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Kinetic Modeling of Peroxydisulfate Pre-Treatment of Algae Slurry (Pasir Gudang, Malaysia) for Increasing Methane Generation from Anaerobic Digestion: Fertilizer Recovery

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This study looked into the possibility of using peroxydisulfate pretreatment to enhance biogas production from anaerobic fermentation of algal slurry. The results demonstrate that a peroxydisulfate added system with a dose of 0.02 g peroxydisulfate/g algal sludge TSS produces the most accumulative methane after 61 days of fermentation. At 0.02, 0.03, 0.06, 0.2, 0.3, 0.6, and 1.2 g peroxydisulfate/g algal sludge TSS cumulative methane generation was 1.16, 1.09, 1.15, 1.14, 1.09, 0.77, and 0.16 times higher than control. After 120 minutes of pre-treatment, the SCOD in the system continued to rise when the peroxydisulfate dosage was enhanced. To simulate the methane yield, a one-substrate model might be utilized. After dosing with peroxydisulfate, the hydrolysis rate reduced, and the maximum resultant and anticipated cumulative methane output was achieved with 0.02 g peroxydisulfate/g algal sludge TSS. After digestion, microcystin-LR in algae slurry was mostly eliminated. Heavy metals could be released from algae cells into the effluent as a result of the greater peroxydisulfate dosage. From the fermented effluent, sludge recapture was 0.09 m^3 sludge/m^3. The supplementation of peroxydisulfate to algae slurry may boost cumulative methane generation while also lowering microcystin-LR levels.

Keywords: Anaerobic digestion, Algae slurry, Methane, Peroxydisulfate, Microcystin-LR.

INTRODUCTION

Presently, the globe is dealing with two corresponding concerns *viz*. proper waste management in manufacturing sectors and a scarcity of creative energy sources to fulfill rising energy demands [1]. Simultaneous environmental fights and dwindling fuel supplies have prompted extensive research to increase energy reserve [2]. By 2050, biomass is expected to make a significant contribution to commerce (UNIDO). Biomass' industrial potential is estimated to be 18.3 EJ/y [3]. Fig. 1 depicts the biomass potential sector breakdown for 2050, with OECD countries harvesting the top 47%. Because of its high percentage of methane, controlled fermentation of agro-industrial waste creates a gas that can be used as an electrical thermal energy source [4].

Algae slurry taken from ecological ponds has sparked widespread concern as solid waste. Human actions can lead to contaminated drinking water and beaches, shellfish bed closures, hazardous algal blooms, fishery reductions, habitat loss, fish kills and a slew of other human health and natural resource issues. Each 1 ton raw algae taken from Pasir Gudang, Johor, Malaysia (1.4703ºN, 103.9030ºE) pond can eliminate 9 kg N and 1 kg P from the pond. This has been critical to eliminate algae, N and P from this pond to aid in the management and restriction of algal blooms and the degradation of the ecosystem system [5]. The raw algae slurry must be cleaned quickly for avoiding secondary contamination from accessing ponds and re-igniting algal blooms [6]. Simultaneously, algae slurry comprises a lot of organic matter, which allows anaerobic digestion to recover energy from it. In last two decades, much research has concentrated on methane production from algal sludge [7].

The sluggish disintegration and hydrolysis rates of the substrate normally limit methane production from anaerobic fermentation [8]. Because the algal cell walls are hard to breach and the release of intracellular organics is limited, the algae

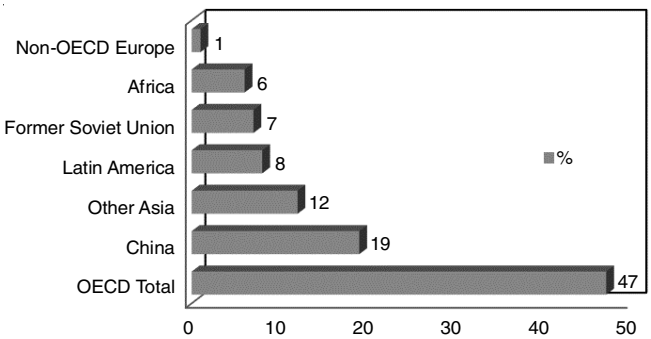

Fig. 1. Without interregional trade, a regional estimate of biomass latent for 2050 (UNIDO), 2012)

have low biodegradability [9]. As a result, before the digesting process, a pretreatment technique, which assist in the breaking of algal cell walls is critical [10]. Because it contains a defensive exterior wall, some microalgae are resistant to breakdown [11]. The advanced oxidation process has gotten a lot of interest for its high efficiency and low cost in improving algal cell disintegration. According to Siddique & Wahid [12], approximately 49.99 mg/L chlorine combined with UV radiation removed 87% of total algal biomass, destroyed cell integrity and released organic matters. Khalid *et al*. [13] explored the pre-treatment of algae with ultrasound and zero-valent iron and found that at a dose of 20 g zero-valent iron/g algal biomass, the largest accumulative methane generation occurred. The cost of the chemicals utilized, as well as the additional energy generated, should be addressed.

