

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

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1	Sulfate removal using rubber wood ash to enhance biogas production from sulfate-
2	rich wastewater generated from a concentrated latex factory
3	
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### 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-CH <sub>4</sub> /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.
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40	Keywords: Wastewater, Latex, Ash, Sulfate removal, Biogas
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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.

Disc bowl centrifuge is used to produce 60% dry rubber content (DRC) 56concentrated latex from field latex, which originally contains approximately 30% DRC. 57The remaining liquid from centrifugation is called 'skim latex', which still contains 4– 58598% 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 60 skimming process, which is non – rubber, is called skim latex serum (SLS). SLS 61 contains high chemical oxygen demand (COD) (35.29 - 43.11 g/L), high sulfate (4,933-62 7,500 mg/L), and low pH (5.0 - 6.0) [3]. Due to high sulfate content, the factory is 63 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 water, air, and soil pollution. 66

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 bacteria (MPB) to use organic substances resulting in lower methane production yield
[6]. However, they also produce H<sub>2</sub>S, which inhibits methane-producing bacteria
(MPB), slowing or stopping methane production [7]. Microorganism inside the biogas
system was found inhibited at sulfate concentration higher than 500 mg/L [8].
Therefore, sulfate in SLS has to be removed to enhance biogas production yield and
lower its sulfate content. Moreover, very high H<sub>2</sub>S content (1-3%) is found in the biogas
generated from rich sulfate SLS [9].

80 Several methods can be used to remove sulfates from wastewater, such as ion exchange, membrane filtration, biological treatment, chemical precipitation, and 81 adsorption. Ion exchange and membrane filtration are not suitable for removing sulfate 82 83 from SLS because SLS has high suspended solids, resulting in fouling problems. Also, biological treatment is not suitable for treating SLS because the high sulfate level can 84 inhibit the microorganism [10]. On the other hand, sulfate precipitation with metallic 85 86 ions and adsorption on metal oxide surface are interesting methods because the sulfate product can be easily separated from the solution. 87

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, rubber glove, and seafood processing. 2.5-3.0% by weight of rubber wood ash (RWA) 90 91 is generated from the combustion [11]. RWA is an industrial waste, which needs to be 92adequately 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%, respectively, at the initial sulfate concentration of 8,364 mg/L [12]. 96

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
190	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).

140 2.3. Biogas production from desulfated SLS

141After the sulfate removal from SLS, desulfated SLS (the separated solution from142RWA and SLS blend) was used as a substrate to produce biogas. The investigation of143biogas production potential was performed in a 500 mL serum bottle with 200 mL144working volume. Raw SLS and desulfated SLS (DSLS) with various initial solid

145loadings 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 147wastewater 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 149to ensure anaerobic conditions before incubated at 35 °C. All experiments were carried 150out in triplicate. The headspace gas was collected every 24 h for biogas volume and biogas composition (methane, carbon dioxide, hydrogen sulfide) determination. pH, 151152COD, total kjeldahl nitrogen (TKN), total alkalinity, total solid (TS), volatile solid (VS), 153ash, total organic carbon (TOC), and sulfate in the substrate were investigated. The anaerobic digestion process was ceased when methane production was constant. The pH 154155and sulfate of effluent were investigated afterward.

156

157 2.4. Analytical methods

The biogas production volume was measured through water displacement. 158Methane, carbon dioxide, and hydrogen sulfite contents in biogas were measured using 159160 gas chromatography (Shimadzu GC 14A equipped with a thermal conductivity detector) fitted with a 2.5 m Porapak S column with Hayesep Q (80/100). Helium was used as a 161 162carrier 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 was injected in triplicate. The procedures described in the standard methods [13] were 164applied to determine the pH, COD, TKN, total alkalinity, TS, VS, ash, and sulfate. TOC 165166 was investigated with TOC-Liquid: multi N/C 3100 TOC analyzer (Analytik Jena). Statistically significant differences in the results were determined using a one-way 167 168analysis of variance) ANOVA) in SPSS v26.0 (IBM, USA).

