identified with X-ray

130 fluorescence (XRF) for element composition, X-ray Diffraction (XRD) for crystalline

131 material structure, Fourier transform infrared (FTIR) spectrometer for sulfate functional

132 group, and scanning electron microscope with Quanta 400 (SEM-Quanta) for

133 morphology property.

134 Moreover, the dissolution of RWA in deionized (DI) water was also

135 investigated. 0.1 mol/L of HCl was used for adjusting DI water before mixing with

136 RWA to attain a pH 5.74 similar to the pH of SLS. Sulfate concentration in DI water at

137 different RWA loading of 5, 10, 15, 20, and 30 g/L were analyzed at 10 min mixing time

138 (DI5, DI10, DI15, DI20, and DI30).

139

140 2.3. Biogas production from desulfated SLS

141 After the sulfate removal from SLS, desulfated SLS (the separated solution from

142 RWA and SLS blend) was used as a substrate to produce biogas. The investigation of

143 biogas production potential was performed in a 500 mL serum bottle with 200 mL

144 working volume. Raw SLS and desulfated SLS (DSLS) with various initial solid

145   loadings of RWA (5, 10, 15, 20, and 30 g/L) were used as substrate at initial loading of

146   8.5 g-COD/L and inoculated with 70% v/v of the inoculum (30g-VS/L). A portion of

147   wastewater was replaced by DI water for blank control. The serum bottle was then

148   closed with a bottle cap and purged with nitrogen gas at a flow rate of 1 L/min for 3 min

149   to ensure anaerobic conditions before incubated at 35 ºC. All experiments were carried

150   out in triplicate. The headspace gas was collected every 24 h for biogas volume and

151   biogas composition (methane, carbon dioxide, hydrogen sulfide) determination. pH,

152   COD, total kjeldahl nitrogen (TKN), total alkalinity, total solid (TS), volatile solid (VS),

153   ash, total organic carbon (TOC), and sulfate in the substrate were investigated. The

154   anaerobic digestion process was ceased when methane production was constant. The pH

155   and sulfate of effluent were investigated afterward.

156

157   2.4. Analytical methods

158   The biogas production volume was measured through water displacement.

159   Methane, carbon dioxide, and hydrogen sulfite contents in biogas were measured using

160   gas chromatography (Shimadzu GC 14A equipped with a thermal conductivity detector)

161   fitted with a 2.5 m Porapak S column with Hayesep Q (80/100). Helium was used as a

162   carrier gas at a flow rate of 30 mL/min. The injection port, oven, and detector

163   temperatures were set at 100, 60, and 110ºC, respectively. A 0.5 mL sample of the gas

164   was injected in triplicate. The procedures described in the standard methods [13] were

165   applied to determine the pH, COD, TKN, total alkalinity, TS, VS, ash, and sulfate. TOC

166   was investigated with TOC-Liquid: multi N/C 3100 TOC analyzer (Analytik Jena).

167   Statistically significant differences in the results were determined using a one-way

168   analysis of variance) ANOVA) in SPSS v26.0 (IBM, USA).

169

3. Results and discussion

3.1. Characteristics of SLS and RWA

Some physicals and chemical characteristics of the SLS collected were analyzed. The result of the analysis carried out is presented in Table 1. High VS of 32-37 g/L and COD of 33-43 g/L indicated a high organic compound content. Therefore, SLS wastewater must be adequately treated before releasing into the environment. The high organic carbon in SLS confirms that it is a promising substrate for producing methane through anaerobic digestion. Nevertheless, since sulfuric acid was used to recover rubber in skim latex, it resulted in a low SLS pH (5.22-5.78), lower than the favorable range for methanogens bacteria growth pH of 7-8.5 [14]. Anaerobic digestion will be inhibited when the pH of the system falls below 6.0. This is because methanogens bacteria do not grow at a low pH and might stop methane production. Therefore, an increase in pH is needed to obtain efficient biogas production from SLS. Sulfate concentration in SLS ranged 4,933 – 7,500 mg/L, which could cause an inhibition on the performance of anaerobic digestion. Hence, to enhance the biogas production yield and quality, sulfate contained in SLS should be first reduced. Alkalinity is the characteristic that reveals the capacity of the buffer to maintain pH drop during the acidogenesis process. The greater the alkalinity, the more stable the anaerobic digestion. Reungsang et al. (2019) reported that the alkalinity of the anaerobic digestion system should not be lower than 2,000 mg-$CaCO_3$/L [15]. Alkalinity range of 2,867-3,287 mg-$CaCO_3$/L was found in SLS, indicating a sufficient buffering capacity.

Table 1 Some physical and chemical characteristics of Skim Latex Serum (SLS).

Parameters	Unit	Value
pH		5.22 - 5.78
TS	(g/L)	33.28 - 44.74
VS	(g/L)	32.64 - 37.94
Ash	(g/L)	6.30 - 7.41
COD	(g/L)	33.02 - 43.11
TOC	(g/L)	14.25 – 15.12
Sulfate	(mg/L)	4,933 – 7,500
Alkalinity	(mg-CaCO$_3$/L)	2,867 - 3,287
TKN	(mg/L)	1,548 – 1,588

193

194   Ca and Si were the main elements found in RWA. K, S, Cl, Mg, and Fe were

195 found in small amounts while a little amount of heavy metal was also observed (Table

196 2). The chemical composition of the ash depends on the composition of fuelwood and

197 combustion temperature. Therefore, in this study, RWA's composition is slightly

198 different from previous studies [16,17].

199

200 **Table 2** Elements composition of raw RWA residues from DSLS10 and DI10.

Element	Composition in RWA (% w/w)		
	Raw RWA	Residue from DSLS10	Residue from DI10
Fluorine (F)	0.178	0.155	0.222
Sodium (Na)	0.068	0.081	0.076
Magnesium (Mg)	2.045	2.171	3.237
Aluminum (Al)	0.950	1.278	1.589
Silicon (Si)	10.529	13.277	18.654

Phosphorus (P)	1.099	2.120	1.879
Sulphur (S)	5.770	5.907	2.195
Chlorine (Cl)	3.151	0.282	0.183
Potassium (K)	6.431	4.146	4.729
Calcium (Ca)	21.825	22.398	19.421
Titanium (Ti)	0.137	0.151	0.192
Chromium (Cr)	0.011	0.013	0.008
Manganese (Mn)	0.298	0.356	0.442
Iron (Fe)	1.491	1.726	1.877
Nickel (Ni)	0.006	0.009	0.006
Copper (Cu)	0.028	0.029	0.038
Zinc (Zn)	0.046	0.754	0.069
Bromine (Br)	0.006	0.000	0.000
Rubidium (Rb)	0.042	0.036	0.040
Strontium (Sr)	0.059	0.074	0.073
Zirconium (Zr)	0.021	0.027	0.027
Lead (Pb)	0.009	0.012	0.044
Total mass (%)	54.200	55.000	55.000

*The results were normalized to 100%, including CHNO from the sample burning.

