



HAL
open science

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

► To cite this version:

Marisa Raketh, Rattana Jariyaboon, Prawit Kongjan, Eric Trably, Alissara Reungsang, et al.. Sulfate removal using rubber wood ash to enhance biogas production from sulfate-rich wastewater generated from a concentrated latex factory. *Biochemical Engineering Journal*, 2021, 173, pp.108084. 10.1016/j.bej.2021.108084 . hal-03319199

HAL Id: hal-03319199

<https://hal.inrae.fr/hal-03319199>

Submitted on 28 Jul 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

3

4 **Marisa Raketh^{1,3}, Rattana Jariyaboon^{2,3,*}, Prawit Kongjan^{2,3}, Eric Trably⁴,**
5 **Alissara Reungsang⁵, Burachat sripitak^{1,3}, Saowapa Chotisuwan²**

6

7 ¹ Energy Technology Program, Faculty of Engineering, Prince of Songkla University,
8 Hat Yai, Songkhla, 90112, Thailand

9 ² Department of Science, Faculty of Science and Technology, Prince of Songkla
10 University (PSU), Pattani 94000, Thailand

11 ³ Bio-Mass Conversion to Energy and Chemicals (Bio-MEC) Research Unit, Faculty of
12 Science and Technology, Prince of Songkla University (PSU), Pattani 94000, Thailand

13 ⁴ INRAE, Univ Montpellier, LBE, Narbonne, France

14 ⁵ Research Group for Development of Microbial Hydrogen Production Process from
15 Biomass, Khon Kaen University, Khon Kaen 40002, Thailand

16

17 *corresponding author at: Department of Science, Faculty of

18 Science and Technology, Prince of Songkla University (PSU), Pattani 94000,

19 Thailand. Tel.: +66 73 313928-50 ext1988, mobile: +66 808721260.

20 E-mail address: rattana.sa@psu.ac.th (R. Jariyaboon).

21

22

23

24

25 **ABSTRACT**

26 Skim latex serum (SLS) is high-strength wastewater generated from latex
27 processing. Anaerobic treatment of SLS can be enhanced by reducing the sulfate
28 content, which is an inhibitor in the biogas production system. This study investigates
29 the effect of mixing time and rubber wood ash (RWA) loading on sulfate removal from
30 SLS. The optimum sulfate removal efficiency of 42% was achieved when 10 g/L of
31 RWA was loaded for 10 min. The biogas production efficiency from both desulfated and
32 raw SLS was investigated. The highest 306.36 mL-CH₄/g-COD of methane production
33 yield was achieved from desulfated SLS using RWA loading of 10 g/L (DSLS10), which
34 is 16% higher than the yield generated using raw SLS as a substrate. Moreover,
35 hydrogen sulfide content in the biogas produced by desulfated SLS was two times lower
36 than raw SLS. The results indicate removing sulfate from SLS using RWA before
37 feeding to the anaerobic digestion enhanced biogas production yield and quality.

38

39

40 **Keywords:** Wastewater, Latex, Ash, Sulfate removal, Biogas

41

42

43

44

45

46

47

48

49 **1. Introduction**

50 Thailand is a leading producer and exporter of natural rubber in several primary
51 products, including concentrated latex, block rubber, and ribbed smoked sheet rubber
52 [1]. The demand for latex in domestic and foreign markets has increased significantly in
53 the concentrated rubber latex industry, which produces concentrated latex as raw
54 material for other downstream industries such as rubber gloves, medical, surgical items,
55 boots, and balloons.

56 Disc bowl centrifuge is used to produce 60% dry rubber content (DRC)
57 concentrated latex from field latex, which originally contains approximately 30% DRC.
58 The remaining liquid from centrifugation is called 'skim latex', which still contains 4–
59 8% DRC. Skim latex is doped with sulfuric acid to coagulate the remaining rubber
60 particles to produce rubber sheets or rubber blocks [2]. Wastewater from the rubber
61 skimming process, which is non – rubber, is called skim latex serum (SLS). SLS
62 contains high chemical oxygen demand (COD) (35.29 - 43.11 g/L), high sulfate (4,933-
63 7,500 mg/L), and low pH (5.0 – 6.0) [3]. Due to high sulfate content, the factory is
64 facing a serious odor problem with the nearby community. Hence, treating this
65 wastewater to meet the environmental standard is crucial; otherwise, it may result in
66 water, air, and soil pollution.

67 The anaerobic digestion process is an attractive choice to treat SLS. Some latex
68 factories have replaced the old wastewater treatment method with the anaerobic process.
69 Due to high sulfate content, there is a need to dilute the wastewater before feeding it to
70 the anaerobic digester. Under anaerobic conditions, sulfate-reducing bacteria (SRB) use
71 sulfate as a terminal electron acceptor to suppress organic compounds [4], [5]. The
72 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 H₂S, 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 H₂S 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 °C. 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 110°C, 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