Because of its powerful and non-selective oxidation ability, peroxydisulfate (PDS) had been frequently applied for resistant deterioration [14]. PDS was found to have a favorable influence on hexachloroethane breakdown in a heat pre-treated co-digestion process [15] and said to have a great ability to disintegrate extracellular polymeric substrates (EPS), thus improve the slurry dewatering capacity [16]. PDS can be converted into reactive oxygen species (ROSs) such as $SO_4^{\bullet}$ and $^{\bullet}OH$, which can act with organics efficiently [17]. Some co-existing organic matters (already present in the process or those created recently by the fragmentation system), may devour PDS and reduce its use efficacy. PDS pretreatment to treat slurry was examined by Li *et al*. [18], who concluded that PDS is an efficient approach for improving slurry dissolution. However, the usage of PDS pretreatment has not been thoroughly investigated and this can have an impact on the system. The gap between feasibility study and fertilizer recovery of pretreated algae slurry was not studied so far.

Therefore, the goal of this work was to find the viability and system of peroxydisulfate (PDS) treatment for increasing methane production from algae slurry and fertilizer recovery. PDS dosages ranging from 0.02 to 1.2 g PDS/g algae total suspended solids were investigated. The character changes in algae slurry while the initial 2 h of treatment were investigated. The final accumulative methane output and fatty acid generation after three days of digestion were also compared. During 60 day digestion, the cumulative methane generation, the algae yield efficiency and the hydrolysis rate were measured. The findings of the study may help in the development of low-cost technologies for processing the algae slurry for methane generation.

EXPERIMENTAL

Sample and seeding source and characteristics: The major constituents employed as algae slurry for fermentation tests investigation were *Microcystis* sp. [19]. The algal slurry and seed employed were gathered according to the method of Li *et al*. [19]. Fresh microalgae had an initial TSS of 6.5 ± 0.20 g/L and a VSS of 5.99 ± 0.17 g/L. The preliminary concentrations of soluble polysaccharides and proteins in algae slurry were 3.62 ± 0.17 mg/L and 15.29 ± 0.31 mg/L, respectively. Total suspended solids and volatile suspended solids of the inoculum were 22 ± 0.5 g/L and 20 ± 0.16 g/L, respectively. The TS, VS, TSS, VSS, TCOD, SCOD, and pH values were 8.07 ± 0.08, 7.6 ± 0.18, 6.50 ± 0.11, 6.08 ± 0.19, 12792.23 ± 763, 697 ± 18.20 and 7.15 ± 0.17, respectively for the algal sample. Besides, the TS, VS, TSS, VSS, TCOD and SCOD values were 58 ± 0.26, 58 ± 0.40, 22 ± 0.46, 21 ± 0.16, 34605 ± 1979, 344 ± 25, respectively for the inoculum.

Pretreatment techniques for peroxydisulfate (PDS): peroxydisulfate ($Na_2S_2O_8$) was procured from Permula Sdn. Bhd., Malaysia, which has a molar mass of 238.03 g/mol. PDS was applied to each digester D_0 to D_7 at doses of 0, 0.02, 0.03, 0.06, 0.20, 0.30, 0.60 and 1.2 g PDS/g algae slurry, respectively. The algae slurry was combined with the appropriate amount of PDS and carefully mixed for 120 min with a mechanical agitator. The soluble polysaccharide, protein, SCOD of the sample were examined every 0.5 h at the time of the PDS treatment.

Biomethane potential testing and modelling: The biomethane potential experiment was performed to assess the methane output efficiency of algae that had been pretreated with various doses of PDS. The detailed system of the biomethane potential experiment was performed according to Li *et al*. [20]. Hydrolysis rate and biomethane potential (BMP) are two important indicators in the methane production process (B_0). After various PDS pretreatments, these 2 metrics were applied to compare methane generation kinetic and yield efficiency. The cumulative methane produced at day t, B(t) was expressed by eqn 1:

$$B(t) = B_0 (1-e^{-kt}) \quad (1)$$

Effects of PDS treatment on bioprocesses: During the digesting system hydrolysis, acidogenesis, acetogenesis and methanogenesis are significant. Using model organic matter, the possible influence of PDS on methane generation from algal biomass was investigated. A total of twelve serum bottles of 500 mL were utilized. The digesters were grouped into four experiments.

In blank experiment, PDS dose 0.02 and 0.2 g PDS/g algae (dry weight basis) were the three PDS-treated conditions employed. It was chosen depending upon variations in PDS dosages and cumulative methane generation findings. After the BMP test, the slurry utilized for every experiment was taken from the reactor (semi-continuous). For removing any significant residual PDS or chemicals, the mixed slurry was

centrifuged at 4000 rpm for 10 min and rinsed three times with tap water. Subsequently, the washed slurry was employed as an inoculum for the anaerobic experiment, which was used to determine the varied substrates utilization rates by the mixed slurry.

Experiment-1: In this experiment, 30 mL mixed slurry pre-treated with 0, 0.02 and 0.2 g PDS/g total suspended solids algae slurry, as well as 270 mL synthetic substrate, were added to three reactors. Bovine serum albumin, a model protein molecule, was used to make the synthetic wastewater at a concentration of 6 g/L. The testing lasted three days and the bovine serum albumin concentration was checked every day. At the end of experiment, the VSS was evaluated and the (v/v) degradation rate of PDS was computed by dividing PDS decrease by volatile suspended solids.

Experiments 2, 3 and 4 were carried out to see how PDS affected the processes of acidogenesis, acetogenesis and methanogenesis, correspondingly. The process was the same as experiment-1, with the exception that the synthetic substrate was changed to glucose and acetates, correspondingly.