*RWA is rubber wood ash, DSLS10 is desulfated SLS using RWA loading of 10 g/L and DI10 is deionized water using RWA loading of 10 g/L.

201 ## 3.2. Using RWA to remove sulfate from SLS

202 ### 3.2.1 Effect of RWA loading and mixing time

203 As shown in Fig. 1a, sulfate concentration in SLS decreased from the initial

204 concentration of 4,933 mg/L after RWA was added. After 10 min of mixing, sulfate

205 concentration in SLS did not significantly decrease for RWA loadings of 5 and 10 g/L

206 because solubility equilibrium was reached. While at RWA loading higher than 10 g/L,

207 the sulfate concentration was constant after 5 min. The maximum sulfate removal

208   efficiency of 42% was found in SLS treated with 10 g/L RWA. The sulfate removal

209   efficiency of RWA loading at 5 g/L was lower than 10 g/L. This might have occurred

210   either due to the number of cations that could precipitate or the low surface area for

211   sulfate adsorption. On the contrary, when RWA loading was higher than 10 g/L, the

212   sulfate removal efficiency was dropped. It might be because the alkaline leachate from

213   the metal oxide in RWA increased the pH of SLS to 6.5-8.2 (as shown in Fig.1b). At a

214   high pH, carbon dioxide in the atmosphere can be easily dissolved into a solution to

215   form bicarbonate or carbonate ions. The solubility product constant (K_{sp}) of $CaCO_3$

216   (1.0×10^{-8}) is lower than $CaSO_4$ (2.0×10^{-4}) [18]; therefore, calcium can easily react to

217   carbonate than sulfate. It was observed that sulfate was also leached from RWA into DI.

218   The more the RWA loading, the more the sulfate released (Fig. 1c). This might also be

219   why the sulfate concentration remaining in SLS was higher when a higher RWA was

220   loaded. The pH of the mixing of DI water with RWA at 10 min mixing time was also

221   investigated and the result is illustrated in Fig. 1d. The pH range was 11.63-12.58,

222   which is higher than the DSLS.

223   Alkalinity is an important parameter to maintain pH during the anaerobic

224   digestion process. The alkalinity of SLS 10 min blending with RWA was investigated,

225   as shown in Fig.1b. It was found that SLS alkalinity increased to 2,950-3,650 mg/L

226   when RWA was loaded, indicating that the further utilization of DSLS for biogas

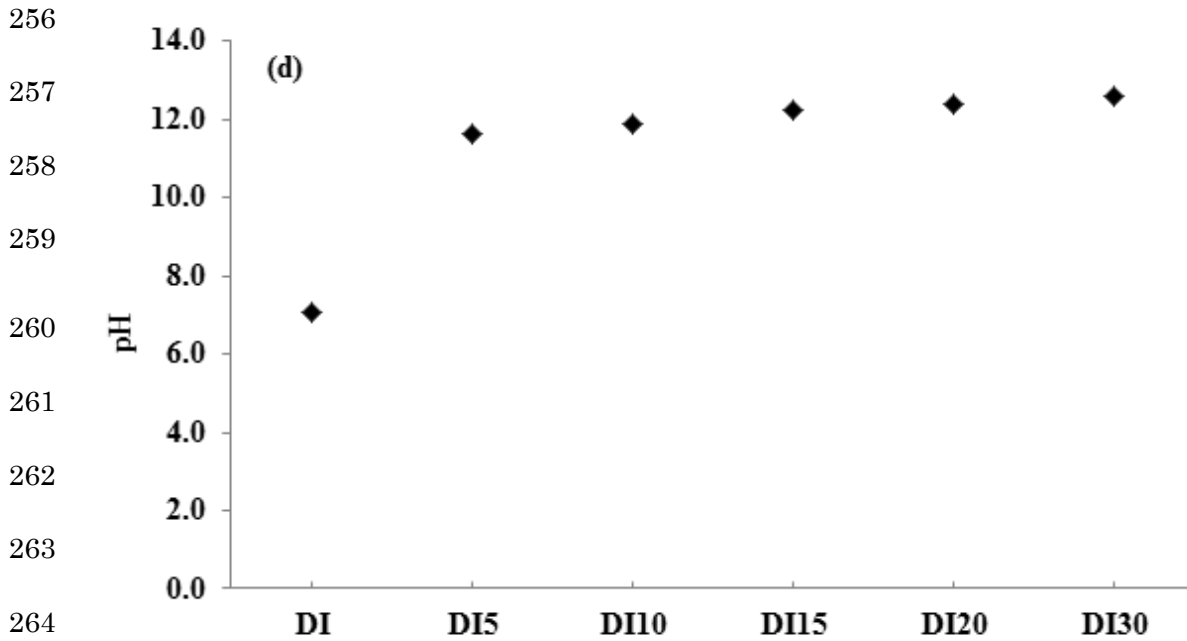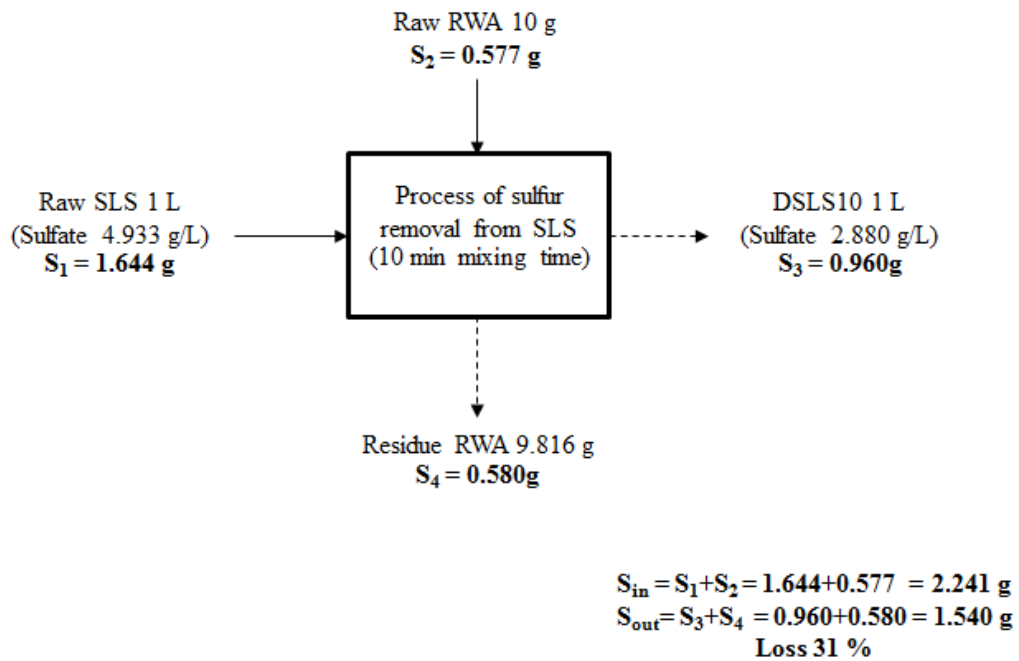227   production could be enhanced.