170 **3. Results and discussion**

171 3.1. Characteristics of SLS and RWA

172 Some physicals and chemical characteristics of the SLS collected were analyzed.
173 The result of the analysis carried out is presented in Table 1. High VS of 32-37 g/L and
174 COD of 33-43 g/L indicated a high organic compound content. Therefore, SLS
175 wastewater must be adequately treated before releasing into the environment. The high
176 organic carbon in SLS confirms that it is a promising substrate for producing methane
177 through anaerobic digestion. Nevertheless, since sulfuric acid was used to recover
178 rubber in skim latex, it resulted in a low SLS pH (5.22-5.78), lower than the favorable
179 range for methanogens bacteria growth pH of 7-8.5 [14]. Anaerobic digestion will be
180 inhibited when the pH of the system falls below 6.0. This is because methanogens
181 bacteria do not grow at a low pH and might stop methane production. Therefore, an
182 increase in pH is needed to obtain efficient biogas production from SLS. Sulfate
183 concentration in SLS ranged 4,933 – 7,500 mg/L, which could cause an inhibition on
184 the performance of anaerobic digestion. Hence, to enhance the biogas production yield
185 and quality, sulfate contained in SLS should be first reduced. Alkalinity is the
186 characteristic that reveals the capacity of the buffer to maintain pH drop during the
187 acidogenesis process. The greater the alkalinity, the more stable the anaerobic digestion.
188 Reungsang et al. (2019) reported that the alkalinity of the anaerobic digestion system
189 should not be lower than 2,000 mg-CaCO₃/L [15]. Alkalinity range of 2,867-3,287 mg-
190 CaCO₃/L was found in SLS, indicating a sufficient buffering capacity.

191

192 **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

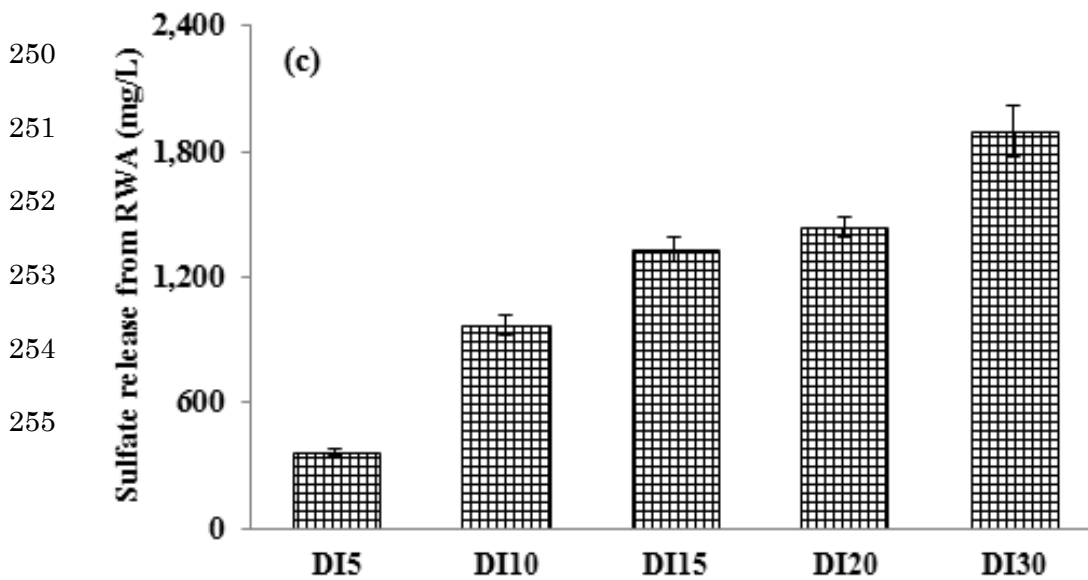
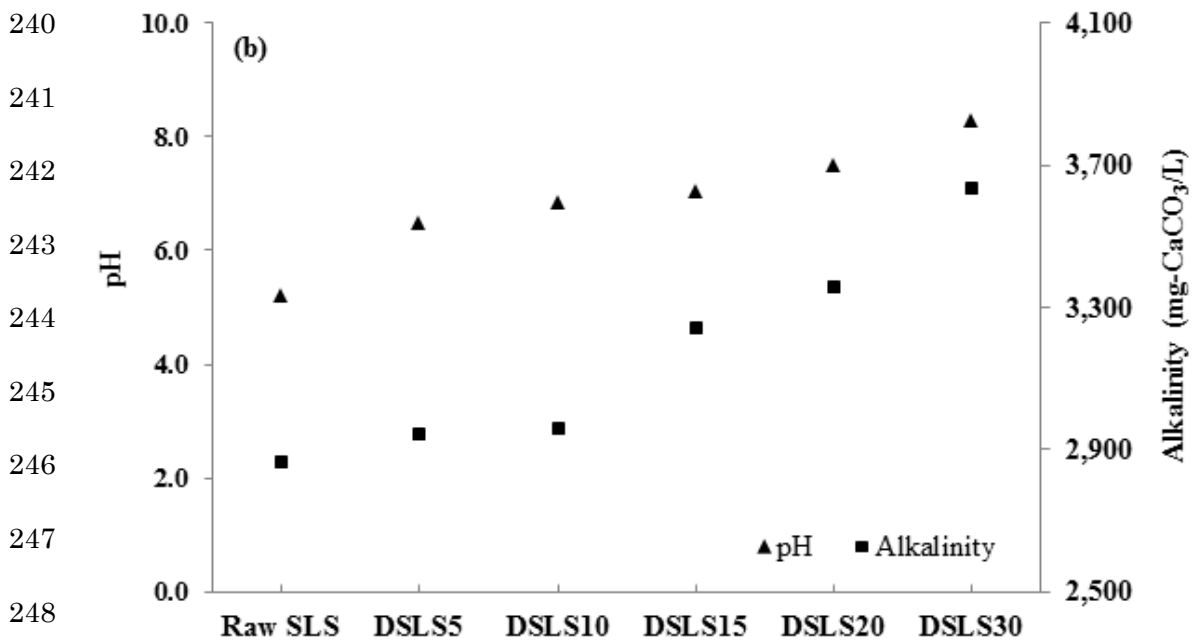
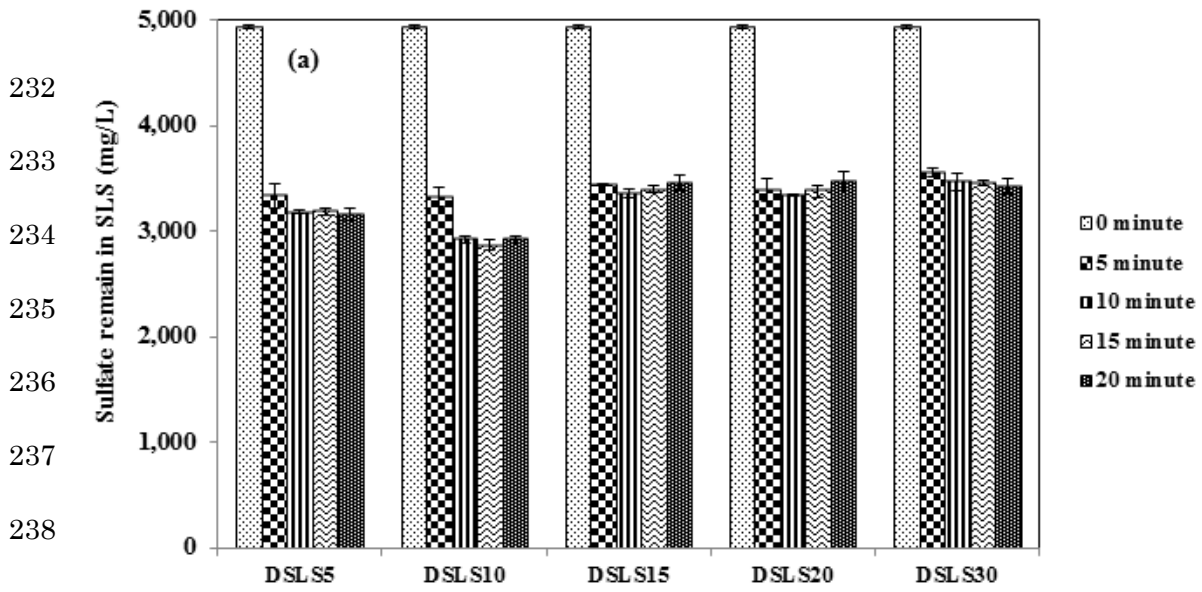
202 3.2.1 Effect of RWA loading and mixing time