Analytical methods for basic parameters: Standard procedures were used to test the basic properties of seed sludge, BSA and algal sludge [21]. The possibility for oxidation decrease after 60 days of digestion, the mixed sludge's oxidation-reduction potential (ORP) was assessed. Ion chromatography (USA) was used to assess the generation of fatty acids in each reactor after three days of digestion. To quantify the heavy metals in the solution before and after digestion and Microcystin-LR was used [18]. The pH, heavy metals, moisture contents, turbidity and suspended solids were measured as described earlier [22].

Role of K_2SO_4, H_2SO_4, H_2O_2, $SO_4^{\bullet-}$, $^1O_2$ and $^\bullet OH$ to PDS aided digestion: During the digestive process, PDS can be degraded into a variety of intermediates, comprising K_2SO_4, H_2SO_4, H_2O_2, $SO_4^{\bullet-}$, $^1O_2$ and $^\bullet OH$. Several fermentation tests were carried out to determine the role of these distinct intermediates and oxidation reactive species. Each serum vial had 140 mL algae sludge and 100 mL seed sludge added to it. Other samples were introduced to the 10 reactors, including PDS 0.0319 g, 0.00393 g H_2O_2, 0, 0.02049 g K_2SO_4, 0.01155 g H_2SO_4, 0.0319 g PDS + 1 M methanol, 1 M methanol, 0.0319 g PDS +1 M *tert*-butanol, 1 M *tert*-butanol, 0.0319 g PDS +1 M *tert*-butanol.

The whole mixture was then made up of 250 mL of MilliQ water in every digester. Subsequently, the digesters were purged with nitrogen for 5 min to ensure anaerobic conditions, airtight by a rubber cork and placed in a shaker for seven days of fermentation at 35 ºC. Subsequent operational settings were the same as described earlier; the fermentation lasted 7 days and the cumulative methane output was measured. The PDSs and intermediates were supplemented at 0.02 g PDS/g algae TSS, based on the PDS dosage. Methanol was employed to generate $SO_4^{\bullet-}$ and $^\bullet OH$, while *tert*-butanol was applied to capture $^\bullet OH$.

Statistical analysis: Three replicates were used for all the samples used in the experiment. All measured parameters were subjected to statistical analysis (standard deviation) by using Microsoft EXCEL 2013.

RESULTS AND DISCUSSION

Influence of PDS pretreatment on algal sludge disintegration: Within 120 min, the soluble polysaccharides, proteins, and SCODs of algal slurry pre-treated with varying doses of PDS were evaluated (Fig. 2). In all reactors, the soluble polysaccharides and SCODs of the algae slurry were rised over time. The concentrations of soluble polysaccharide and SCOD are significantly correlated with the PDS dose ($p < 0.01$ for polysaccharides, $p < 0.01$ for SCODs at 39 min and $p < 0.05$ for SCODs at 2 h) (Table-1). The PDS dose had a strong negative connection with the soluble protein concentration. Protein's decrease was sluggish in the PDS state of 0.02-0.2 g PDS/g algae total suspended solids, but this was faster in the concentrated and PDS level of 0.3-1.2 g PDS/g algae total suspended solids.

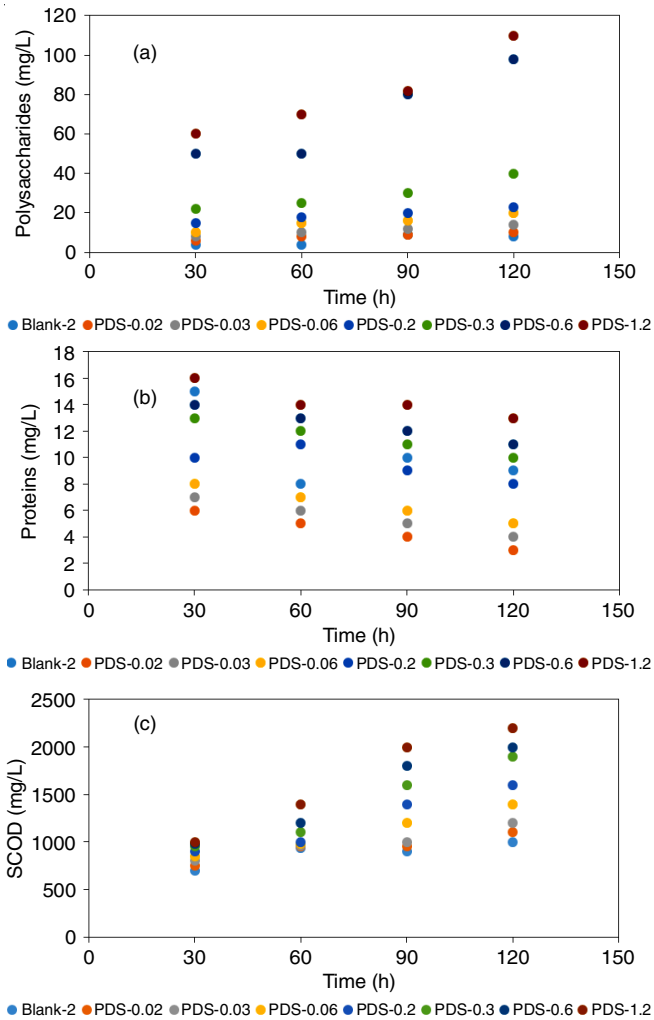

Fig. 2. Soluble polysaccharides (a), proteins (b), SCODs (c) of the algae slurry at the time of pretreatment with PDS