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(a)

(b)

(c)
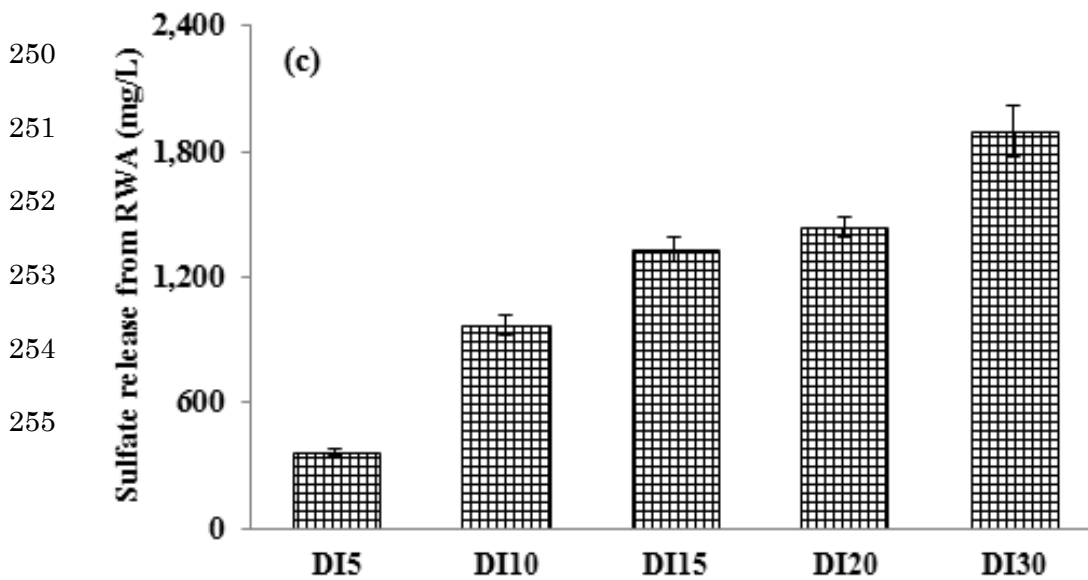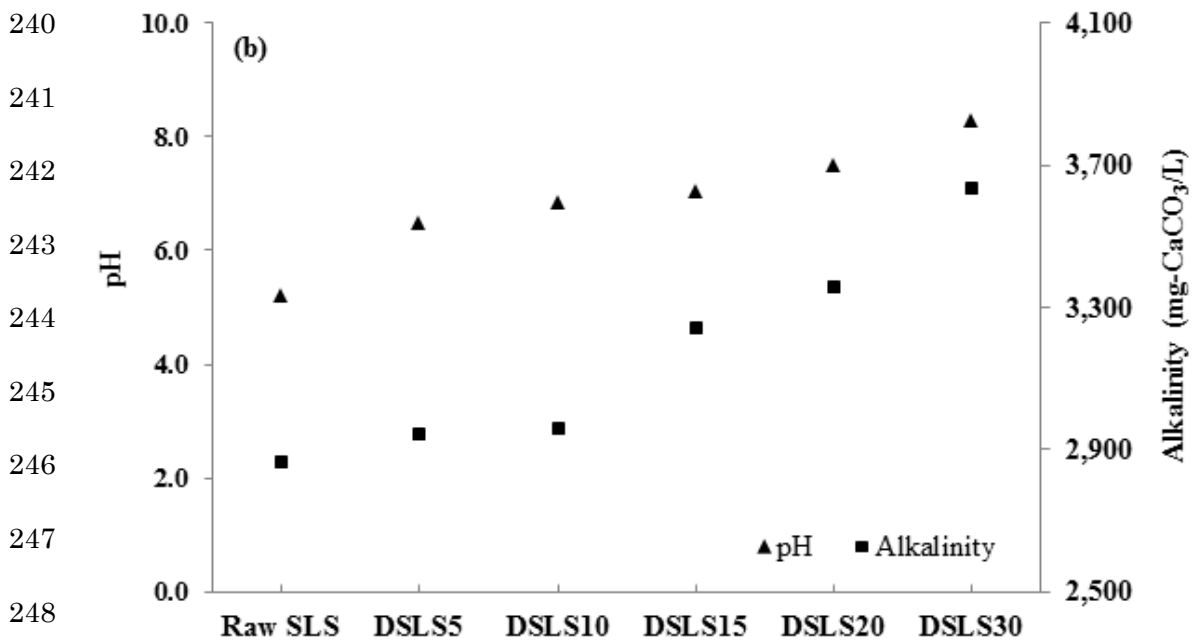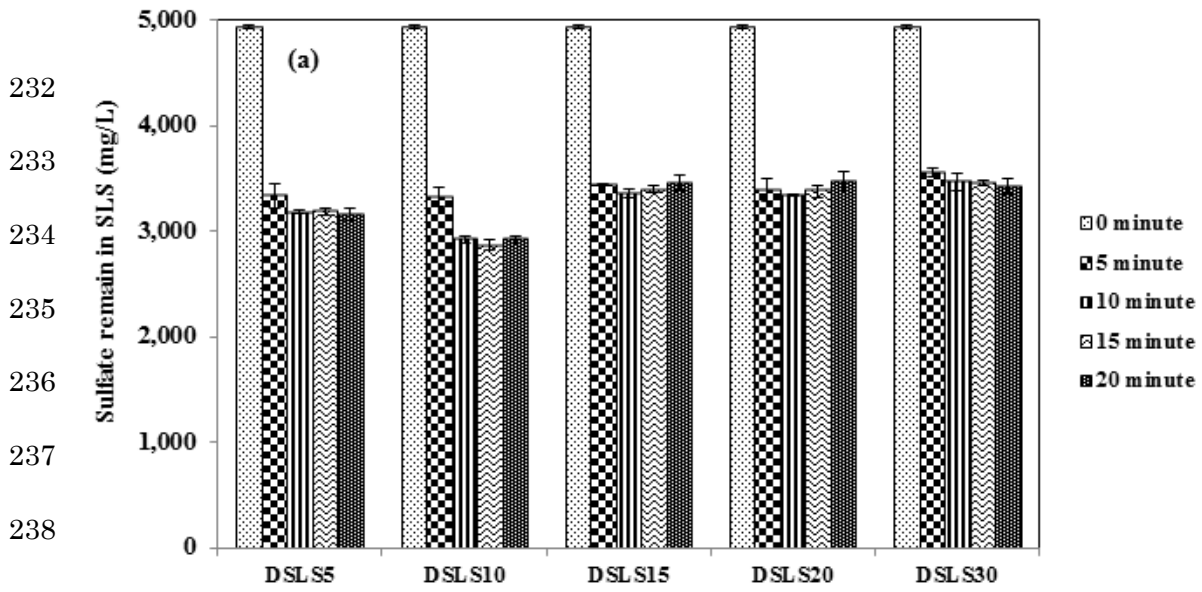
Fig. 1 The removal of sulfate after mixing with RWA: (a) sulfate concentration in DSLS, (b) pH and alkalinity of SLS at 10 min mixing time, (c) sulfate concentration in DI with RWA at 10 min mixing time, and (d) pH of DI with RWA at 10 min mixing time.