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.

228
229
230
231



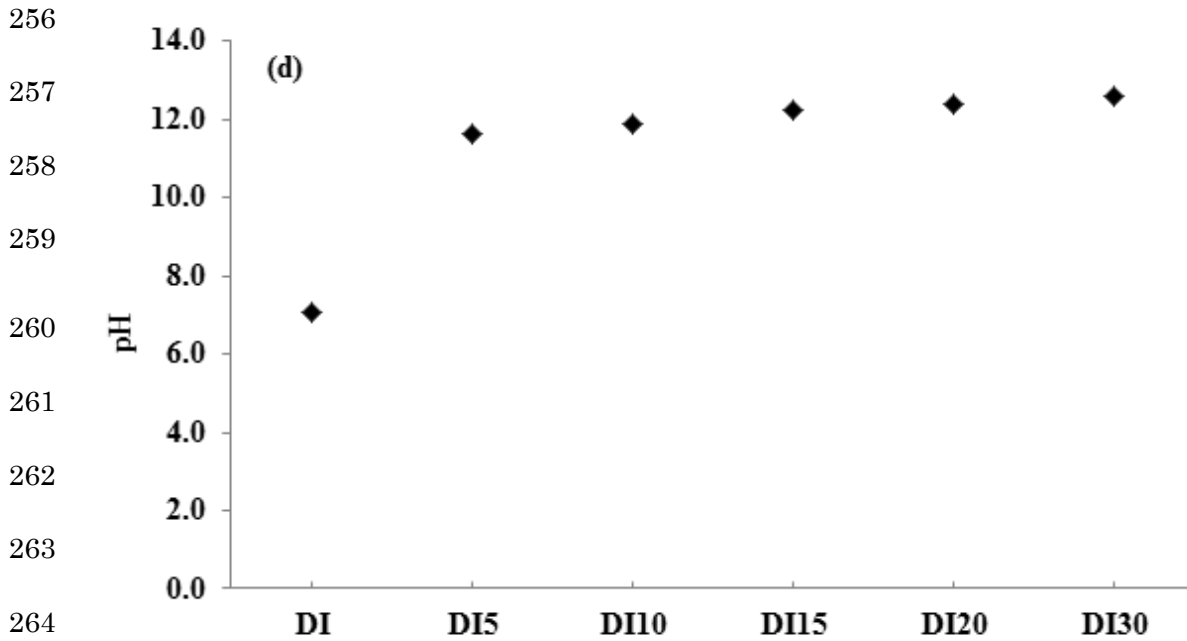


Fig. 1 The removal of sulfate after mixing with RWA: (a) sulfate concentration in DSLS, (b) pH and alkalinity of SLS at 10 min mixing time, (c) sulfate concentration in DI with RWA at 10 min mixing time, and (d) pH of DI with RWA at 10 min mixing time.

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.