The oxidation-reduction potential for individual digester enhanced as the PDS dose was raised after 2 h of PDS pretreatment, indicating that the addition of PDS resulted in a larger oxidation potential (Table-2). It showed that PDS treatment might increase algae cell breakdown, resulting in the release of peptidoglycans from the algal cells and polysacc-

TABLE-1
CORRELATION BETWEEN PEROXYDISULFATE DOSE AND THE SOLUBLE POLYSACCHARIDES, PROTEINS AND SCODS OF THE ALGAE SLURRY AT 120 min

	Peroxy-disulfate dose	Polysaccharides				Proteins				SCODs			
		30 min	60 min	90 min	120 min	30 min	60 min	90 min	120 min	30 min	60 min	90 min	120 min
Peroxydisulfate dosage	1												
Polysaccharides 30 min	.956**	1											
Polysaccharides 60 min	.977**	.994**	1										
Polysaccharides 90 min	.933**	.996**	.987**	1									
Polysaccharides 120 min	.946**	.996**	.993**	.998**	1								
Protein 30 min	-.772*	-.649	-.662	-.590	-.607	1							
Protein 60 min	-.843**	-.897**	-.865**	-.877**	-.867**	.797*	1						
Protein 90 min	-.833*	-.873**	-.843**	-.853**	-.836**	.806*	.986**	1					
Protein 120 min	-.816*	-.852**	-.831*	-.833*	-.815*	.789*	.972**	.985**	1				
SCOD 30 min	.969**	.994**	.998**	.990**	.995**	-.627	-.846**	-.823*	-.800*	1			
SCOD 60 min	.930**	.897**	.925**	.882**	.883**	-.579	-.718*	-.745*	-.750*	.918**	1		
SCOD 90 min	.958**	.898**	.937**	.885**	.899**	-.603	-.676	-.681	-.671	.937**	.969**	1	
SCOD 120 min	.815*	.887**	.891**	.892**	.888**	-.338	-.687	-.678	-.697	.890**	.914**	.854**	1

**$p < 0.01$, *$p < 0.05$

TABLE-2
STATES OF THE EXPERIMENTS

Digesters	States of the experiments
Blank	100 mL seed sludge + 145 mL MiliQ water
D0	100 mL seed sludge + 145 mL Algae sludge
D1	100 mL seed sludge + 145 mL Algae sludge pretreated with 0.02 g PDS/g algae TSS
D2	100 mL seed sludge + 145 mL Algae sludge pretreated with 0.03 g PDS/g algae TSS
D3	100 mL seed sludge + 145 mL Algae sludge pretreated with 0.06 g PDS/g algae TSS
D4	100 mL seed sludge + 145 mL Algae sludge pretreated with 0.20 g PDS/g algae TSS
D5	100 mL seed sludge + 145 mL Algae sludge pretreated with 0.30 g PDS/g algae TSS
D6	100 mL seed sludge + 145 mL Algae sludge pretreated with 0.60 g PDS/g algae TSS
D7	100 mL seed sludge + 145 mL Algae sludge pretreated with 1.20 g PDS/g algae TSS

harides from the intracellular material into the solutions [23]. In addition, SCODs were utilized to indicate the results that the extent of algal disintegration was in an optimistic relationship with the peroxymonosulfate dose [9]. As the PDS dose enhanced, the damages to algal cell structures and protein breakdown also enhanced as well. This could also imply that the best product recovery *via* methane generation may not have taken place in the presence of the maximum PDS dose [24]. Greater PDS concentrations may cause mineralization of feed wastes and decrease organic material concentrations, resulting in poorer methane yields [25,26].

Methane generation with and without PDS treatment at various dosages: Fig. 3a shows the cumulative methane production in reactors with varying PDS dosages after 60 days of digestion. The cumulative effect pretreated at 0, 0.02, 0.03, 0.06, 0.2, 0.3, 0.6 and 1.2 g PDS/g algae slurry, methane generation was 293, 337, 317, 334, 331, 318, 223, and 45 L methane/kg TCOD algal slurry, respectively.

With 0.02 g PDS/g algae slurry supplied, D_3 had the largest cumulative methane generation. When compared to D_0, D_1, D_3, D_4, D_5, D_6 and D_7, it is 15%, 6%, 1%, 2%, 6%, 51% and 657%, respectively. This means that the accumulative methane