Sulfur mass balance was calculated based on RWA initial loading of 10 g/L and 10 min mixing time. The calculation result is presented in Fig. 2. Two input sulfur streams comprised 1.644 g sulfur in raw SLS and 0.577 g sulfur in RWA. After 10 min mixing time, sulfur in SLS decreased to 0.960 g. While sulfur contained in residue RWA was a little higher than its initial loading. The overall sulfur mass calculation resulted in an imbalance with approximately 31% sulfur mass loss from the output streams. This loss might have occurred due to experimental errors such as measuring a small quantity of ash in the solution, estimating the element in RWA and residue RWA using XRF, and sulfate determination using the turbidimetric method.

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Raw RWA 10 g
$S_2 = 0.577$ g

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Raw SLS 1 L   Process of sulfur   DSLS10 1 L
(Sulfate 4.933 g/L)   removal from SLS   (Sulfate 2.880 g/L)
$S_1 = 1.644$ g   (10 min mixing time) $S_3 = 0.960$g

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Residue RWA 9.816 g
$S_4 = 0.580$g

287

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$S_{in} = S_1 + S_2 = 1.644 + 0.577 = 2.241$ g
$S_{out} = S_3 + S_4 = 0.960 + 0.580 = 1.540$ g
Loss 31 %

289

290   **Fig. 2** Sulfur mass distribution of DSLS10.

291

292   3.2.2. Sulfate adsorption as the main mechanism

293   Several dissolved elements in raw SLS, DSLS10, and DI10 were detected, as

294   shown in Table 3. Ca, Mg, Na, P, K, and Zn mainly appeared in raw SLS, whereas Co,

295   Cu, Fe, Mn, and Ni were found in small amounts. After RWA was added into raw SLS,

296   most of the elements solution increased due to leaching from RWA. The experiment of

297   DI10 was carried out to investigate the dissolvable element in RWA. It was found that

298   Ca, Mg, and K was the main element while Co, Cu, Fe, Mn, Na, Ni, P, and Zn were

299   present in little amounts. This indicates that the disappearance of sulfate was not mainly

300   from the precipitation with metal ions. Therefore, the possible mechanism to describe

301   the removal of sulfate from the SLS solution might be adsorption on the RWA surface.

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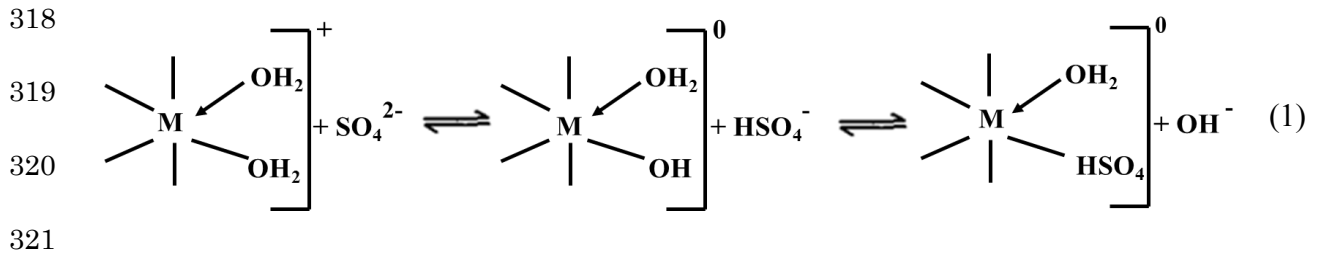303   **Table 3** Dissolved elements in raw SLS, DSLS10, and DI10.

Dissolved elements	Concentration (mg/L)		
	Raw SLS	DSLS10	DI10
Calcium (Ca)	12.91 ± 0.05	302.40 ± 6.56	275.00 ± 5.57
Cobalt (Co)	< 0.003	< 0.003	< 0.003
Copper (Cu)	< 0.016	0.18 ± 0.02	< 0.016
Iron (Fe)	0.60 ± 0.02	1.34 ± 0.02	0.30 ± 0.01
Magnesium (Mg)	32.41 ± 0.06	66.41 ± 0.10	12.61 ± 0.29
Manganese (Mn)	0.14 ± 0.00	2.69 ± 0.00	0.17 ± 0.00
Sodium (Na)	10.62 ± 0.02	12.22 ± 0.09	2.21 ± 0.07
Nickel (Ni)	< 0.005	0.06±0.01	< 0.005
Phosphorus (P)	223.90 ± 2.64	209.20 ± 1.56	1.33 ± 0.07
Potassium (K)	3,728.00 ± 47.85	4,015.00 ± 59.26	403.80 ± 4.47
Zinc (Zn)	295.70 ± 3.93	240.80 ± 2.88	< 0.003

304

305   The remaining elements composition in RWA residue of DSLS10 and DI10 were

306 analyzed and the result presented in Table 2. After RWA was added into SLS and DI

307 water, the fraction of high solubility elements such as K and Cl decreased. In contrast,

308 the fraction of the element with low solubilities such as Al, Si, Zn, P, Fe, Sr, and Pb

309 increased. It can also be observed that the sulfur element found in the ash residue of the

310 SLS mixture was a bit higher than in raw RWA and almost 3 times higher than it

311 appeared in the ash residue of the DI water mixture. This result confirms that sulfate

312 transferred from the SLS phase and adsorbed on the surface of RWA.

