Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 52 (2014) 337 – 351

Energy Procedia

2013 International Conference on Alternative Energy in Developing Countries and Emerging Economies

Enhanced Biogas Production from Canned Seafood Wastewater by Co-digestion with Glycerol Waste and *Wolffia arrhiza*

Kiattisak Panpong[a], Galaya Srisuwan[a], Sompong O-Thong[a,b,c*], Prawit Kongjan[d]

[a] *School of Engineering and Resources, Walailak University, Nakhon si thammarat 80161, Thailand*
[b] *Department of Biology,* [c] *Research Center in Energy and Environment, Faculty of Science, Thaksin University, Phatthalung 93110, Thailand*
[d] *Department of Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand*

Abstract

Anaerobic co-digestion of canned seafood wastewater (CSW) with glycerol waste (GW) and *wolffia arrhiza* (WA) for methane production was investigated. Methane yields from anaerobic co-digestion of CSW with 1%GW, CSW with 1%GW and 5%WA, CSW with 1%GW and 10%WA and CSW with 1%GW and 15%WA were 577, 789, 545 and 474 mL CH_4/g VS-added, respectively. Methane production from CSW with 1%GW and 5%WA increased approximately 4-fold when compared with CSW alone (278 mLCH_4/g VS-added). Co-digestion of CSW with 1% GW and 5% WA was the best condition and gave the maximum methane production of 8.8 m^3 CH_4/m^3 mixed wastewater and 96.8% biodegradability. The maximum methane production rate and yield were 3.71 L CH_4/L-reactor.day and 858 mL CH4/g VS-added (352 mLCH4/g COD-removed) at OLR of 4 g COD/L. day in UASB reactor. The methane composition in biogas was 62.3%. The Monod, Modified Stover–Kincannon and Grau second-order models were used to explain the performance of UASB reactor. The results showed that the kinetic coefficient of the Modified Stover–Kincannon model could explain the performance of UASB reactor in term of COD removal efficiency and microbial growth by having the regression coefficient (R^2) as 0.987.

Selection and peer-review under responsibility of the Organizing Committee of 2013 AEDCEE

Keywords: Co-digestion, Biogas production, Canned seafood wastewater, Glycerol waste, *Wolffia arrhiza*

* Corresponding author. Tel.: +66 746 09600 ; fax: +66 746 93992.
E-mail address: sompong.o@gmail.com

Selection and peer-review under responsibility of the Organizing Committee of 2013 AEDCEE
doi:10.1016/j.egypro.2014.07.085

1. Introduction

Canned seafood industry (tuna, sardine, mackerel, etc.) is one of the major exports in Thailand. Most of the canned seafood industry is located in the southern and eastern coast of Thailand. Canned seafood processing requires large amounts of water such as the thawing, butchering and cooking etc. which the wastewater discharges about 14 to 22 m^3/ton of raw material [1]. Generally, the wastewater treatments for canned seafood wastewater are activated sludge, aerated lagoon, oxidation pond and anaerobic lagoon but the anaerobic systems are less used. Anaerobic systems are not very popular due to the problem of high content of organic nitrogen in wastewater which inhibits the anaerobic process [2]. Wastewater from canned seafood processing has a high protein-based nitrogen and sodium concentration. Canned seafood wastewaters are contained of BOD_5 (100–3,000 mg/L), COD (1,000–18,000 mg/L) and total nitrogen (80–1,000 mg/L) [3]. Protein-rich materials have a slow degradation and their degradation products (ammonium) can inhibit the process as well [4]. The ammonia nitrogen concentration ranging between 0.17 and 14 g/L could inhibit methanogenic process and result the methane production reducing of 50% [5, 6]. Methanogenesis was also strongly inhibited by a sodium at the concentration of 10 g/L [3]. Prasertsan et al. [2] reported that the maximal biogas yield from fishery wastewater was 0.75 m^3/kg COD for anaerobic filter treatment at OLR of 1.3 kg COD/m^3.day and HRT of 11 days.

The canned seafood wastewater unsuitable to treat with the anaerobic process due to it was low organic matter content and high nitrogen content. Anaerobic co-digestion of canned seafood wastewater with other waste that has high COD content could be suitable for methane production. Glycerol waste was a by-product of biodiesel production. Glycerol waste was generated around 10% of raw material [7]. Glycerol waste has high COD, low prices, can be stored at room temperature for a long time and easy to digest under anaerobic condition [8]. Generally, glycerol waste was used as a co-substrate to improve the biogas production from pig manure. The maximum methane yield of 0.32 ml CH_4/g COD was achieved at a mixing ratio of 80:20 (glycerol: pig manure) [9]. *Wolfia arrhiza* was a small circular floating weed. The size of *wolfia arrhiza* was about 1 mm of length that lives in tropical and subtropical lakes and marshes. The *Wolfia arrhiza* grows quickly and absorbs large amounts of nutrients [10]. The vegetative frond of *Wolffia arrhiza* may be applicable to the removal of nutrients from treated wastewater or polluted water like that in eutrophic lakes and used to make animal feed. Suppadit [11] reported that the nutrient removal using *Wolffia arrhiza.* It also difficult to dispose and using *Wolffia arrhiza* as a co-substrate in anaerobic digestion could be a suitable way for disposal. However, It still no report on co-digestion of glycerol waste and *Wolffia arrhiza* with industrial wastewater for biogas production.

This work aimed to evaluate the potential of glycerol waste (GW) and *Wolfia arrhiza* (WA) which is used as co-substrates to improve the methane production of canned seafood wastewater (CSW) in laboratory scale. The effect of the feed mixing ratio on the system performance and substrate removal was tested in an up-flow anaerobic sludge blanket reactor (UASB). The experimental data was also used for the kinetic coefficient value determination.