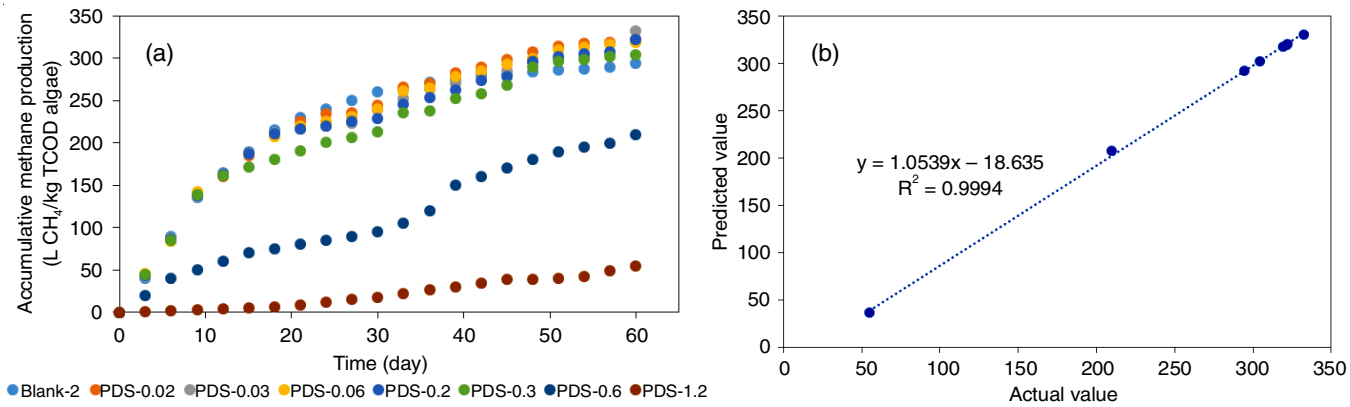

Fig. 3. Accumulative methane production during 60 day anaerobic digestion in each reactor with various pretreatment of algal sludge (a) and the actual and predicted accumulative methane production (b)

TABLE-3
ALGAE SLURRY PROPERTIES AFTER 120 min TREATMENT BY PEROXYDISULFATE

Digesters	Treatment conditions	pH	Oxidation reduction potential (mV)	Polysaccharide (mg/L)	Protein (mg/L)	SCOD (mg/L)
D0	0 g PDS/g algal TSS	7.04	71	8.3	6.42	1095.20
D1	0.02 g PDS/g algal TSS	7.20	74.3	13.50	13.53	1334.75
D2	0.03 g PDS/g algal TSS	7.17	92.9	20.71	13.18	1464.96
D3	0.06 g PDS/g algal TSS	7.13	123.4	22.31	9.52	1559.82
D4	0.20 g PDS/g algal TSS	7.09	179.1	23.80	7.55	1567.55
D5	0.30 g PDS/g algal TSS	7.03	247.4	40.65	6.10	1940.25
D6	0.60 g PDS/g algal TSS	6.96	270.9	95.81	2.76	2022.84
D7	1.2 g PDS/g algal TSS	6.83	329.5	105.69	0.71	2119.07

TABLE-4
ANALYZED HYDROLYSIS RATE, BIOCHEMICAL METHANE POTENTIAL OF ALGAL BIOMASS AT UNALIKE PRETREATMENT CONDITIONS BY ONE-SUBSTRATE MODELLING

Digesters	Blank-2	PDS-0.02	PDS-0.03	PDS-0.06	PDS-0.2	PDS-0.3	PDS-0.6	PDS-1.2
k (d^{-1})	0.0875	0.087	0.0802	0.0776	0.079	0.0798	0.0772	0.0185
B_0	291.51	319.01	330.33	317.28	319.06	302.46	207.41	53.96
Y(60)	289.81	317.54	327.17	314.13	316.92	300.37	205.64	36.82
R^2	0.9919	0.9912	0.9912	0.9902	0.9869	0.986	0.9779	0.8989

produced by the PDS at 0.02, 0.03, 0.06, 0.2, and 0.3 g PDS/g algae slurry after 2 months of co-digestion is identical. A one-substrate model was utilized for fitting the daily cumulative methane produced in each reactor (Table-3, $R_2 > 0.9779$ from D_0 through D_6 and 0.8989 for D_7). At D_2, with 0.02 g PDS/g algae slurry dose, the greatest biological methane generation efficiency computed was 330 L methane/kg TCOD algae. When PDS was added to the reactors, the hydrolysis rate was lowered when compared to the blank (D_0). This meant that after being dosed with PDS, the biological and chemical procedure had transformed, at the very least the hydrolysis rate had decreased. The model determined the forecasted methane generation efficiency for individual digesters (Table-4). The actual and the projected value are highly correlated (Fig. 3b). The addition of PDS to the digesting process may have increased reactive oxidizing species (ROS) and thus algae fragmentation [27]. According to Li *et al*. [28] at 50 ºC, 16 h, 0.5% persulfate pretreatment, pH = 5, and a solid-liquid mass proportion of 1:10 were the best pretreatment conditions. Pretreatment of lignin with thermally activated sodium persulfate reduced it significantly. The production of reducing sugar and volatile fatty acids was significantly higher in the treated group than in the control group. This pattern emerged because heat activation of persulfate predominantly damages the benzene ring in lignin by creating and releasing active sulfate radical; additionally, during the thermal activation, hydroxyl radical and sulfate radical dot operate together. Besides, the daily biogas generation of the groups were pretreated for 15 and 47 h without elution, which was 23% and 27% higher, respectively, than the untreated group. After the pretreatment, the degradation rates of total and volatile solids increased to 61% and 71%, respectively.

Effect of PDS on bioprocess: Using several model substrates, batch tests were performed to investigate the influence of PDS on those bioprocesses. At a dosage of 0, 0.02 and 0.20 g PDS/g algae slurry was investigated (Table-5). The model substrate degradation rate was lowered with the addition of

TABLE-5
DEGRADATION PROPORTION OF BSA, GLUCOSE, BUTYRATE AND ACETATE[a]

Substrates	Peroxydisulfate levels (g peroxydisulfate/g algal TSS)		
	0	0.02	0.2
BSA	6.98 ± 0.47	2.73 ± 0.09	1.06 ± 0.09
Glucose	1.76 ± 0.05	1.94 ± 0.12	1.64 ± 0.07
Butyrate	0.25 ± 0.02	0.29 ± 0.05	0.17 ± 0.03
Acetate	0.99 ± 0.04	0.43 ± 0.03	0.52 ± 0.03

[a]Outcomes are the means and standard deviations of triplicate experiments, the unit is mg/g VS h

PDS, irrespective of the PDS dose; greater PDS dose caused a lower degradation rate. To summarize, the use of PDS miffed the bioprocess such as hydrolysis abilities. Breakdown rates of BSAs, glucose, butyrates and acetates for the untreated sample were 6.98 ± 0.47, 1.76 ± 0.05, 0.25 ± 0.02 and 0.99 ± 0.04 mg/gVSh, respectively. The glucose and butyrate breakdown rates were slightly boosted at D_2, where 0.02 g PDS/g algae slurry was introduced.