313   Ishiguro et al. (2006) reported that sulfate's adsorption mechanism on a volcanic

314 ash soil surface was multilayer adsorption through van der Waals attraction [19]. The

315 mechanism of sulfate adsorption was proposed, as shown in Equation (1) [20]. M is the

316 metal at the surface. The adsorption of sulfate occurs by ligand exchange with the OH

317 group [21].

318

$$\left[\begin{array}{c} \diagdown \ | \ \diagup \diagup \ \text{OH}_2 \\ \text{M} \\ \diagup \ | \ \diagdown \text{OH}_2 \end{array} \right]^{+} + SO_4^{2-} \rightleftharpoons \left[\begin{array}{c} \diagdown \ | \ \diagup \diagup \ \text{OH}_2 \\ \text{M} \\ \diagup \ | \ \diagdown \text{OH} \end{array} \right]^{0} + HSO_4^{-} \rightleftharpoons \left[\begin{array}{c} \diagdown \ | \ \diagup \diagup \ \text{OH}_2 \\ \text{M} \\ \diagup \ | \ \diagdown \text{HSO}_4 \end{array} \right]^{0} + OH^{-} \quad (1)$$

Also, the functional groups of raw RWA and RWA residue after mixing with

SLS were tested using FTIR, as shown in Fig. 3. The asymmetric stretching vibration of

the carbonate (CO_3^{2-}) band was assigned to a strong band near 1440 cm^{-1}. The peak

observed at 875 cm^{-1} was due to out-of-plane bending vibration (CO_3^{2-}) of carbonate. A

weak doublet was observed in the lower region at 678 and 596 cm^{-1}. The observation

might have resulted from the in and out-of-plane bending (SO_4^{2-}) vibration of sulfate

[22]. The FTIR spectra indicated that there were sulfate and carbonate compounds in

raw RWA (a) and the residue of DSLS10 (b). Moreover, the residues peak intensity was

higher than raw RWA, indicating a higher sulfate and carbonate deposit.
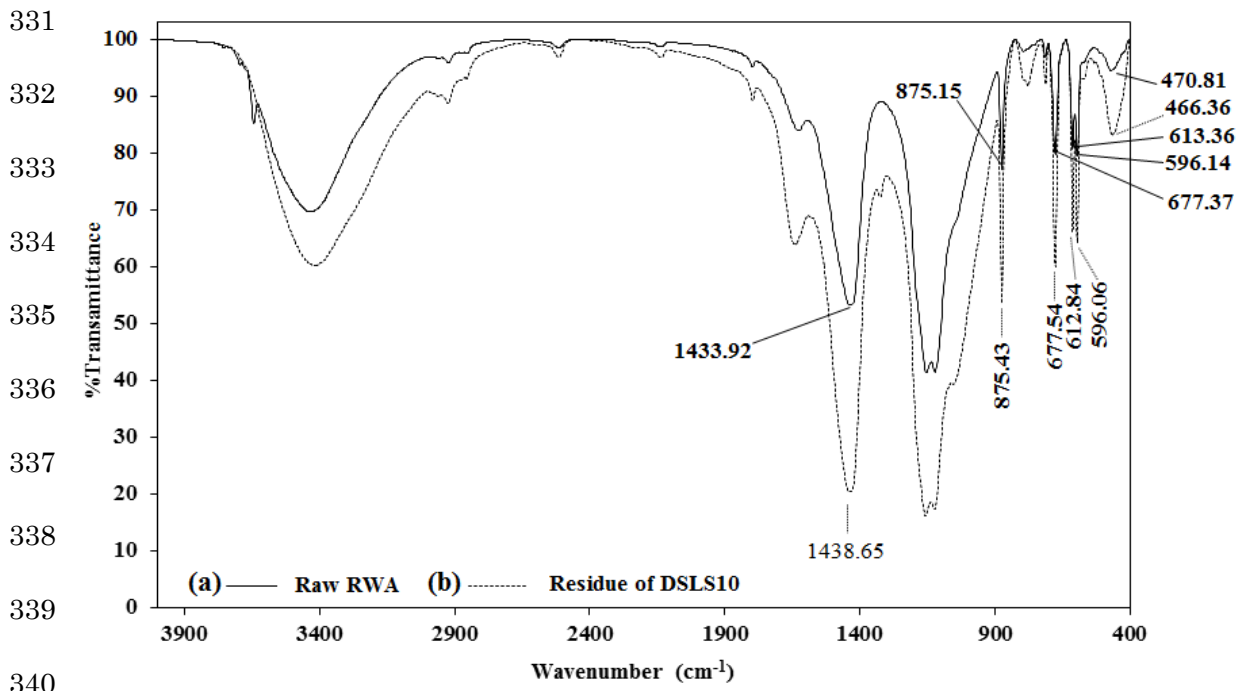
Fig. 3 FTIR spectra: (a) Raw RWA and (b) residue of DSLS10.

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343   Moreover, XRD analysis was also carried out to confirm the surface deposit

344   structure of RWA. XRD patterns of raw RWA and residue RWA are shown in Fig. 4. It

345   confirms that both raw RWA and residue RWA contains $CaSO_4$. However, the $CaSO_4$

346   crystals structure (lattice constant) of raw RWA and residue were different. The $CaSO_4$

347   (anhydrite) of raw RWA has an Amma space group with a lattice constant of a=7.006 Å,

348   b=6.998 Å, and c=6.245 Å. While for residue RWA, the space group of $CaSO_4$

349   (anhydrite, syn) was Bbmm with lattice constant a=6.240 Å, b=6.980 Å, and c=6.970 Å.

350   The lattice constant was affected by several factors such as the surface reconstruction,

351   recrystallization, precipitation and process condition, pressure, temperature [23], [24],

352   and solvent [25]. Therefore, the structure change of $CaSO_4$ found in the residue RWA

353   after mixing with SLS might confirm that the sulfate removal occurred by being

354   adsorbed on the RWA surface.