Nomenclature

a	$S_0 /(k_s \cdot X)$ (per day)
b	constant for Grau second-order model
E	substrate removal efficiency (S_i-S_e/S_i)
K_B	saturation value constant (g COD/L-day)
K_d	death rate constant (per day)
K_S	half saturation concentration (g COD/L)
k_s	Grau second-order substrate removal rate constant (per day)
Q	inflow rate (L/day)

Nomenclature (Cont'd)

X, X_e	concentrations of biomass in the feed and reactor effluent (g VSS/L)
U_{max}	maximum utilization rate constant (g COD/L-day)
V	reactor volume (L)
Y	yield coefficient (g VSS/ g COD removal)
θ_C	mean cell-residence time (day)
θ_H	hydraulic retention time (day)
μ, μ_{max}	specific growth rate and, maximum specific growth rate, respectively (per day)
CSW	canned seafood wastewater
GW	glycerol waste
WA	*wolffia arrhiza*

2. Methodology

2.1 Substrates and seed inoculum

Canned seafood wastewater (CSW) was collected from Kuang Pei San Food Products Public Co., Ltd., Trang province, Thailand. Glycerol waste (GW) was collected from the biodiesel plant at Prince of Songkhla University, Songkhla, Thailand. *Wolffia arrhiza* (WA) was obtained from a local villager at Sakonnakhon, Thailand. The anaerobic seed was collected from wastewater treatment plant of the Kiang Huat Sea Gull Trading Frozen Food Public Company, Songkhla, Thailand. The substrate and seed were stored at 4^{o}C and put aside at room temperature before using in the experiment. The chemical characterizations of substrate tested in this study were shown in Table 1.

Table 1. Chemical characterization of substrates used in the experiments

Parameter	CSW	GW	WA
pH	6.3	8.8	10.4
COD(mg/L)	10,400	1,760,000	45,000
VFA(mg/L)	2,230	6,650	1,000
ALK(mg/L)	2,560	35,050	1,050
TN(mg/L)	870	1,670	1,010
TP(mg/L)	53.6	71,500	6,600
TS(g/L)	9.37	969	29.80
VS(g/L)	7.76	910	26.73
Protein(g/L)	3.90	1.28	9.10
Carbohydrate(g/L)	1.91	845	14
Lipids(g/L)	0.13	63.76	3.40
C/N ratio	11	949	40

2.2 Bio-methane potential test

All experiments were conducted with 5 conditions of CSW alone, CSW(99%)+GW(1%), CSW (96%)+GW(1%)+WA(5%), CSW(89%)+GW(1%)+WA(10%) and CSW(84%)+GW(1%)+WA(15%). The bio-methane potential was investigated in serum bottle size 1,000 mL with working volume 900 mL. The experiment was performed for 64 days under mesophilic (37^{o}C) conditions. The initial seed used in bio-methane potential test was 125 ml in all tests. The biogas production was measured by the water displacement method. The serum bottles were sealed with rubber stoppers and aluminium caps. The biogas composition was measured by a gas chromatography (GC).

2.3 Methane production in UASB reactor

The UASB reactor working volume of 2.58 L was conducted under mesophilic (37^{o}C) conditions and using the initial seed of 322.5 ml (125ml/L). Mixing of CSW with 1%GW and 5%WA was fed into the reactor with an organic loading rate (OLR) of OLR as 2, 4 and 6 g COD/L. day and HRT of 14, 7 and 5 days. The composition and volume of biogas, pH, VFA/alkalinity ratio and concentration of COD, volatile fatty acid (VFA), alkalinity were monitored daily.

2.4 Analytical methods

pH was measured using a pH meter model Sartorius Docu. Chemical oxygen demand (COD), total solid (VS), volatile suspended solid (VSS), total nitrogen (TN), total phosphorus (TP), volatile fatty acid, alkalinity, protein, carbohydrate, fat and total ammonia nitrogen (TAN) were analyzed using the standard method for the examination of water and wastewater [12]. The biogas volume and composition were measured by the displacement of water and analyzed by gas chromatography (GC-8A Shimadzu) equipped with thermal conductivity detector and filled with 2.0 m packed column (Shin-Carbon ST 100/120 Restex) [13]. The synergistic effect was calculated using the methane production from the best condition in bio-methane potential test by comparing to the methane production of single CSW, GW (%) and WA (%) [14]. Theoretical methane yield was calculated according Bushwell's formula which is derived from the stoichiometric conversion of the compound to CH_4, CO_2 and NH_3 [15].

3. Substrate removal kinetic method

3.1 Monod model

For an UASB reactor without biomass recycle, the biomass growth rate and substrate consumption rate were expressed as equations (1) and (2):

$$\frac{dX}{dt} = \frac{QX_i}{V} - \frac{QX_e}{V} + \mu X - K_d X \tag{1}$$

$$-\frac{dS}{dt} = \frac{QS_i}{V} - \frac{QS_e}{V} - \frac{\mu X}{Y} \tag{2}$$

The ratio of the total biomass in the UASB reactor to wasted biomass per given time represents mean cell-residence time (θ_C) was calculated from an equation (3):

$$\theta_C = \frac{VX}{QX_e} \tag{3}$$

The correlation between the specific growth rate ($\mu_{\max}$) and the rate limiting substrate concentration was expressed by the Monod in an equation (4):

$$\mu = \frac{\mu_{\max} S_e}{K_s + S_e} \tag{4}$$

If it is assumed that the concentration of biomass in the influent could be neglected at the steady-state condition (dX/dt = 0 and –dS/dt = 0) and the HRT (θ_H). It was defined as the volume of the reactor divided by the flow rate of the influent, following equations was obtained by substituting equations (3) - (4) into equations (1) and (2):

$$\mu = \frac{1}{\theta_c} + K_d \tag{5}$$

$$\frac{\mu_{\max} S_e}{K_s + S_e} = \frac{1}{\theta_c} + K_d \tag{6}$$

The kinetic parameters Y and K_d for the Monod model was obtained by rearranging equation as shown below

$$\frac{S_i - S_e}{\theta_H X_e} = \frac{1}{Y}\frac{1}{\theta_C} + \frac{1}{Y} K_d \tag{7}$$