#### 3. Results and discussion 170

1713.1. Characteristics of SLS and RWA

Some physicals and chemical characteristics of the SLS collected were analyzed. 172The result of the analysis carried out is presented in Table 1. High VS of 32-37 g/L and 173174COD 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 175176organic carbon in SLS confirms that it is a promising substrate for producing methane 177through 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 178179 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 increase in pH is needed to obtain efficient biogas production from SLS. Sulfate 182concentration in SLS ranged 4,933 – 7,500 mg/L, which could cause an inhibition on 183184 the performance of anaerobic digestion. Hence, to enhance the biogas production yield 185and 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 should not be lower than 2,000 mg-CaCO<sub>3</sub>/L [15]. Alkalinity range of 2,867-3,287 mg-189 190 CaCO<sub>3</sub>/L was found in SLS, indicating a sufficient buffering capacity. 191



Parameters	Unit	Value
рН		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 <sub>3</sub> /L)	2,867 - 3,287
TKN	(mg/L)	1,548 – 1,588

Ca and Si were the main elements found in RWA. K, S, Cl, Mg, and Fe were found in small amounts while a little amount of heavy metal was also observed (Table 2). The chemical composition of the ash depends on the composition of fuelwood and combustion temperature. Therefore, in this study, RWA's composition is slightly different from previous studies [16,17].

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

	Composition in RWA (% w/w)			
Element	Raw RWA	Residue from	Residue from	
		DSLS10	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

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 <sub>3</sub>
216	$(1.0 \times 10^{-8})$ is lower than CaSO <sub>4</sub> $(2.0 \times 10^{-4})$ [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

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

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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.

271Sulfur 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 272273streams 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 274275was a little higher than its initial loading. The overall sulfur mass calculation resulted in 276an imbalance with approximately 31% sulfur mass loss from the output streams. This 277loss might have occurred due to experimental errors such as measuring a small quantity 278of ash in the solution, estimating the element in RWA and residue RWA using XRF, and sulfate determination using the turbidimetric method. 279



Dissolved	Concentration (mg/L)			
elements	Raw SLS	DSLS10	<b>DI10</b>	
Calcium (Ca)	$12.91 \pm 0.05$	$302.40\pm6.56$	$275.00 \pm 5.57$	
Cobalt (Co)	< 0.003	< 0.003	< 0.003	
Copper (Cu)	< 0.016	$0.18\pm0.02$	< 0.016	
Iron (Fe)	$0.60\pm0.02$	$1.34\pm0.02$	$0.30\pm0.01$	
Magnesium (Mg)	$32.41\pm0.06$	$66.41 \pm 0.10$	$12.61\pm0.29$	
Manganese (Mn)	$0.14\pm0.00$	$2.69\pm0.00$	$0.17\pm0.00$	
Sodium (Na)	$10.62\pm0.02$	$12.22\pm0.09$	$2.21\pm0.07$	
Nickel (Ni)	< 0.005	$0.06 \pm 0.01$	< 0.005	
Phosphorus (P)	$223.90\pm2.64$	$209.20 \pm 1.56$	$1.33\pm0.07$	
Potassium (K)	$3,\!728.00 \pm 47.85$	$4,\!015.00\pm59.26$	$403.80\pm4.47$	
Zinc (Zn)	$295.70\pm3.93$	$240.80\pm2.88$	< 0.003	

<sup>304</sup> 

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 SLS mixture was a bit higher than in raw RWA and almost 3 times higher than it 310 311 appeared in the ash residue of the DI water mixture. This result confirms that sulfate transferred from the SLS phase and adsorbed on the surface of RWA. 312313 Ishiguro et al. (2006) reported that sulfate's adsorption mechanism on a volcanic ash soil surface was multilayer adsorption through van der Waals attraction [19]. The 314 mechanism of sulfate adsorption was proposed, as shown in Equation (1) [20]. M is the 315metal at the surface. The adsorption of sulfate occurs by ligand exchange with the OH 316

317 group [21].



322Also, 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 323the carbonate  $(CO_3^{2-})$  band was assigned to a strong band near 1440 cm<sup>-1</sup>. The peak 324observed at 875 cm<sup>-1</sup> was due to out-of-plane bending vibration ( $CO_3^{2-}$ ) of carbonate. A 325weak doublet was observed in the lower region at 678 and 596 cm<sup>-1</sup>. The observation 326 might have resulted from the in and out-of-plane bending  $(SO_4^{2-})$  vibration of sulfate 327 328[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 329330 higher than raw RWA, indicating a higher sulfate and carbonate deposit.