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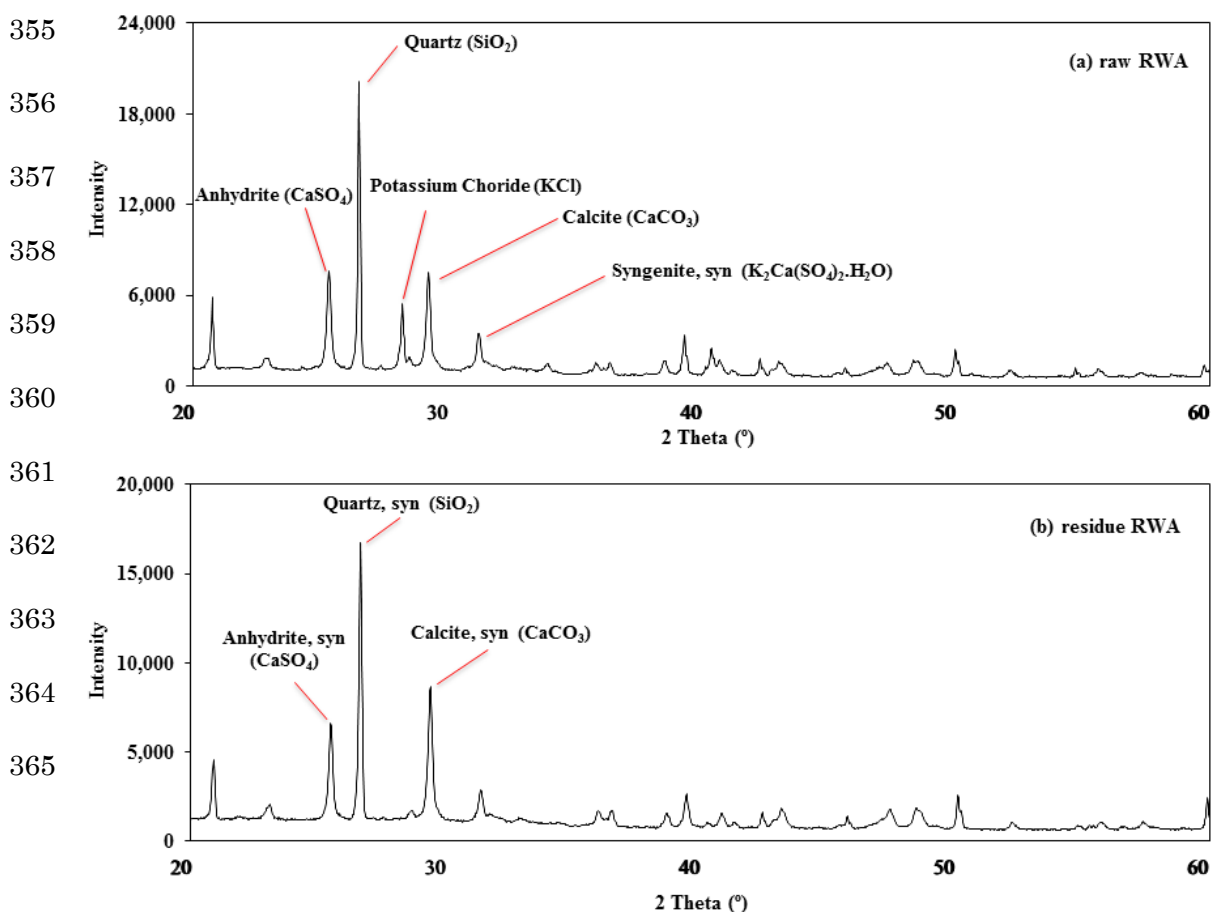
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367 **Fig**. **4** XRD patterns: (a) raw RWA and (b) residue RWA.

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369   Aside from FTIR spectra and XRD pattern, the morphology of RWA was studied

370 by scanning electron microscopes with Quanta 400 (SEM-Quanta), and the difference

371 between raw RWA and RWA residue after mixing with SLS was observed (Fig. 5a and

372 b). It was found that from the scanning electron micrographs, the deposit and many

373 irregularly structured inorganic particles were found on the residue of DSLS10 surface

374 as present in Fig. 5b. In contrast, raw RWA had a few deposits on its surface (Fig. 5a).

375 Thus, FTIR spectra and Scanning electron microscopy (SEM) photographs confirmed

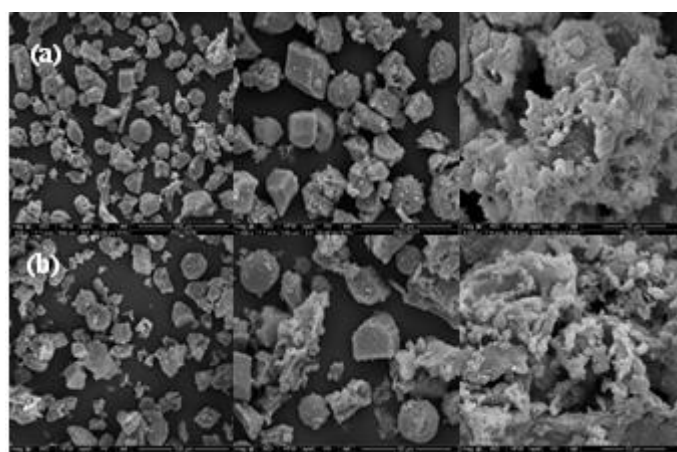376 that the SO_4 was adsorbed onto the surface.

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384 **Fig. 5** Scanning electron microscopy (SEM) photographs, 500X (left), 1000X (middle)

385 and 3500X (right): (a) raw RWA, and (b) residue of DSLS10.

386

387   Inthong (2008) reported that sulfate from latex rubber industry wastewater could

388 be reduced using fly ash from Phuket incinerator, lime, and ash from rubber wood. The

389 result showed that sulfate reduction efficiency was 2.4%, 3.21%, and 5.32%,

390 respectively, at the initial sulfate concentration of 8,364 mg/L. When fly ash, lime, and

391 rubber wood ash were loaded at 1 g/L, the ash from rubber wood had a high adsorption

392 ability than other materials [12]. The sulfate removal efficiency retrieved from In Thong

393 (2008) was about 10 times lower than the efficiency recorded in this study. This is

394 because the study of In Thong (2008) loaded less ash, which is 10% lower than this

395 current study. Moreover, the removal of sulfate in sulfate-rich laboratory wastewater

396 using $CaCl_2$ was studied by Benatti et al. (2009). They reported that Ca^{2+} at a

397 concentration of 80 g/L was precipitated with sulfate and achieved a sulfate removal

398 efficiency of over 99%. However, the highest sulfate removal efficiency obtained in this

399 study was only 42% due to the solubility limit of RWA [26]. Using an RWA supplement

400 with another calcium compound might give more sulfate removal efficiency. However,

401 an additional chemical cost is required.

402

403 3.3. Desulfated SLS for enhanced biogas production

404   The RWA residue was separated from SLS before further use to produce biogas

405 to prevent sulfate desorption and reduce total solid content. The biogas production

406 potential of raw SLS and desulfated SLS (DSLS) using different RWA loading was

407 carried out. The cumulative biogas production in the mesophilic anaerobic condition is

408 presented in Fig.6a. Less than 1 day of lag time was found in all substrate types because

409 the substrate was diluted to 8.5 g-COD/L initial loading. As expected, DSLS was a

410 superior substrate for biogas production compared to raw SLS. After 12 days of the

411 anaerobic digestion process, a nearly steady biogas production rate was observed. This

412 indicated that the organic matter in SLS was easily biodegraded.