The value of $\mu_{\max}$ and K_s were determined by plotting an equation (8):

$$\frac{\theta_C}{1 + \theta_C K_d} = \frac{K_S}{\mu_{\max}}\frac{1}{S_e} + \frac{1}{\mu_{\max}} \tag{8}$$

The effluent COD concentrations of the UASB reactor were predicted using an equation (9):

$$COD_{effluent} = \frac{K_S(K_d + \frac{1}{\theta_C})}{\mu_{\max} - K_d - \frac{1}{\theta_C}} \tag{9}$$

3.2 Modified Stover–Kincannon model

The Stover-Kincannon model was explained by an equation (10):

$$\frac{dS}{dt} = \frac{Q}{V}(S_i - S_e) \tag{10}$$

The dS/dt was a substrate removal rate (g/L. day) and determined as follows:

$$\frac{dS}{dt} = \frac{U_{\max}(QS_i / V)}{k_B + (QS_i / V)} \tag{11}$$

Thus, Eq. (10) was explained as follows:

$$(\frac{dS}{dt})^{-1} = \frac{V}{Q(S_i - S_e)} = \frac{k_B}{U_{\max}} \frac{V}{QS_i} + \frac{1}{U_{\max}} \tag{12}$$

The organic loading rate (OLR) was defined as follows:

$$OLR = \frac{S_i Q}{V} \tag{13}$$

By substituting an equation (13) into an equation (12) was illustrated as follows:

$$(\frac{dS}{dt})^{-1} = \frac{V}{Q(S_i - S_e)} = \frac{k_B}{U_{\max}} \frac{1}{OLR} + \frac{1}{U_{\max}} \tag{14}$$

The effluent COD concentrations of the UASB reactor were predicted using an equation (15):

$$COD_{effluent} = S_i - \frac{U_{\max} S_i}{k_B + OLR} \tag{15}$$

3.3 Grau second-order multi component substrate removal model

The general equation of the second-order model was described by an equation (16) [16]:

$$-(\frac{dS}{dt}) = k_S X (\frac{S_i}{S_e})^2 \tag{16}$$

If an equation (16) was integrated and then linearized, an equation (17) will be obtained [17]:

$$\frac{S_i \theta_H}{S_i - S_e} = \theta_H + \frac{S_i}{k_S X} \tag{17}$$

If $S_i/(k_sX)$ was considered as a constant (a) and $(S_i-S_e)/S_i$ replaced by the substrate removal efficiency (E). An equation (17) was modified as follows [18]:

$$\frac{\theta_H}{E} = b\theta_H + a \tag{18}$$

The effluent COD concentrations of the UASB reactor were predicted using an equation (19):

$$COD_{effluent} = S_i (1 - \frac{\theta_H}{a + b\theta_H}) \tag{19}$$

4. Result and Discussion

4.1 Substrate composition and bio-methane potential

The CSW had a low C/N ratio. Mixing of CSW with GW and WA increased C/N ratio in the range of 20-27 and could be reduced toxic chemicals in the form of total ammonia nitrogen (TAN) which was directly toxic to methanogenic bacteria. CSW with GW and WA compositions was shown in Table 2. TAN was produced by the biological degradation in the substrate had protein as a main component [19]. The optimal C/N ratio for anaerobic digestion was suggested in the range of 20-30 [20] while a higher C/N ratio could be expected to release lower concentrations of ammonia-N within the anaerobic systems [6]. The co-digestion of CSW (94%) with GW (1%) and WA (5%) enhanced maximum methane production of 7.9 LCH_4/L mixed waste and methane yield 789 $mLCH_4$/g VS-added with 96.75% of biodegradability. The cumulative methane production and methane yield in bio-methane potential test were shown in Fig. 1 and 2. The cumulative methane production and methane yield of other mixing ratio were in the range of 5.2-7.9 L CH_4/L mixed waste and 474-789 $mLCH_4$/g VS-added. Additionally, the cumulative methane production and methane yield of CSW, GW (1%) and WA (5%) alone were 1.95, 0.95, 0.29 L CH_4/L waste and 278, 211, 192 $mLCH_4$/g VS-added. Adding of GW and WA was also increased COD concentration in the range of 25.6-30.4 g/L resulted in a higher biogas production rate. Mshandete et al. [22] also reported that the highest methane yield of 620 $mLCH_4$/g VS-added when co-digested between 33% fish waste and 67% sisal pulp. Methane production rate and methane yield were increased by 307% and 184% when compared to CSW alone. After adding of co-substrates, pH values in the pH range from 6.9 – 7.2 compared with CSW alone pH to 6.3. The advantages in using GW as a co-substrate can be adjusted the pH of CSW a higher and saved the cost of chemicals used to adjust the neutral pH. The optimum pH for the methanogens and combined cultures ranged from 6.8 – 7.4 [23].

Table 2. Composition of CSW and CSW mixed with GW and WA

Experiment	COD (g/L)	VS (g/L)	TN (g/L)	TAN (g/L)	C/N ratio	COD/VS (gCOD/gVS)
CSW	10.40	7.76	0.870	0.78	11	1.34
WA(5%)	2.40	1.53	0.095	*ND	23	1.57
GW(1%)	16.00	4.50	0.025	*ND	576	3.56
CSW(99%)+GW(1%)	25.60	9.98	0.887	1.66	26	2.57
CSW(94%)+GW(1%)+WA(5%)	27.20	11.15	0.992	1.04	27	2.44
CSW(89%)+GW(1%)+WA(10%)	28.80	12.66	1.192	*ND	22	2.27
CSW(84%)+GW(1%)+WA(15%)	30.40	13.99	1.342	*ND	20	2.17

*ND=Not determine

The high methane yield form co-digestion compared to digestion alone caused the synergism of bacteria within an anaerobic system [24]. The co-digestion of CSW (94%) with GW (1%) and WA (5%) was the best condition of methane production. The results of the synergism showed in Fig 3. The methane yield was 789 $mLCH_4$/g VS-added (Theoretical methane yield = 830 mL CH_4/g VS-added) compared to the methane yield of CSW, GW (1%) and WA (5%) alone were 278, 211 and 192 mL CH_4/g VS-added. The yield of a synergistic methane yield (Syn-MY) was 108 mL CH_4/gVS-added which increased the methane production.