This could explain why the acidogenesis and acetogenesis rates were somewhat enriched at 0.02 g PDS/g algae slurry [29]. It could also explain the reason of the cumulative methane generated was extraordinary in D_2 [30].

Removal of microcystin-LR and heavy metals: After algae slurry digestion, microcystin-LR and heavy metal elimination were estimated (Table-6). The heavy metals like Cd, Pb and Cr in effluent were elevated in comparison to algal sludge, whereas Zn was considerably reduced. It meant that the algae slurry employed contained higher concentrations of heavy metals mixed with the substrates as indicated by the fermentation process. Many previous studies have looked into using algal biomass to uptake heavy metals from wastewaters, with some algal species such as *C. aculeolate*, reaching a maximum uptake capability of 106 mg/g for heavy metals lead, cadmium, and zinc [31]. Since heavy metals reduction in the liquid state might be transported to the slurry state while fermentation, heavy metals in the effluent should be counted throughout the

TABLE-6
POLLUTANTS ELIMINATION DURING FERMENTATION SYSTEM

Treatment conditions	Cd (µg/L)	Pb (µg/L)	Zn (µg/L)	Cr (µg/L)	*Microcystin-LR* in fluid state (µg/L)	*Microcystin-LR* in slurry state (µg/g dry sludge)
Algae slurry	0.13	0.89	2564.78	28.65	1.22	1394.64
Seeding slurry	0.11	7.12	284.00	164.17	–	–
0 g PDS/g algal TSS	–	–	–	–	0.33	12.86
0.02 g PDS/g algal TSS	0.09	4.75	264.82	168.74	–	6.37
0.03 g PDS/g algal TSS	0.18	9.73	97.86	134.46	–	3.52
0.06 g PDS/g algal TSS	0.16	4.86	85.34	218.17	–	2.82
0.20 g PDS/g algal TSS	0.04	1.64	30.44	147.06	–	2.37
0.30 g PDS/g algal TSS	0.06	4.74	128.30	387.53	–	2.87
0.60 g PDS/g algal TSS	0.08	4.80	66.36	613.13	–	2.92
1.2 g PDS/g algal TSS	0.08	12.86	619.24	352.28	–	2.17

algae slurry rescue system. Microcystin-LR in the fluid state was decreased from 1.3 g/L to out of detection in PDS supplemented process and to 0.33 g/L to the untreated process at the same time.

With the addition of PDS, the microcystin-LR in the slurry state of algae slurry was reduced from 1394.64 g/g dry algae slurry to 2.17-6.37 g/g dry assimilated algae slurry. The end sludge phase microcystin-LR in the reactor without PDS is 12.86 g/L, which is two-folds greater compared to the levels in the PDS-supplemented process. This meant that using PDS enhanced microcystin-LR removal in both the fluid and slurry phases, with microcystin-LR removal in the sludge phase increasing considerably after fermentation. This demonstrates that algae slurry digestion has the potential to significantly reduce microcystin-LR contamination in the environment.

Contribution of PDS to the digestive process: As a highly oxidative compound, PDS has the potential to cause harm. The breakdown into a variety of intermediates, which are then transformed into three major free radicals: $SO_4^{\bullet-}$, $^1O_2$ and $^\bullet OH$. The cumulative methane generation for the 1 week fermentation in individual digester was compiled with first-order kinetic equation (Fig. 4), 0.0693, 0.0597, 0.0551, 0.0437, 0.0350, 0.0334, 0.0178, 0.0064, 0.0008 and 0.0008 were the corresponding k values. It is clearly observed that when *tert*-butanol was added, accumulative methane production was virtually completely stopped. The k value for the PDS, H_2O_2 added reactor and control was rather high, indicating that in the PDS supplemented process, OH may have the greatest influence, whereas SO_4^- has only minor influences [32,33].

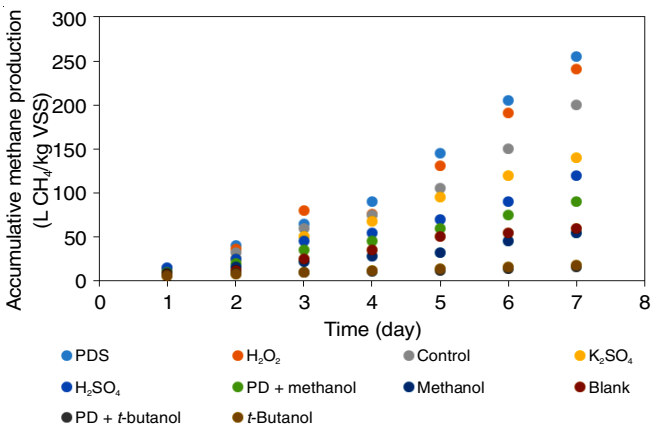

Fig. 4. Influences of PDS and its breakdown products on algae slurry methane generation (Control: only algal sludge and seed sludge were added; Blank: only MilliQ instead of algal sludge, and seed sludge were added) (0.0693, 0.0597, 0.0551, 0.0437, 0.0350, 0.0334, 0.0178, 0.0064, 0.0008 and 0.0008 were the corresponding k values)