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

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 <sub>4</sub> . However, the CaSO <sub>4</sub>
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.



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

- 369 Aside from FTIR spectra and XRD pattern, the morphology of RWA was studied by scanning electron microscopes with Quanta 400 (SEM-Quanta), and the difference 370 371between raw RWA and RWA residue after mixing with SLS was observed (Fig. 5a and 372b). It was found that from the scanning electron micrographs, the deposit and many 373irregularly structured inorganic particles were found on the residue of DSLS10 surface as present in Fig. 5b. In contrast, raw RWA had a few deposits on its surface (Fig. 5a). 374375Thus, FTIR spectra and Scanning electron microscopy (SEM) photographs confirmed 376 that the SO<sub>4</sub> was adsorbed onto the surface.
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- 383



Fig. 5 Scanning electron microscopy (SEM) photographs, 500X (left), 1000X (middle)
and 3500X (right): (a) raw RWA, and (b) residue of DSLS10.

386

Inthong (2008) reported that sulfate from latex rubber industry wastewater could
be reduced using fly ash from Phuket incinerator, lime, and ash from rubber wood. The

- 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.

403 3.3. Desulfated SLS for enhanced biogas production

The RWA residue was separated from SLS before further use to produce biogas 404 to prevent sulfate desorption and reduce total solid content. The biogas production 405406 potential of raw SLS and desulfated SLS (DSLS) using different RWA loading was carried out. The cumulative biogas production in the mesophilic anaerobic condition is 407 presented in Fig.6a. Less than 1 day of lag time was found in all substrate types because 408 409 the substrate was diluted to 8.5 g-COD/L initial loading. As expected, DSLS was a superior substrate for biogas production compared to raw SLS. After 12 days of the 410 anaerobic digestion process, a nearly steady biogas production rate was observed. This 411 412indicated that the organic matter in SLS was easily biodegraded.

Fig.6b shows the average methane content in biogas was between 58.2 - 74.8%,
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:	Acetate $\longrightarrow$ CH <sub>4</sub> + CO <sub>2</sub>	(2)
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421 Hydrogenotrophic methanogenesis pathway:  $H_2 + CO_2 \longrightarrow CH_4$  (3)

422Methane production yield was also calculated and shown in Fig. 6c. It can be 423seen that raw SLS and DSLS using different RWA loading gave a significantly different 424methane production yield. Desulfated SLS using RWA 10 g/L (DSLS10) gave the 425highest cumulative methane 520 mL and a maximum methane yield of 306.36 mL-426 CH<sub>4</sub>/g-COD corresponding to 11.00 kJ/g-COD of energy production. The maximum 427methane yield achieved in this study was equal to 77.58% of theoretical yield (350 mL-CH<sub>4</sub>/g-COD at STP). Raw SLS gave the lowest methane yield production of 264.38 428mL-CH<sub>4</sub>/g-COD, which was 16% lower than the DSLS. The result confirms that RWA 429430 does not reduce the sulfate to lower than the inhibition level (500 mg/L) due to the 431equilibrium limit and sulfate contained in RWA released into SLS. However, RWA 432obviously enhanced the biogas production.

433 H<sub>2</sub>S concentration in biogas was monitored and illustrated in Fig. 6d. H<sub>2</sub>S was 434 detected after the  $3^{rd}$  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<sub>2</sub>S concentration of 52,299 ppm on the  $11^{th}$  day of the anaerobic digestion 437 process. At the same time, the maximum H<sub>2</sub>S concentration of 28,000 ppm was 438 generated from DSLS10 digestion. Visser et al. (1996) reported that at a pH below 6.9 (acidic condition), MPB would outcompete SRB. Whereas, at a pH above 7.7 (alkaline
condition), SRB will perform better than MPB [28]. The pH's influent range of
DSLS15, DSLS20, and DSLS25 was 7.69-7.75, respectively, while DSLS5 and
DSLS10 were 7.49-7.60 (as shown in Table 4). Therefore, H<sub>2</sub>S concentration in biogas
produced from DSLS15, DSLS20, and DSLS25 was higher than in DSLS5 and
DSLS10.