Considering the energy content of CH_4 was 36 MJ/m^3, 10 kWh/m^3 was achieved anaerobic digestion with conversion efficiency of approximate 40% in a gas motor [14]. The maximum methane production of co-digestion of CSW (94%) with GW (1%) and WA (5%) was 8.8 m^3 CH_4/m^3 of mixed wastewater and electricity production of 1 m^3 mixed wastewater would be 317 MJ or 88 kWh of electricity.

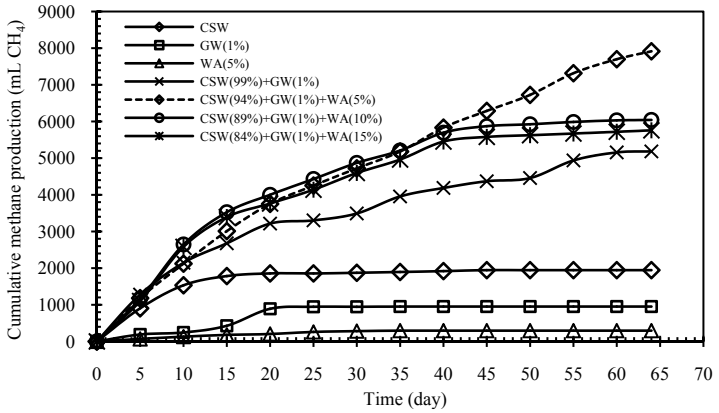

Fig. 1. Cumulative methane production from anaerobic co-digestion of CSW with GW and WA

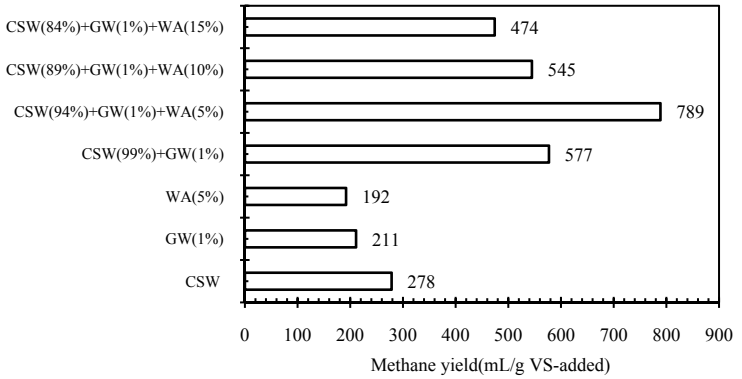

Fig. 2. Methane yield from anaerobic co-digestion of CSW with GW and WA

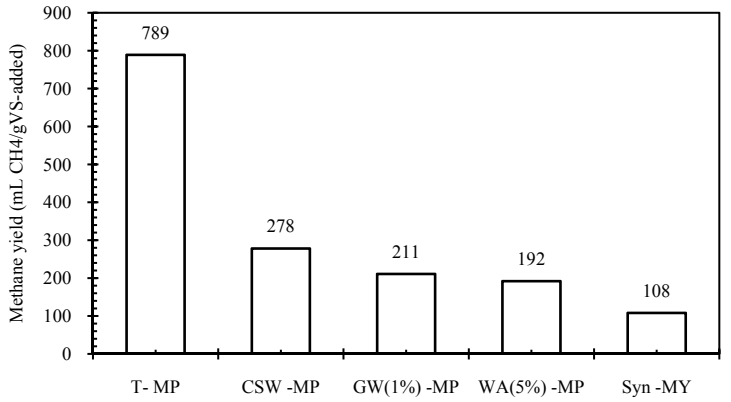

Fig. 3. The synergetic effect of co-digestion CSW with GW and WA at mixing ratio of 94: 1: 5; T-MP (Total methane production), CSW-MP (Canned seafood wastewater methane production), GW (1%)-MP(Glycerol waste (1%) methane production, WA(5%)-MP (*Wolffia arrhiza* (5%) methane production) and Syn-MY (Synergistic methane yield)

4.2 Methane production in UASB reactor

The anaerobic co-digestion of CSW (94%) with GW (1%) and WA (5%) was the best condition of methane production. This condition was selected to operate in the UASB reactor. UASB could adapt quickly because the seed was collected from anaerobic digestion of same wastewater type with CSW. Early stages of the acclimation, the CSW was fed into the UASB reactor at OLR between 0.5 and 1 g COD/L. day. When the seed could adapt to the new environment then gradually increased OLR as 2, 4 and 6 g COD/L. day which was done by increasing inflow rate of influent (fixed initial COD was 27.2 g/L). The effect of OLR on the performance of the UASB reactor was investigated. The results found that methane production rate increased from 8.5 to 9.5 L/day when enhanced OLR from 2 to 4 g COD/L. day. However, the methane production rate gradually dropped down to 3.6 L/day when increased OLR to 6 g COD/L. day (Fig 4C). The COD removal efficiency at OLR of 2, 4 and 6 g COD/L. day was 85, 72 and 60% (Fig 4A), respectively. The maximum methane yield was approximately 858 mL CH_4/g VS-added (352 mLCH_4/g COD removed) and the methane composition was 62.28% on an average that the OLR was 4 g COD/L. day (Fig 4C). The methane yield from UASB was similar to the methane yield from batch test (789 mL CH_4/g VS-added). Nuchdang and Phalakornkule [9] reported that maximum methane yield of 320 mL CH_4/g COD-removed at OLR of 1.6 g COD/L. day in a case of co-digestion with glycerol and pig manure which had the methane content of 54% in UASB reactor.