Other compounds have also restricted the methane production, indicating a negative impact on the digestion process in addition to contribute ROS in order to promote digestion. The solo-PDS process has been upgraded to break down into a variety of intermediates, which are then transformed into three major free radicals mentioned previously. The accumulative methane output at the highest k value implied that employing the PDS treatment method may boost methane generation. It may be due to the greater reactive oxygen species levels of the process. When compared to a methanol-only process, the PDS and methanol co-added process still produce more methane, and the $^1O_2$ that remains in the process contributes to the oxidation process. The significant methane production in the control set suggests that SO_4^- may have contributed to the inhibition of methane synthesis, which should be avoided.

Fertilizer recovery: Co-fermentation of the organic substrates could result in irrigation liquid and fertilizer for agriculture [24]. Table-7 shows the qualities of the fermented waste. From the fermented waste, sludge recapture was 0.09 m^3 sludge/m^3 wastewater and water recapture was 0.86 (m^3 sludge/m^3 wastewater). To evaluate their prospective usage, the qualities of the sludge were compared to the standards established in the current Malaysia recommendations. Sludge may be used as an agricultural input if the heavy metal content is below the limitations. Thus, the fermented slurry can be used as fertilizer and the produced liquid can also be used for irrigation.

Conclusion

In this work, the effects of treatment by different doses of peroxydisulfate (PDS) on algal methane generation were examined. The outcomes showed that algae slurry prepared with 0.02 g PDS/g produced the best results. Even though the SCOD and polysaccharide levels rise with increased PDS dose, the ultimate cumulative methane output doesn't follow the same pattern. At 0.02 g PDS/g algal TSS, the potential of acidogenesis and acetogenesis was improved. The cumulative methane production in the digesters examined could be explained by a single substrate model, with the maximum projected cumulative methane generation occurring at 0.02 g PDS/g algae total suspended solids.

TABLE-7
PHYSICO-CHEMICAL PROPERTIES OF DECOMPOSED SLURRY TREATED WITH 0.02 g PEROXYDISULFATE/g ALGAL TSS

	Solid portion		Water portion
Recovery of sludge (m^3 sludge m^{-3} substrate)	0.09	Recovery of water (m^3water m^{-3}substrate)	0.86
Moisture (%)	96	COD (g/L)	0.31
Zn (g/kg dry weight)	0.59	Turbidity (unfiltered turbidity, UNF)	1291
Ni (g/kg dry weight)	0.19	Suspended solids (g/L)	0.06
Cu (g/kg dry weight)	0.20		
Cr (g/kg dry weight)	0.04		
Hg (g/kg dry weight)	0.003		
Pb (g/kg dry weight)	7.4×10^{-3}		
Cd (g/kg dry weight)	2.7×10^{-4}		