280
 281
 282
 283
 284
 285
 286
 287
 288
 289
 290
 291
 292
 293
 294
 295
 296
 297
 298
 299
 300
 301
 302
 303

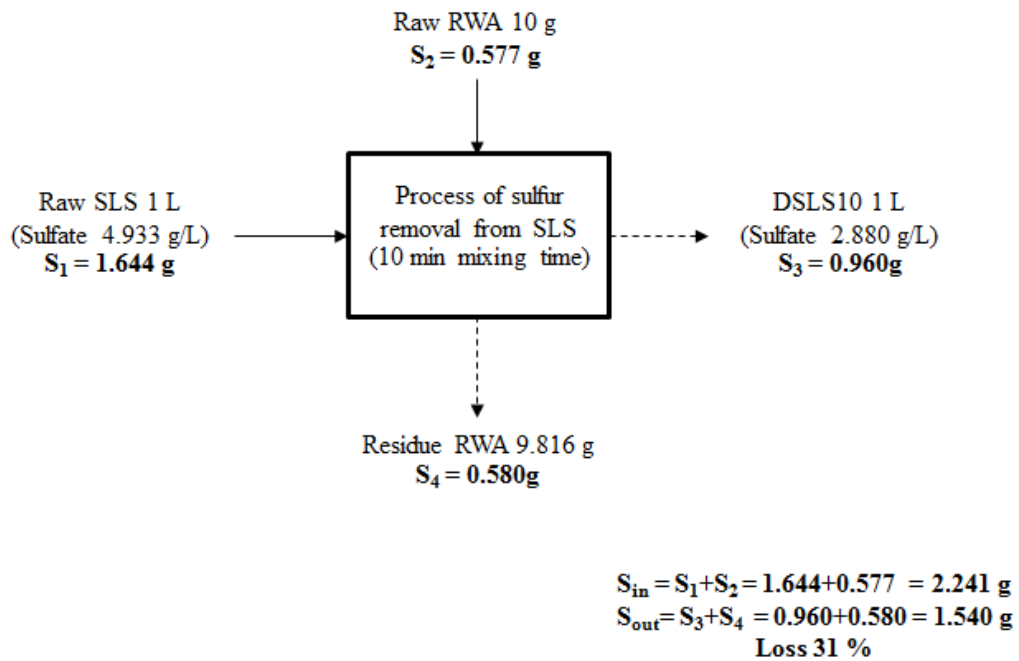


Fig. 2 Sulfur mass distribution of DSLS10.

3.2.2. Sulfate adsorption as the main mechanism

Several dissolved elements in raw SLS, DSLS10, and DI10 were detected, as shown in Table 3. Ca, Mg, Na, P, K, and Zn mainly appeared in raw SLS, whereas Co, Cu, Fe, Mn, and Ni were found in small amounts. After RWA was added into raw SLS, most of the elements solution increased due to leaching from RWA. The experiment of DI10 was carried out to investigate the dissolvable element in RWA. It was found that Ca, Mg, and K was the main element while Co, Cu, Fe, Mn, Na, Ni, P, and Zn were present in little amounts. This indicates that the disappearance of sulfate was not mainly from the precipitation with metal ions. Therefore, the possible mechanism to describe the removal of sulfate from the SLS solution might be adsorption on the RWA surface.

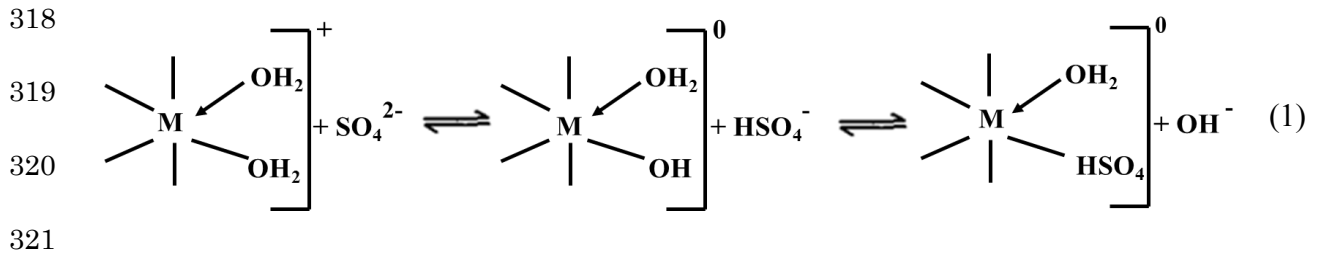
Table 3 Dissolved elements in raw SLS, DSLS10, and DI10.

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].



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

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

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

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

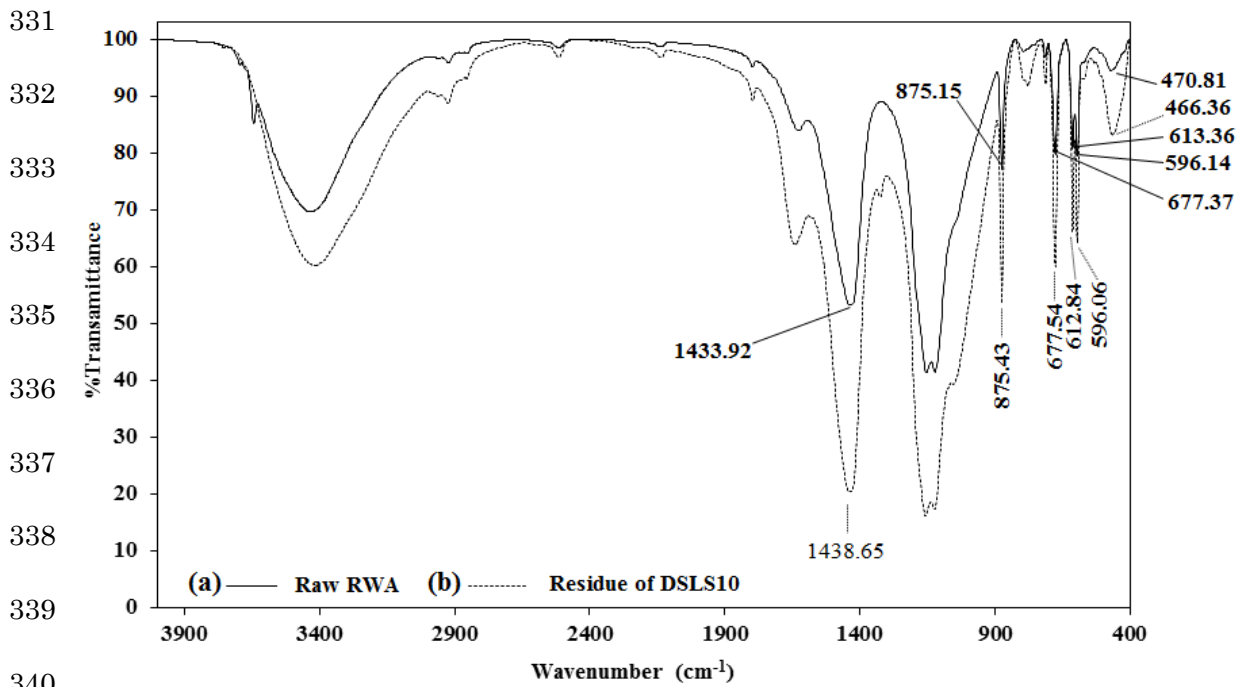
326 weak doublet was observed in the lower region at 678 and 596 cm^{-1} . The observation