The total VFA was potential inhibitors to the anaerobic process, their determination was important for control of anaerobic digestion process. The alkalinity measurements used for evaluating the buffering capacity of the systems [25]. In this experiment, the total VFA increased in the range of 500 - 1,500 mg/L when enhanced the OLR (Fig 4B). Additionally, the increase of OLR effected the accumulation of total VFA that resulted pH values in the system reduced. If a high concentration of the VFA, the pH will be reduced and would inhibit the methanogenic bacteria severely or even may die which was important had buffering capacity in the system [23]. The VFA and alkalinity in anaerobic systems should be in the range of 500 – 2,000 mg/L and 1,000-5,000 mg/L and should have VFA/alkalinity ratio less than 0.4 [26, 27]. If the VFA/alkalinity ratio greater than 0.8, the pH of the system decreased quickly. Finally, the VFA/alkalinity ratio in this experiment was in the range between 0.1 and 0.5 which showed the high performance of UASB reactor.

4.3 Evaluation of kinetic modelling

4.3.1 Monod model

The experimental data at steady-states were used to define the kinetic parameters. Fig 5(A) was plotted from an equation (7) for defining kinetic parameters which Y and k_d were calculated from the intercept and the slope of the plot line of 3.058 gVSS/gCOD and 0.018 per day ($R^2 = 0.977$), respectively. The values of the maximum specific growth rate (μ_{max}) and half saturation concentration (K_s) were defined from Fig 5(B) by using an equation (8) which had a values as 0.548 per day and 15.487 g/L ($R^2 = 0.980$). The effluent COD concentration of UASB can be predicted by using an equation (20).

$$COD_{effluent} = \frac{15.487(0.018 + \frac{1}{\theta_C})}{0.548 - 0.018 - \frac{1}{\theta_C}} \quad (20)$$

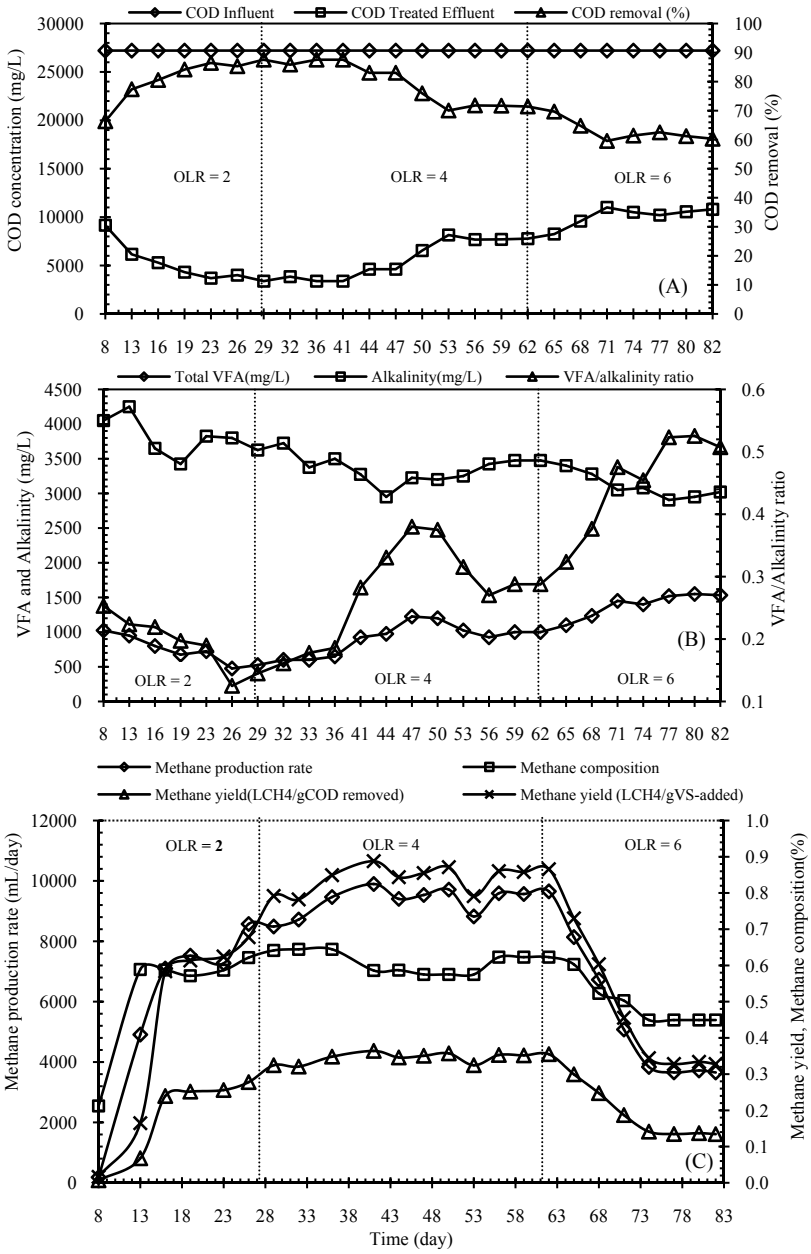

Fig. 4. The profile of COD removal (A), Total VFA, Alkalinity and VFA/alkalinity ratio (B), Methane production rate, methane composition (%) and methane yield (C) in UASB reactor.