With the supplementation of PDS, the hydrolysis rate was somewhat lowered, according to the modeling results. PDS had the potentiality to be employed as a successful pretreatment technique for treating algae slurry as an organic material rescue process. The digested slurry may be used as fertilizer and the liquid that is produced can be used for irrigation.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. R.E.C. Amaral, J. Brito, M. Buckman, E. Drake, E. Ilatova, P. Rice, C. Sabbagh, S. Voronkin and Y.S. Abraham, *Sustainability*, **12**, 5337 (2020); https://doi.org/10.3390/su12135337
2. T. Wiedmann, M. Lenzen, L.T. Keyßer and J.K. Steinberger, *Nat. Commun.*, **11**, 3107 (2020); https://doi.org/10.1038/s41467-020-16941-y
3. M.N.I. Siddique, M.S. Abdul Munaim and A.W. Zularisam, *J. Clean. Prod.*, **106**, 380 (2015); https://doi.org/10.1016/j.jclepro.2014.08.003
4. P.K. Sadh, S. Duhan and J.S. Duhan, *Bioresour. Bioprocess.*, **5**, 1 (2018); https://doi.org/10.1186/s40643-017-0187-z
5. W.W. McNeary and L.E. Erickson, *J. Environ. Protec.*, **4**, 9 (2013); https://doi.org/10.4236/jep.2013.411A002
6. D. Liu, P. Wang, G. Wei, W. Dong and F. Hui, *Environ. Sci. Pollut. Res.*, **20**, 60 (2013); https://doi.org/10.1007/s11356-012-1052-4
7. A.J. Ward, D.M. Lewis and F.B. Green, *Algal Res.*, **5**, 204 (2014); https://doi.org/10.1016/j.algal.2014.02.001
8. M.N. Islam Siddique, Z.B. Khalid and M.Z.B. Ibrahim, *J. Environ. Chem. Eng.*, **8**, 103569 (2020); https://doi.org/10.1016/j.jece.2019.103569
9. M.N.I. Siddique and Z.A. Wahid, *Water Environ. Res.*, **90**, 835 (2018); https://doi.org/10.2175/106143017X15131012153031
10. S. Bleakley and M. Hayes, *Foods*, **6**, 33 (2017); https://doi.org/10.3390/foods6050033
11. L. Machado, G. Carvalho and R.N. Pereira, *Biomass*, **2**, 80 (2022); https://doi.org/10.3390/biomass2020006
12. T. Garoma and R.E. Yazdi, *BMC Plant Biol.*, **19**, 18 (2019); https://doi.org/10.1186/s12870-018-1614-9
13. Z.B. Khalid, M.N.I. Siddique, A. Nayeem, T.M. Adyel, S.B. Ismail and M.Z. Ibrahim, *J. Environ. Chem. Eng.*, **9**, 105489 (2021); https://doi.org/10.1016/j.jece.2021.105489
14. Y. Wan, X. Chen, Q. Liu, H. Hu, C. Wu and Q. Xue, *Environ. Pollut.*, **293**, 118586 (2022); https://doi.org/10.1016/j.envpol.2021.118586
15. T. Hou, J. Zhao, Z. Lei, K. Shimizu and Z. Zhang, *J. Clean. Prod.*, **314**, 127942 (2021); https://doi.org/10.1016/j.jclepro.2021.127942
16. Z. Chen, J. Li, M. Chen, K.Y. Koh, Z. Du, K.Y.-H. Gin, Y. He, C.N. Ong and J.P. Chen, *Water Res.*, **201**, 117263 (2021); https://doi.org/10.1016/j.watres.2021.117263
17. X.-Y. Pei, H.-Y. Ren, G.-S. Liu, G.-L. Cao, G.-J. Xie, D.-F. Xing, N.-Q. Ren and B.-F. Liu, *J. Hazard. Mater.*, **424**, 127254 (2022); https://doi.org/10.1016/j.jhazmat.2021.127254
18. C. Li, V. Goetz and S. Chiron, *Sci. Total Environ.*, **806**, 150768 (2022); https://doi.org/10.1016/j.scitotenv.2021.150768
19. R. Li, M. Cai, Z. Xie, Q. Zhang, Y. Zeng, H. Liu, G. Liu and W. Lv, *Appl. Catal. B*, **244**, 974 (2019); https://doi.org/10.1016/j.apcatb.2018.12.043
20. R. Li, J. Kong, H. Liu, P. Chen, Y. Su, G. Liu and W. Lv, *Chem. Eng. J.*, **331**, 809 (2018); https://doi.org/10.1016/j.cej.2017.09.025
21. S. Vinardell, S. Astals, K. Koch, J. Mata-Alvarez and J. Dosta, *Bioresour. Technol.*, **330**, 124978 (2021); https://doi.org/10.1016/j.biortech.2021.124978
22. A. González-González, F. Cuadros, A. Ruiz-Celma and F. López-Rodríguez, *Bioresour. Technol.*, **136**, 109 (2013); https://doi.org/10.1016/j.biortech.2013.02.031
23. H. Zhou, D. Lu, S. Fang, C. Liu, Y. Chen, Y. Hu and Q. Luo, *J. Environ. Manage.*, **287**, 112294 (2021); https://doi.org/10.1016/j.jenvman.2021.112294
24. A. Singh, R. Sharma, D. Pant and P. Malaviya, *Sci. Total Environ.*, **774**, 145676 (2021); https://doi.org/10.1016/j.scitotenv.2021.145676
25. Z. Zahan and M.Z. Othman, *Bioresour. Technol.*, **281**, 286 (2019); https://doi.org/10.1016/j.biortech.2019.01.129
26. S.D. Neve, S. Sleutel, S. Sleutel and G. Hofman, *Nutr. Cycl. Agroecosyst.*, **67**, 13 (2003); https://doi.org/10.1023/A:1025113425069
27. J.W.R. Chong, G.Y. Yew, K.S. Khoo, S.-H. Ho and P.L. Show, *J. Environ. Manage.*, **293**, 112782 (2021); https://doi.org/10.1016/j.jenvman.2021.112782
28. X. Li, G. Fang, L. Chen, R. Guo, D. Zou and Y. Liu, *Biomass Bioenergy*, **154**, 106216 (2021); https://doi.org/10.1016/j.biombioe.2021.106216
29. R. Zhang, X. Lu, Y. Tan, T. Cai, Y. Han, D. Kudisi, C. Niu, Z. Zhang, W. Li and G. Zhen, *Bioresour. Technol.*, **339**, 125547 (2021); https://doi.org/10.1016/j.biortech.2021.125547
30. Y. Li, Z. Wang, Z. Jiang, L. Feng, J. Pan, M. Zhu, C. Ma, Z. Jing, H. Jiang, H. Zhou, H. Sun and H. Liu, *Bioresour. Technol.*, **344**, 126353 (2022); https://doi.org/10.1016/j.biortech.2021.126353
31. C. Yu, H. Pang, J.-H. Wang, Z.-Y. Chi, Q. Zhang, F.-T. Kong, Y.-P. Xu, S.-Y. Li and J. Che, *Sci. Total Environ.*, **813**, 151891 (2021); https://doi.org/10.1016/j.scitotenv.2021.151891
32. J. Dou, J. Cheng, Z. Lu, Z. Tian, J. Xu and Y. He, *Appl. Catal. B*, **301**, 120832 (2022); https://doi.org/10.1016/j.apcatb.2021.120832
33. P. Malik and S.K. Saha, *Sep. Purif. Technol.*, **31**, 241 (2003); https://doi.org/10.1016/S1383-5866(02)00200-9