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

328 [22]. The FTIR spectra indicated that there were sulfate and carbonate compounds in

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

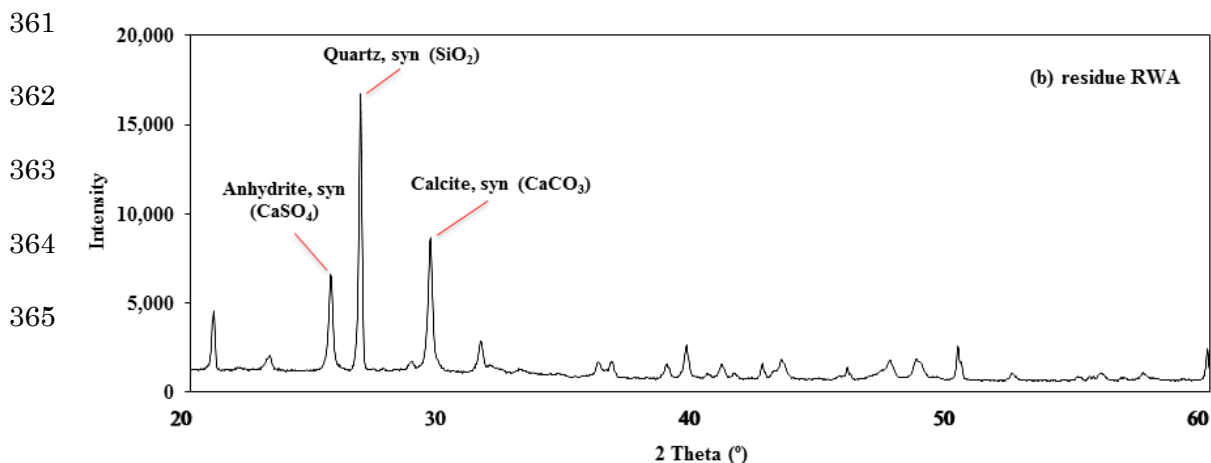
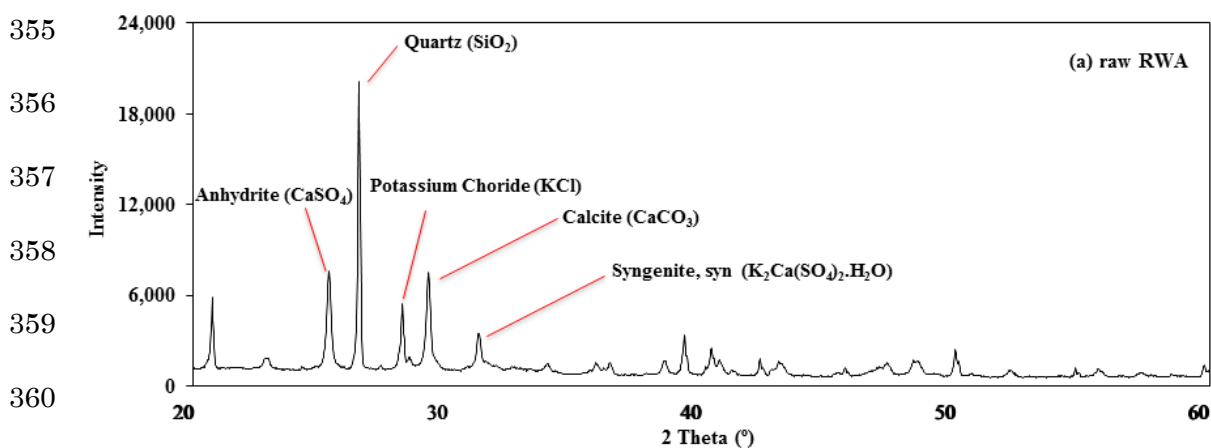
330 higher than raw RWA, indicating a higher sulfate and carbonate deposit.



341 **Fig. 3** FTIR spectra: (a) Raw RWA and (b) residue of DSLS10.

342

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 $a=7.006 \text{ \AA}$,
348 $b=6.998 \text{ \AA}$, and $c=6.245 \text{ \AA}$. While for residue RWA, the space group of CaSO_4
349 (anhydrite, syn) was Bbmm with lattice constant $a=6.240 \text{ \AA}$, $b=6.980 \text{ \AA}$, and $c=6.970 \text{ \AA}$.
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.



366

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

368

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 SO₄ was adsorbed onto the surface.