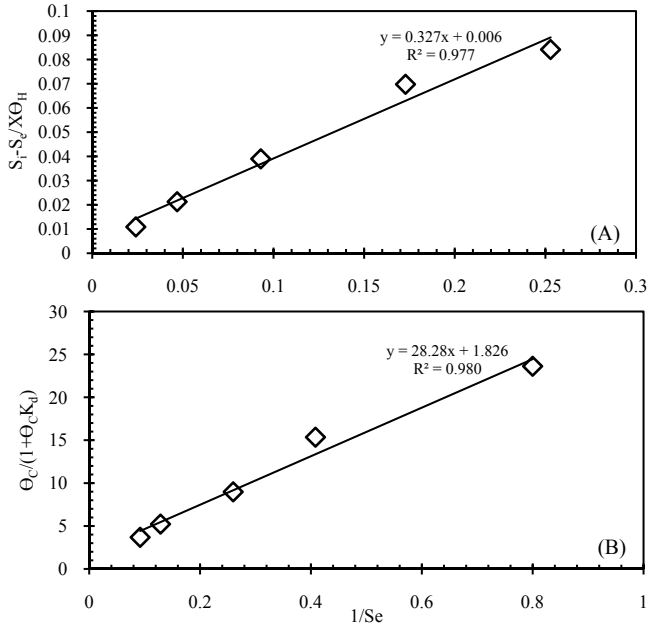

Fig. 5. Linearized plots of Monod model for the determination of Y and k_d (A) and plots of Monod model for the determination of μ_{max} and K_s (B).

4.3.2 Modified Stover–Kincannon model

The kinetic values of Modified Stover–Kincannon model were U_{max} and K_S base on the equation (14). Fig 6 showed the graph plotted between $V/Q(S_i\text{-}S_e)$ and 1/OLR which had K_B/ U_{max} as the slope and $1/U_{max}$ as the intercept point. Thus, the K_B and U_{max} from calculating were 10 and 9.96 g/L. day. The correlation coefficient was 0.999 that could confirm the application of the Modified Stover–Kincannon model. The effluent COD concentration of UASB can be predicted by using an equation (21).

$$COD_{effluent} = 27.200 - \left[\frac{(10.000)(27.200)}{9.960 + OLR} \right] \tag{21}$$

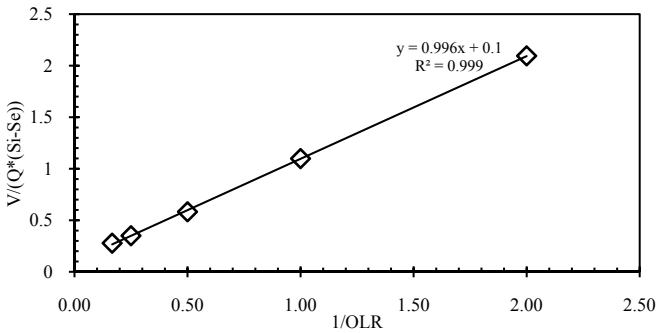

Fig. 6. Linearized plots of Modified Stover–Kincannon model

4.3.3 Grau second-order multicomponent substrate removal model

The Grau second-order model coefficients were defined by plotting an equation (18). Fig 7 showed the graph plotted between HRT/E and θ_H. The values of a and b by calculating from the intercept and slope of the plot line were 2.905 per day and 0.992 ($R^2 = 0.999$). The k_s was 0.276 per day by calculating from an equation (22) which indicated substrate removal of microorganism in the process. The effluent COD concentration of UASB can be predicted by using an equation (23).

$$k_s = \frac{S_i}{(X).(a)} \tag{22}$$

$$COD_{effluent} = S_i\left[1 - \frac{\theta_H}{(2.095) + (0.992)(\theta_H)}\right] \tag{23}$$

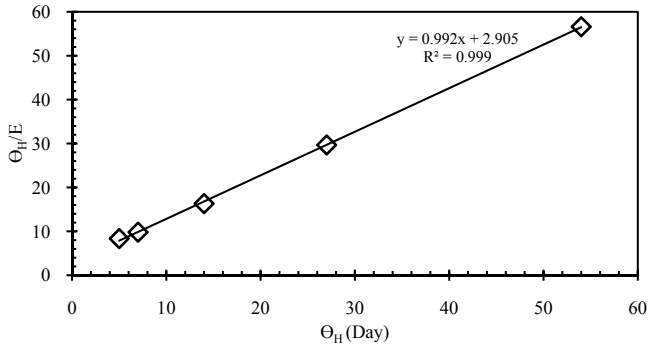

Fig. 7. Linearized plots of Grau second-order multi-component substrate removal model

4.4 Model evaluation

The kinetic models explained performance of the UASB and predicted COD effluent in the anaerobic system base on the Monod, Modified Stover–Kincannon and Grau second-order multicomponent substrate removal models compared to experimental data which obtained from the study of resulted OLR (Fig 8). A model to study (Monod, Modified Stover–Kincannon and Grau second-order multicomponent substrate removal models) was suitable for predicting COD effluent which had a regression coefficient higher than 0.95 under mesophilic condition. The kinetic coefficients of all models in this experiment were summarized and compared to the coefficients obtained from the other experiment which showed in Table 3. The coefficients of the Monod model (Y and μ_{max}) in the case of CSW (94%) + GW (1%) + WA (5%) value were 3.058 g VSS/g COD and 0.548 per day compared with the report of Isik and Sponza [17] which had a value of 0.125 g VSS/g COD and 0.105 per day, respectively. However, the μ_{max} (0.548 per day) obtained in this experiment which had a higher μ_{max} value (0.105 per day) of Isik and Sponza [17]. The reason for the μ_{max} differed because the difference of microorganism used in the experimental and the results of the co-digestion was adjusted the balance C: N ratio resulting the toxicity in system decreased which resulting the enhanced μ_{max}. By increasing the value of μ_{max} corresponded to higher Y value (3.058 g VSS/g COD) as a result of microorganism in the system can be adapted and substrate can be used as well.