Sulfate and COD in the influent and effluent were also monitored and are presented
in Table 4. It was fond that sulfate removal efficiency (84-88%) achieved from all SLS
digestion were similar. While more than 70 % COD removal was observed for DSLS
digestion. Most especially, DSLS10 gave the highest COD removal (76.37%), while
65.90 % of COD removal was achieved from raw SLS.

450





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	рН		Sulfate (mg/L)		COD (g-COD)			
Substitute	Influent	Effluent	Influent	Effluent	$\mathbf{RE}^{*}$	Influent	Effluent**	$\mathbf{RE}^*$
Raw SLS	$7.27\pm0.03$	$7.34\pm0.01$	$1,625 \pm 32$	$250\pm11$	$84.42\pm2.0$	$1.72\pm0.01$	$0.59{\pm}~0.02$	$65.90 \pm 1.0$
DSLS5	$7.49 \pm 0.05$	$7.33\pm0.02$	$1{,}040\pm20$	$145\pm8$	$86.11\pm0.5$	$1.72\pm0.01$	$0.46{\pm}~0.02$	$73.28\pm2.0$
DSLS10	$7.60\pm0.02$	$7.34\pm0.01$	$850 \pm 23$	$102\pm5$	$88.00 \pm 1.0$	$1.72\pm0.01$	$0.41 \pm 0.01$	$76.37 \pm 1.5$
DSLS15	$7.69\pm0.03$	$7.34\pm0.02$	$980\pm19$	$145\pm9$	$86.00\pm1.5$	$1.72\pm0.01$	$0.44 \pm 0.03$	$74.38\pm2.5$
DSLS20	$7.73\pm0.01$	$7.35\pm0.01$	$1,230 \pm 15$	$149\pm7$	$87.89\pm2.0$	$1.72\pm0.01$	$0.52 \pm 0.04$	$70.05\pm1.0$
DSLS30	$7.75 \pm 0.01$	$7.37 \pm 0.03$	$1,300 \pm 25$	$170 \pm 10$	86.92 ± 1.0	$1.72 \pm 0.01$	$0.47 \pm 0.02$	$72.70 \pm 1.5$

\*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 CO <sub>2</sub> to CH <sub>4</sub> [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

anions. However, fermenter elements will be typically diluted in a practical continuous
process, thus lowering their inhibition effects. According to Fig.1 and Table 3 when
RWA loading into SLS increased, the pH, alkalinity, and mineral ions increased to a
more favorable level for the related anaerobic microorganisms. However, the biogas
did not increase due to the increase in RWA loading. Hence, the increase in gas
production was mainly enhanced due to the sulfate reduction in SLS.

Furthermore, pH had a significant role in microbial growth in anaerobic digestion. 510511It should be kept at a neutral range due to the sensitivity of microorganisms [32]. Batch 512experiment was performed in this study using 70% inoculum to ensure sufficient microorganism exists in the biomethane production potential (BMP) protocol [33]. 513514Furthermore, since the inoculum used had a pH of 7.91, all experiments had an appropriate initial pH range of 7.27-7.93. However, in the practical aspect, higher 515516organic loading will be used to obtain higher productivity. Therefore, when raw SLS is used as a substrate, the fermenter's pH will be lower than the pH observed in this 517experiment and may be lower than the optimum level, leading to a lower methane 518519production yield. When RWA is used to remove sulfate from SLS, the pH of DSLS 520increases; thus, an external chemical is not necessarily used to keep the pH in the 521fermenter for efficient biogas production.

A recent site visit to some concentrated latex factories producing biogas using wastewater revealed that it is first diluted to reduce sulfate concentration and adjust pH before feeding to the biogas reactor. Thus, using RWA is a promising method to enhance wastewater treatment and biogas production since RWA can reduce sulfate in SLS, increase pH to methanogens for favorable environment growth, and achieve 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

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<sub>2</sub> emission. 543

544 **4.** Conclusions

RWA can be utilized to remove sulfate in SLS with the maximum removal efficiency of 42%. Adsorption is a possible main mechanism to describe sulfate removal. Asides from sulfate reduction, the pH and alkalinity in SLS were also increased to meet the desired level for efficient anaerobic SLS treatment to produce biogas after RWA was blended. Biogas production from the anaerobic digestion of desulfated SLS with 10 g/L RWA loading was 16% higher than raw SLS. This study revealed the promising concept for practical application to treat rich sulfate wastewater 552generated from a concentrated latex factory.

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