377

378

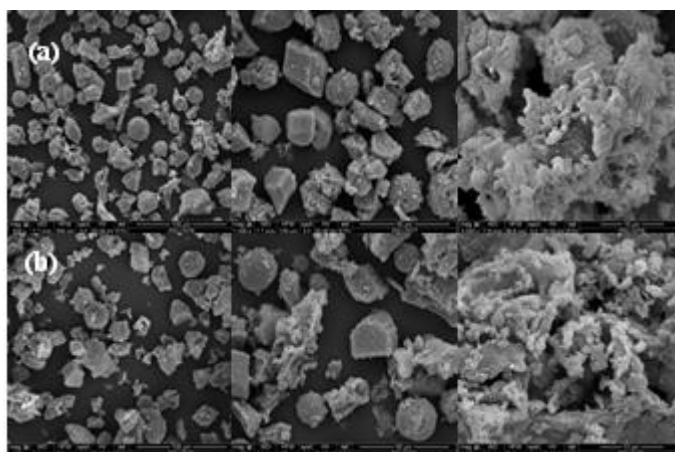
379

380

381

382

383



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: $\text{Acetate} \longrightarrow \text{CH}_4 + \text{CO}_2$ (2)

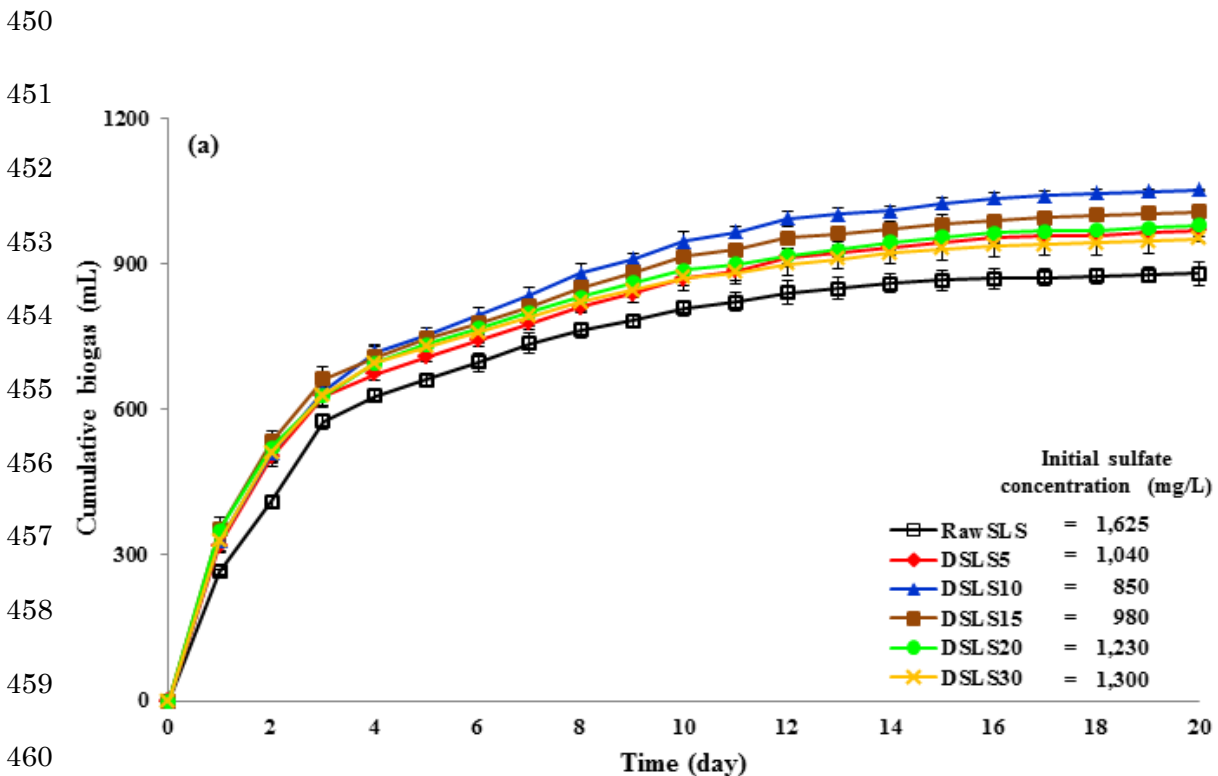
421 Hydrogenotrophic methanogenesis pathway: $\text{H}_2 + \text{CO}_2 \longrightarrow \text{CH}_4$ (3)

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 $\text{CH}_4/\text{g-COD}$ 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 $\text{CH}_4/\text{g-COD}$ at STP). Raw SLS gave the lowest methane yield production of 264.38
429 mL- $\text{CH}_4/\text{g-COD}$, 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, H₂S 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 found 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.



487

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

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

490

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

492 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 ± 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 ± 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 ± 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 ± 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

494 Additional essential mineral leached from RWA is one reason for the improvement
495 in methane production from DSLS. Fe acts as an electron acceptor and donor involving
496 energy metabolism and can be utilized by methanogens to reduce CO₂ to CH₄ [29]. Ni is
497 a crucial coenzyme harbored in methanogens [30]. Ca and Mg, the coenzyme in the
498 anaerobic process [15] found in DSLS, did not exceed the limit value of 2500 mg/L and
499 1,000 mg/L, respectively. Co, Cu, Fe, and Ni were also lower than the concentration
500 inhibits to microorganisms (2.8, 1, 5.5, and 2 mg/L, respectively). While, K, P, and Zn
501 presented in raw SLS was over the recommended levels (3.9 mg/L [15], 2.5 mg/L [15],
502 and 12.5 mg/L [31], respectively). After RWA was added to SLS, a decrease in P and
503 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 CO₂ emission.

543

544 **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.