Table 3. Comparison of the kinetic coefficients in the Monod model, Modified Stover–Kincannon model and Grau second-order multicomponent substrate removal model

Model	Substrate	Reactor type	Organic loading rate (g COD/L-day)	Ks (gCOD/L)	Y (g VSS/g COD remove)	μ_{max} (day^{-1})	K_d (day^{-1})	Reference
Monod	CSW+GW(1%)+ WA(5%)	UASB	2-6	15.487	3.058	0.548	0.018	This study
	Textile wastewater	UASB	1-15.8	>4.0	0.125	0.105	0.0065	[17]
Model	Substrate	Reactor type	Organic loading rate (g COD/L-day)	U_{max} (g COD/L-day)		K_B (g COD/L-day)		Reference
Modified Stover–Kincannon	CSW+GW(1%)+ WA(5%)	UASB	2-6	10		9.96		This study
	Textile wastewater	UASB	1-15.8	7.5		8.2		[17]
	Saline wastewater	UASB	2.3-4.44	7.05		5.3		[28]
	Glucose digestion	UASB	1.3-2.6	27.78		27.19		[9]
	Glycerol digestion	UASB	1.3-2.6	13.7		13.51		[9]
	Co-digestion of glycerol and pig manure	UASB	1.3-2.6	66.67		69.8		[9]
Model	Substrate	Reactor type	Organic loading rate (g COD/L-day)	a (day^{-1})		b	k_s (day^{-1})	Reference
Grau second-order	CSW+GW(1%)+ WA(5%)	UASB	2-6	2.905		0.992	0.276	This study
	Textile wastewater	UASB	1-15.8	0.562		1.095	0.337	[17]

A comparison of kinetic values as shown in Table 3 which illustrated the value of U_{max} and K_B base on Modified Stover–Kincannon model in this experiment which had a value as 10 and 9.96 g COD/L. day similar to the experimental values of Isik and Sponza [17] and Kapdan and Erten [28] from simulated textile wastewater (7.5 and 8.2 g COD/L. day) and saline wastewater (7.50 and 5.3 g COD/L. day). The values of U_{max} and K_B in this study were less than when compared to the simulated glucose digestion (27.78 and 27.19 g COD/L. day), glycerol digestion (13.70 and 13.51 g COD/L. day) and co-digestion between glycerol and pig manure (66.67 and 69.80 g COD/L. day) in the experiments of Nuchdang and Phalakornkule [9] because substrates can be digested more easily when compared with CSW (94%) + GW (1%) + WA (5%) which were composed of the main protein. Additionally, the parameter values (a, b) of Grau second-order multicomponent substrate removal model calculating from the experimental data were 2.905 per day and 0.992. The kinetic coefficient (k_s) of Grau second-order multicomponent substrate removal model depended on the initial substrate (S_i) and microorganism concentrations (X) in the reactor as 0.337 per day [17] which was similar to the values in this experiment (0.276 per day).

The results showed that the kinetic coefficient of the Modified Stover–Kincannon model having the highest regression coefficient (R^2=0. 987) when compared to Monod and Grau second-order component substrate removal model which confirming the suitability of the model used in this experiment.

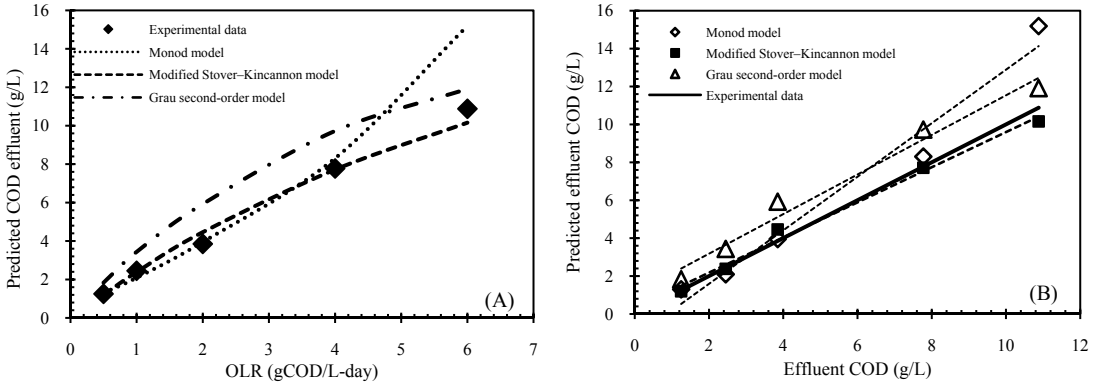

Fig. 8. (A) Predicted COD effluent base on the Monod (R^2=0.981), Modified Stover–Kincannon (R^2=0.987), and Grau second-order multicomponent substrate removal model (R^2=0.971), (B) Linear relationship between predicted COD effluent and experiment data.

5. Conclusion

Using the GW and WA as co-substrate could enhance the methane production in anaerobic co-digestion of CSW which had 94% CSW, 1% GW and 5%WA as the best mixture. Methane production from a mixture of 94% CSW, 1% GW and 5%WA had the highest methane yield of 789 mL CH_4/g VS-added with 96.75% biodegradability. The methane yield of mixture increased by 184% when compared to digested CSW alone. The maximum methane production of CSW (94%) with GW (1%) and WA (5%) was 8.8 m^3 CH_4/m^3 of mixed wastewater which could calculate the electricity production of 1 m^3 of mixed wastewater as 317 MJ or 88 kWh of electricity. In continuous system, the maximum methane yield was approximately 858 mLCH_4/g VS-added (352 mLCH_4/g COD removed) and the methane composition was 62.28% on an average that the OLR was 4 g COD/L. day in UASB reactor. The kinetic models (base on the Monod, Modified Stover–Kincannon and Grau second-order models) and kinetic parameters were achieved by linear regression with correlation coefficients (R^2) higher 97%.