413   Fig.6b shows the average methane content in biogas was between 58.2 – 74.8%,

414 indicating a favorable anaerobic digestion pathway was performed. The percentage of

415   methane in biogas probably presents the metabolic pathways as shown in Equation (2)

416   and (3) [27], respectively. As shown in Fig.6b, the profile of methane content in

417   produced biogas during anaerobic digestion of all substrates (raw SLS and DSLS) were

418   similar. Thus, the increase in gas production in anaerobic digestion is mainly not due to

419   changing metabolic pathways.

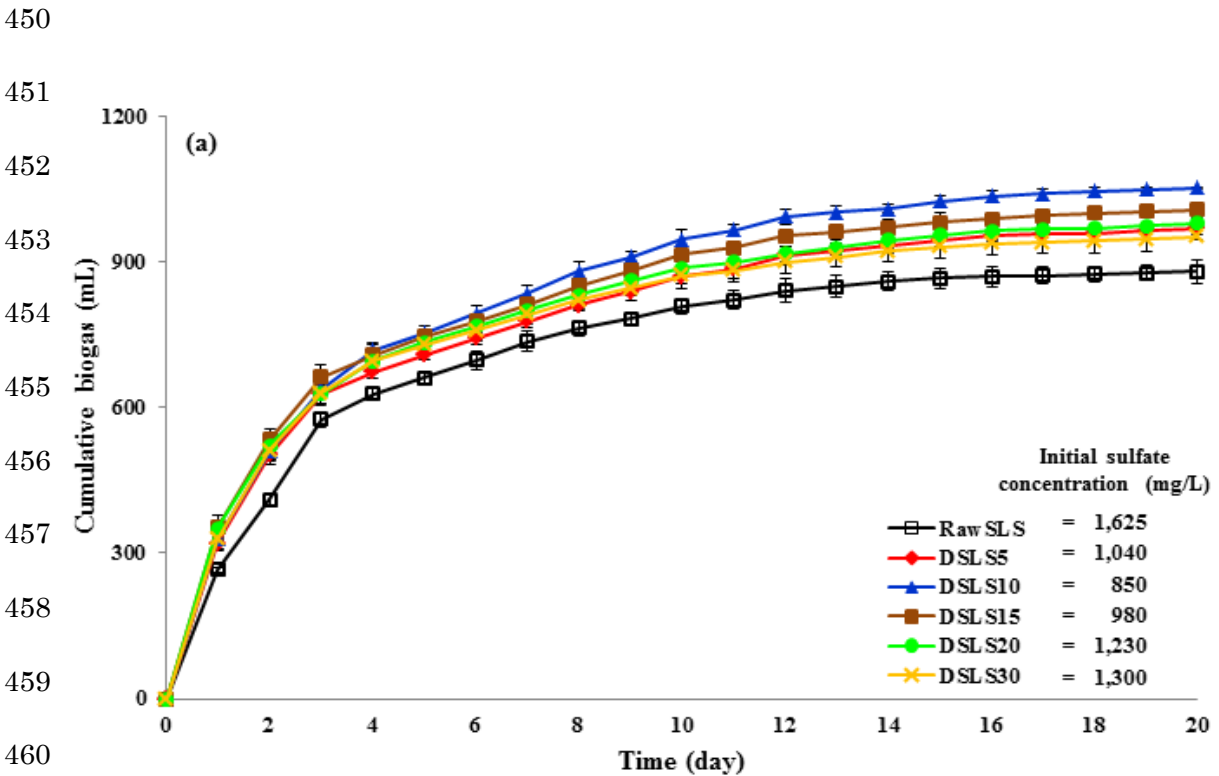420   Acetoclastic methanogenesis pathway: $\quad$ Acetate $\longrightarrow CH_4 + CO_2$ $\qquad\qquad$ (2)

421   Hydrogenotrophic methanogenesis pathway: $H_2 + CO_2 \longrightarrow CH_4$ $\qquad\qquad$ (3)

422   Methane production yield was also calculated and shown in Fig. 6c. It can be

423   seen that raw SLS and DSLS using different RWA loading gave a significantly different

424   methane production yield. Desulfated SLS using RWA 10 g/L (DSLS10) gave the

425   highest cumulative methane 520 mL and a maximum methane yield of 306.36 mL-

426   CH_4/g-COD corresponding to 11.00 kJ/g-COD of energy production. The maximum

427   methane yield achieved in this study was equal to 77.58% of theoretical yield (350 mL-

428   CH_4/g-COD at STP). Raw SLS gave the lowest methane yield production of 264.38

429   mL-CH_4/g-COD, which was 16% lower than the DSLS. The result confirms that RWA

430   does not reduce the sulfate to lower than the inhibition level (500 mg/L) due to the

431   equilibrium limit and sulfate contained in RWA released into SLS. However, RWA

432   obviously enhanced the biogas production.

433   H_2S concentration in biogas was monitored and illustrated in Fig. 6d. H_2S was

434   detected after the 3rd day of the anaerobic digestion process because microorganisms

435   need time to acclimatize to a new environment. Raw SLS digestion generated the

436   highest H_2S concentration of 52,299 ppm on the 11th day of the anaerobic digestion

437   process. At the same time, the maximum H_2S concentration of 28,000 ppm was

438   generated from DSLS10 digestion. Visser et al. (1996) reported that at a pH below 6.9

439 (acidic condition), MPB would outcompete SRB. Whereas, at a pH above 7.7 (alkaline

440 condition), SRB will perform better than MPB [28]. The pH's influent range of

441 DSLS15, DSLS20, and DSLS25 was 7.69-7.75, respectively, while DSLS5 and

442 DSLS10 were 7.49-7.60 (as shown in Table 4). Therefore, H_2S concentration in biogas

443 produced from DSLS15, DSLS20, and DSLS25 was higher than in DSLS5 and

444 DSLS10.

445 Sulfate and COD in the influent and effluent were also monitored and are presented

446 in Table 4. It was fond that sulfate removal efficiency (84-88%) achieved from all SLS

447 digestion were similar. While more than 70 % COD removal was observed for DSLS

448 digestion. Most especially, DSLS10 gave the highest COD removal (76.37%), while

449 65.90 % of COD removal was achieved from raw SLS.