553

554 **Acknowledgments**

555 The authors would like to thank the Thailand Research Fund through the Royal
556 Golden Jubilee Ph.D. Program (Grant No. PHD/0216/2559) and SAT ASEAN research
557 grant (budget year 2559-2560, contract number SAT590908S) for financial support. The
558 fifth author is supported by the Thailand Research Fund for Senior Research Scholar
559 (Grant No. RTA6280001). The authors are also grateful to the Language Center, Prince
560 of Songkla University, Pattani Campus, for proofreading the article. In addition, the
561 authors would like to thank Top Glove Technology (Thailand).Co., Ltd and Top Glove
562 Medical (Thailand) .Co., Ltd for providing materials to our research.

563

564 **References**

- 565 [1] W. Jawjit, P. Pavasant, C. Kroeze, Evaluating environmental performance of
566 concentrated latex production in Thailand, *J Clean Prod.* 98 (2015) 84-91,
567 <https://doi.org/10.1016/j.jclepro.2013.11.016>
- 568 [2] S.T. Leong, S. Muttamara, P. Laortanakul, Reutilization of wastewater in a rubber-
569 based processing factory: a case study in Southern Thailand, *Res Con Recycle.* 37
570 (2003) 37:159-72, [https://doi.org/10.1016/S0921-3449\(02\)00073-3](https://doi.org/10.1016/S0921-3449(02)00073-3)
- 571 [3] P. Kongjan, R. Jariyaboon, S. O-Thong, Anaerobic digestion of skim latex serum
572 (SLS) for hydrogen and methane production using a two-stage process in a series of
573 up-flow anaerobic sludge blanket (UASB) reactor, *Int J Hydrogen Energy.* 39 (2014)
574 19343-19348, <https://doi.org/10.1016/j.ijhydene.2014.06.057>
- 575 [4] J.W.H.O.E. Stefanie, A. Visser, L W.H. Pol, A.J.M .Stams, Sulfate reduction in

576 methanogenic bioreactors, FEMS Microbiol Rev. 15 (1994) 119-36,
577 <https://doi.org/10.1111/j.1574-6976.1994.tb00130.x>

578 [5] T. Mu, J. Xing, M. Yang, Sulfate reduction by a haloalkaliphilic bench-scale sulfate-
579 reducing bioreactor and its bacterial communities at different depths, Biochem Eng J.
580 147 (2019) 100-109, <https://doi.org/10.1016/j.bej.2019.04.008>

581 [6] J. Gustavsson, S. Shakeri Yekta, C. Sundberg, A. Karlsson, J. Ejlertsson, U.
582 Skyllberg, B.H. Svensson, Bioavailability of cobalt and nickel during anaerobic
583 digestion of sulfur-rich stillage for biogas formation, Appl Energy. 112 (2013) 473-
584 477, <https://doi.org/10.1016/j.apenergy.2013.02.009>

585 [7] L. Pokorna-Krayzelova, K.E. Mampaey, TPW. Vannecke, J. Bartacek, P. Jenicek,
586 EIP. Volcke, Model-based optimization of microaeration for biogas desulfurization in
587 UASB reactors, Biochem Eng J. 125 (2017) 171-179,
588 <https://doi.org/10.1016/j.bej.2017.06.009>

589 [8] I. Angelidaki, D. Karakashev, D.J. Batstone, C.M. Plugge, A.J.M. Stams, Chapter
590 sixteen -Biomethanation and Its Potential .in :*Methods in Enzymology*,)Eds (.A.C .
591 Rosenzweig, S.W. Ragsdale, Academic Press pp. 494 (2011) 327-51,
592 <https://doi.org/10.1016/B978-0-12-385112-3.00016-0>

593 [9] R. Saelee, J. Chungsiriporn, J. Intamane, C. Bunyakan, Removal of H₂S in biogas
594 from concentrated latex industry with iron (III) (chelate in packed column, J. Sci .
595 Technol. 31 (2009) 195–203 .

596 [10] P. Kijjanapanich, G. A. P. Annachatre, E. D. Esposito, P. van Hullebusch, N. L. .
597 Lens, Biological sulfate removal from gypsum contaminated construction and
598 demolition debris, J Environ Manag. 131 (2013) 82-91,
599 <https://doi.org/10.1016/j.jenvman.2013.09.025>

- 600 [11] J. Hytönen, J. Nurmi, N. Kaakkurivaara, T. Kaakkurivaara, Rubber Tree)Hevea
601 brasiliensis (Biomass, Nutrient Content, and Heating Values in Southern Thailand, J
602 Forests. 10 (2019) 638, <https://doi.org/10.3390/f10080638>
- 603 [12] W. Inthong, Sulfate Removal from Latex Rubber Industry Wastewater by Using
604 Phuket Incinerator Fly Ash, MS thesis, Prince of Songkla University, Thailand, 2008.
- 605 [13] APHA .Book of data .22th ed .Washington DC .USA :Standard methods for the
606 examination of water and wastewater; 2012.
- 607 [14] R. Chandra, H. Takeuchi, T. Hasegawa, Methane production from lignocellulosic
608 agricultural crop wastes :A review in context to second generation of biofuel
609 production, Renew Sustain Energy Rev. 16 (2012) 1462-1476,
610 <https://doi.org/10.1016/j.rser.2011.11.035>
- 611 [15] A. Reungsang, Book of data .First ed .Khon Kaen University, Thailand:Microbial-
612 Derived Biofuels and Biochemicals; 2019.
- 613 [16] T. Rattanaya, P. Sawasdisan, P. Srichuay, A. Samanwiwat, P. Kongjan, P. Yuso, M.
614 Waehamah, R. Jariyaboon, A. Reungsang, Application of Waste Rubberwood Ash
615 in Carbon Dioxide Absorption, Int J Environ Sci Educ. 12 (2017) 2275–2287.
- 616 [17] M. Masae, L. Sikong, P. Kongsong, P. Phoempoon, S. Rawangwong, W. Sririkun,
617 Application of rubber wood ash for removal nickel and copper from aqueous
618 solution, Environ Nat Resour J. 11 (2013) 17-27 .
- 619 [18] W.G. Breck, R.J.C. Brown, J.D. McCowan, Book of data .McGraw-Hill:Chemistry
620 for Science and Engineering;1989.
- 621 [19] M. Ishiguro, T. Makino, Y. Hattori, Sulfate adsorption and surface precipitation on
622 a volcanic ash soil)allophanic andisol(, J Colloid Interface Sci. 300 (2006) 504-
623 510, <https://doi.org/10.1016/j.jcis.2006.04.032>