Acknowledgements

I would like to thank the Office of the Higher Education Commission (OHEC) for financial support in this research.

References

[1] Palenzuela-Rollon A. Anaerobic Digestion of Fish Processing Wastewater with Special Emphasis on Hydrolysis of Suspended Solids. *Taylor and Francis* 1999, London.
[2] Prasertsan P, Jung S, Buckle KA. Anaerobic filter treatment of fishery wastewater. *World J. Microbiol. Biotechnol.* 1994; **10**: 11–13.
[3] Chowdhury p, Viraraghavan T, Srinivasan A. Biological treatment processes for fish processing wastewater – A review .*Bioresource Technology* 2010; **10**: 439–449.
[4] Regueiro L, Carballa M, Álvarez JA, Lema JM. Enhanced methane production from pig manure anaerobic digestion using fish and biodiesel wastes as co-substrates. *Bioresource Technology* 2012; **123**(0): 507-513.
[5] Chen Y, Cheng JJ, Creamer KS. Inhibition of anaerobic digestion process: A review. *Bioresource Technology* 2008; **99**(10): 4044-4064.

[6] Zeshan OP, Karthikeyan. Effect of C/N ratio and ammonia-N accumulation in a pilot-scale thermophilic dry anaerobic digester. *Bioresource Technology* 2012; **113**(0): 294-302.
[7] Yazdani SS, Gonzalez R. Anaerobic fermentation of glycerol: A path to economic viability for the biofuels industry. *Current Opinion in Biotechnology* 2007*;* **18**: 213-219.
[8] Jingxing M, Mariane VW, Marta C, Willy V. Improvement of the anaerobic treatment of potato processing wastewater in a UASB reactor by co-digestion with glycerol. *Biotechnology Letter* 2008; **30**: 861–867.
[9] Nuchdang S, Phalakornkule C. Anaerobic digestion of glycerol and co-digestion of glycerol and pig manure. *Journal of Environmental Management* 2012; **101**(0): 164-172.
[10] Fujita M, Mori K, Kodera T. Nutrient removal and starch production through cultivation of Wolffia arrhiza. *Biotechnology and Bioengineering* 1999; **87**: 194–198.
[11] Suppadit T. Nutrient removal of effluent from quail farm through cultivation of Wolffia arrhiza. *Bioresource Technology* 2011; **102**: 7388–7392.
[12] APHA. Standard methods for the examination of water and wastewater 22th edn, American Public Health Association, Washington DC, USA; 2012.
[13] Mamimin C, Thongdumyu P, Hniman A, Prasertsan P, Imai T. O-thong S. Simultaneous thermophilic hydrogen production and phenol removal from palm oil mill effluent by Thermoanaerobacterium-rich sludge. *International Journal of Hydrogen Energy* 2012; **37**(20):15598-15606.
[14] O-Thong S, Boe K, Angelidaki I. Thermophilic anaerobic co-digestion of oil palm empty fruit bunches with palm oil mill effluent for efficient biogas production. *Applied Energy* 2012; **93**(0): 648-654.
[15] Symons GE, Bushwell AM. The methane fermentation of carbohydrate. *Journal of American Chemistry Society* 1993; **55**: 2028–39.
[16] Grau P, Dohanyas M, Chudoba J. Kinetics of multicomponent substrate removal by activated sludge. *Water Res*earch 1975; **9**: 637–642.
[17] Isik M, Sponza T. Substrate removal kinetics in an upflow anaerobic sludge blanket reactor decolorising simulated textile wastewater. Process Biochemistry 2005; **40**: 1189–1198.
[18] Ni SQ, Sung S, Yue QY, Gao BY. Substrate removal evaluation of granular anammox process in pilot-scale upflow anaerobic blanket reactor. *Ecological Engineering* 2012; **38**: 30-36.
[19] Kayhanian M. Ammonia inhibition in high-solids biogasification: an overview and practical solutions. *Environmental Technology* 1999; **20**: 355–365.
[20] Li Y, Park SY, Zhu J. Solid-state anaerobic digestion for methane production from organic waste. *Renewable and Sustainable Energy Reviews* 2011;**15**(1): 821-826.
[21] Borja B, Sgnchez E, Weiland P. Influence of ammonia concentration on thermophilic anaerobic digestion of cattle manure in upflow anaerobic sludge blanket(UASB) reactors. *Process Biochemistry* 1996; **31**(5): 477-483.
[22] Mshandete A, Kivaisi A, Rubindamayugi M, Mattiasson B. Anaerobic batch co-digestion of sisal pulp and fish wastes. *Bioresource Technology* 2004; **95**: 19–24.
[23] Khanal SK. Anaerobic Biotechnology for Bioenergy Production: Principles and Applications. *Wiley-Blackwell*; 2008, p.43-63.
[24] Wang X, Yang G. Optimizing feeding composition and carbon–nitrogen ratios for improved methane yield during anaerobic co-digestion of dairy, chicken manure and wheat straw. Bioresource Technology 2012; **120**(0): 78-83.
[25] Pandian M, NGO HH, Pazhaniappan S. Substrate removal kinetics of an anaerobic hybrid reactor treating pharmaceutical wastewater. *Journal of Water Sustainability* 2011; **1**(3): 301-312.
[26] Halbelt EJ. Process operation and monitoring : poisons and inhibitors. *Proceeding of the 1st ASEAN Seminar Workshop on Biogas Technology*, Manila, Philippines 1981; 369-385.
[27] MetCalf, Eddy. Wastewater Engineering : Treatment disposal and reuse. *McGraw-Hill*, Inc. New York; 1982.
[28] Kapdan IK, Erten B. Anaerobic treatment of saline wastewater by *Halanaerobium lacusrosei*. *Process Biochemistry* 2007; **42**: 449–453.