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(b)

Methane concentration (%)

Legend: □ Raw SLS ◆ DSLS5 ▲ DSLS10 ■ DSLS15 ● DSLS20 ✕ DSLS30

Time (day)

(c)

Methane production yield (mL/g-COD)

Raw SLS (a) — DSLS5 (b) — DSLS10 (c) — DSLS15 (d) — DSLS20 (e) — DSLS30 (f)

(d)

Hydrogen sulfide concentration (ppm)

Legend: □ Raw SLS ◆ DSLS5 ▲ DSLS10 ■ DSLS15 ● DSLS20 ✕ DSLS30

Time (Day)

Fig. 6 Biogas production: (a) Cumulative biogas, (b) Methane concentration, (c)

Methane production yield, and (d) Hydrogen sulfide concentration.

490

Table 4 pH, sulfate and COD of the influent and effluent in the biogas production

system.

Substrate	pH		Sulfate (mg/L)			COD (g-COD)		
	Influent	Effluent	Influent	Effluent	RE[*]	Influent	Effluent**	RE[*]
Raw SLS	7.27 ± 0.03	7.34 ± 0.01	$1{,}625 \pm 32$	250 ± 11	84.42 ± 2.0	1.72 ± 0.01	0.59 ± 0.02	65.90 ± 1.0
DSLS5	7.49 ± 0.05	7.33 ± 0.02	$1{,}040 \pm 20$	145 ± 8	86.11 ± 0.5	1.72 ± 0.01	0.46 ± 0.02	73.28 ± 2.0
DSLS10	7.60 ± 0.02	7.34 ± 0.01	850 ± 23	102 ± 5	88.00 ± 1.0	1.72 ± 0.01	0.41 ± 0.01	76.37 ± 1.5
DSLS15	7.69 ± 0.03	7.34 ± 0.02	980 ± 19	145 ± 9	86.00 ± 1.5	1.72 ± 0.01	0.44 ± 0.03	74.38 ± 2.5
DSLS20	7.73 ± 0.01	7.35 ± 0.01	$1{,}230 \pm 15$	149 ± 7	87.89 ± 2.0	1.72 ± 0.01	0.52 ± 0.04	70.05 ± 1.0
DSLS30	7.75 ± 0.01	7.37 ± 0.03	$1{,}300 \pm 25$	170 ± 10	86.92 ± 1.0	1.72 ± 0.01	0.47 ± 0.02	72.70 ± 1.5

*RE = Removal efficiency

**Remaining COD in the effluent was calculated from COD balance.

493

Additional essential mineral leached from RWA is one reason for the improvement

in methane production from DSLS. Fe acts as an electron acceptor and donor involving

energy metabolism and can be utilized by methanogens to reduce CO_2 to CH_4 [29]. Ni is

a crucial coenzyme harbored in methanogens [30]. Ca and Mg, the coenzyme in the

anaerobic process [15] found in DSLS, did not exceed the limit value of 2500 mg/L and

1,000 mg/L, respectively. Co, Cu, Fe, and Ni were also lower than the concentration

inhibits to microorganisms (2.8, 1, 5.5, and 2 mg/L, respectively). While, K, P, and Zn

presented in raw SLS was over the recommended levels (3.9 mg/L [15], 2.5 mg/L [15],

and 12.5 mg/L [31], respectively). After RWA was added to SLS, a decrease in P and

Zn's amount occurred due to the adsorption on the RWA surface or precipitation with

504   anions. However, fermenter elements will be typically diluted in a practical continuous

505   process, thus lowering their inhibition effects. According to Fig.1 and Table 3 when

506   RWA loading into SLS increased, the pH, alkalinity, and mineral ions increased to a

507   more favorable level for the related anaerobic microorganisms. However, the biogas

508   did not increase due to the increase in RWA loading. Hence, the increase in gas

509   production was mainly enhanced due to the sulfate reduction in SLS.

510   Furthermore, pH had a significant role in microbial growth in anaerobic digestion.

511   It should be kept at a neutral range due to the sensitivity of microorganisms [32]. Batch

512   experiment was performed in this study using 70% inoculum to ensure sufficient

513   microorganism exists in the biomethane production potential (BMP) protocol [33].

514   Furthermore, since the inoculum used had a pH of 7.91, all experiments had an

515   appropriate initial pH range of 7.27-7.93. However, in the practical aspect, higher

516   organic loading will be used to obtain higher productivity. Therefore, when raw SLS is

517   used as a substrate, the fermenter's pH will be lower than the pH observed in this

518   experiment and may be lower than the optimum level, leading to a lower methane

519   production yield. When RWA is used to remove sulfate from SLS, the pH of DSLS

520   increases; thus, an external chemical is not necessarily used to keep the pH in the

521   fermenter for efficient biogas production.

522   A recent site visit to some concentrated latex factories producing biogas using

523   wastewater revealed that it is first diluted to reduce sulfate concentration and adjust pH

524   before feeding to the biogas reactor. Thus, using RWA is a promising method to

525   enhance wastewater treatment and biogas production since RWA can reduce sulfate in

526   SLS, increase pH to methanogens for favorable environment growth, and achieve

527   nutrients needed by microorganisms.

528   On the other hand, the RWA residue from the sulfate removal process was stable

529 because the alkaline is leached out. The RWA residue can produce fertilizers because it

530 provides many trace elements that plants need to thrive without causing alkaline soil

531 problems. It can also be used as a soil amendment to increase soil physicochemical

532 characteristics [34]. According to Notification of The National Environmental Board

533 (Thailand) No.25, B.E.2547: The Soil quality standard, soil should contain for example

534 Cr < 300 mg/kg, Pb < 400 mg/kg, Ni <1600 mg/kg, Mn < 1800 mg/kg, Hg < 23 mg/kg,

535 As < 23 mg/kg, Cd < 37 mg/kg. It can be seen that all heavy metals found in RWA

536 residue have a concentration lower than the regulation except Mn, which was found to

537 be 0.356 % (3560 mg/kg) [35]. Hence, RWA residue could be used as a soil amendment

538 after blending with soil or other organic residues in the proper portion.

539   After biogas upgrading, it can be used as biofuel similar to the application of

540 natural gas. At the same time, effluent from biogas is commonly used in agricultural

541 cultivation [36]. Consequently, this conceptual scheme would combine waste

542 transformation to energy with zero waste release and a mightily reduced CO_2 emission.

543

4. Conclusions

545   RWA can be utilized to remove sulfate in SLS with the maximum removal

546 efficiency of 42%. Adsorption is a possible main mechanism to describe sulfate

547 removal. Asides from sulfate reduction, the pH and alkalinity in SLS were also

548 increased to meet the desired level for efficient anaerobic SLS treatment to produce

549 biogas after RWA was blended. Biogas production from the anaerobic digestion of

550 desulfated SLS with 10 g/L RWA loading was 16% higher than raw SLS. This study

551 revealed the promising concept for practical application to treat rich sulfate wastewater

552   generated from a concentrated latex factory.

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