- 624 [20] S.M. Rao, A .Sridharan, Mechanism of Sulfate Adsorption by Kaolinite, Clays and
625 Clay Minerals. 32 (1984) 414-418, <https://doi.org/10.1346/CCMN.1984.0320510>
- 626 [21] R.L. Parfitt, Anion Adsorption by Soils and Soil Materials .in :Advances in
627 Agronomy,) Ed (.N.C .Brady, Academic Press pp. 30 (1979) 1-50,
628 [https://doi.org//10.1016S6-60702\(08\)2113-0065](https://doi.org//10.1016S6-60702(08)2113-0065)
- 629 [22] C. Kamaraj, S. Lakshmi, C. Rose, C. Muralidharan, Wet Blue Fiber and Lime
630 from Leather Industry Solid Waste as Stabilizing Additive and Filler in Design of
631 Stone Matrix Asphalt, Asian J of Research in Soc Sci and Hum. 7 (2017) 240-257.
- 632 [23] Y. Ma, Q. Zhou, Z. He, F. Li, K. Yang, Q. Cui, G. Zou, High-pressure and high-
633 temperature study of the phase transition in anhydrite, J Phys Condens Matter. 19
634 (2007) 425221.
- 635 [24] H.T. Evans, The thermal expansion of anhydrite to 1000° C, Phys Chem Minerals 4
636 (1979) 77-82, <https://doi.org/10.1007/BF00308361>
- 637 [25] Y. Li, Y. Yu, H. Wang, F. Zhao, Effect of process parameters on the recrystallization
638 and size control of puerarin using the supercritical fluid antisolvent process, Asian J
639 pharm Sci 11 (2016) 281-291, <https://doi.org/10.1016/j.ajps.2015.12.001>
- 640 [26] C.T. Benatti, C.R.G. Tavares, E. Lenzi, Sulfate removal from waste chemicals by
641 precipitation, J Environ Manage. 90 (2009) 504-511, <https://doi.org//10.1016j.jenvman.2007.12.006>
- 642 jenvman.2007.12.006
- 643 [27] Z. Simjanoski, MASTER'S THESIS, 2012, 10.13140/RG.2.2.21874.66246
- 644 [28] A. Visser, L.W.H. Pol, G. Lettinga, Competition of methanogenic and sulfidogenic
645 bacteria, Water Sci Technol. 33 (1996) 99-110, [https://doi.org/10.1016/0273-1223\(96\)00324-1](https://doi.org/10.1016/0273-1223(96)00324-1)
- 646 1223(96)00324-1
- 647 [29] Y.Y. Choong, I. Norli, A.Z. Abdullah, M.F. Yhaya, Impacts of trace element

648 supplementation on the performance of anaerobic digestion process :A critical
649 review, *Bioresour Technol.* 209 (2016) 369-379, [https://doi.org/10.1016/j.biortech.](https://doi.org/10.1016/j.biortech.2016.03.028)
650 2016.03.028

651 [30] C. Yin, Y. Shen, N. Zhu, Q. Huang, Z. Lou, H. Yuan, Anaerobic digestion of waste
652 activated sludge with incineration bottom ash :Enhanced methane production and
653 CO₂ sequestration, *Appl Energy.* 215 (2018) 503-511, [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.apenergy.2018.02.056)
654 [apenergy.2018.02.056](https://doi.org/10.1016/j.apenergy.2018.02.056)

655 [31] A. Mudhoo, S. Kumar, Effects of heavy metals as stress factors on anaerobic
656 digestion processes and biogas production from biomass, *Int J Environ Sci*
657 *Technol.* 10 (2013) 1383–1398.

658 [32] A.J. Ward, P.J. Hobbs, P.J. Holliman, D.L. Jones, Optimisation of the anaerobic
659 digestion of agricultural resources, *Bioresour Technol.* 99 (2008) 7928-40,
660 <https://doi.org/10.1016/j.biortech.2008.02.044>

661 [33] I. Angelidaki, W. Sanders, Assessment of the anaerobic biodegradability of
662 macropollutants, *Rev Environ Sci Biotechnol.* 3 (2004) 117-129.

663 [34] M. Khan Jamil, M. Qasim, Integrated use of boiler ash as organic fertilizer and soil
664 conditioner with NPK in calcareous soil, *Songklanakarin J Sci Technol.* 30 (2008)
665 281-289.

666 [35] National Environmental Board)Thailand(, Define of soil quality standards. 25
667 (2004) 170-181.

668 [36] K. Möller, W. Stinner, Effects of organic wastes digestion for biogas production on
669 mineral nutrient availability of biogas effluents, *Nut Cyc Agroecosys.* 87 (2010)
670 395-413, <https://doi.org/10.1007/s10705-010-9346-8>

671