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Carbon balance of anaerobic granulation process: Carbon credit

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ABSTRACT

The concept of carbon credit arose out of increasing awareness of the need to reduce emissions of greenhouse gases to combat global warming which was formalized in the Kyoto protocol. In addition to contribution to sustainable development with energy recovery in the form of methane, carbon credits can be claimed by application of advanced anaerobic processes in wastewater treatment for reducing emissions of greenhouse gases. As anaerobic granular systems are capable of handling high organic loadings concomitant with high strength wastewater and short hydraulic retention time, they could render much more carbon credits than other conventional anaerobic systems. This study investigated the potential carbon credit derived from laboratory-scale upflow anaerobic sludge blanket (UASB) reactors based on a carbon balance analysis. Methane emission reduction could be calculated by calculating the difference of UASB reactors and open lagoon treatment systems. Based on the 2.5 l bench-scale reactor, the total CH₄ emissions reduction was calculated as 29 kg CO₂/year. On scaling up to a typical full-scale anaerobic digester, the total CH₄ emissions reduction could achieve 46,420 tons CO₂ reduction/year. The estimated carbon credits would amount to 278,500 US\$ per year by assuming a carbon price of 6 US\$ per metric ton CO₂ reduction. The analysis postulated that it is financially viable to invest in advanced anaerobic granular treatment system from the revenue generated from carbon credits.

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1. Introduction

Global warming arising from unprecedented emissions of greenhouse gases presents the greatest test humans have ever faced. Increasing global concerns over diminishing crude oil reserve and greenhouse gas emission through combustion of fossil fuels have called for a need for alternative fuels. Keller and Hartley (2003) and Cakir and Stenstrom (2005) highlighted the issue of greenhouse gas emission from wastewater treatment facilities. Rosso and Stenstrom (2008) estimated the carbon sequestration potential of municipal wastewater treatment using aerobic processes. Use of anaerobic processes for extracting carbon pollutants in wastewater to biofuel energy clearly better fit this need (Greenfield and Batstone, 2005; Harteley and Lant, 2006; Urban et al., 2007; Cantrell et al., 2008; Fanqueiro et al., 2008; Kikuchi and do Amaral, 2008; Ward et al., 2008).

Anaerobic processes have been employed over the last few decades in industrial wastewater treatment. The processes have attracted increasing attention owing to their capability of energy production in the form of biogas. Many systems have been developed to treat a variety of wastewaters. The systems which are based on anaerobic granular sludge appear to be the most promising,

especially in treating high strength wastewaters. These reactor systems provide efficient and stable operational performance, attributable to its effective retention of the fast settling granules associated with high biomass concentration and rich microbial diversity. Anaerobic granular systems are designed in wastewater treatment to maximize biomass retention and methane yield. Methane – a greenhouse gas can be effectively captured and reused rendering great potential for the clean development mechanism (CDM) initiatives under the Kyoto protocol. Under CDM project implementation, ‘carbon credit’ represents the amount of decrease of greenhouse gas emissions from an emission source. To improve treatment efficiency and to claim carbon credits, many existing aerobic and low-rate anaerobic treatment such as those pond systems have been upgraded to anaerobic granular-sludge systems.

Volatile fatty acids (VFA) such as acetate, propionate, butyrate, are major intermediate products in acidogenesis and acetogenesis stages of anaerobic biochemical degradation. The stability of overall biochemical reactions relied on the degradation of VFA by the anaerobes to the final gaseous products. Under favorable condition, more than 75% of acetate can be converted to methane (Mountfort and Asher, 1978; Gujer and Zehnder, 1983; Zinder, 1993). Butyrate degradation differs from that of acetate as it includes an acetogenesis step in the biochemical reactions. Conversion of butyrate to acetate is not thermodynamically favorable unless the acetate and hydrogen produced by the acetogens can be readily removed

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by acetotrophic and hydrogenotrophic bacteria, respectively (Gujer and Zehnder, 1983).

In an UASB reactor, bacteria aggregate to form biogranules which have high microbial activity. However, formation of granules relies on the syntrophic association of various bacterial groups (Fang et al., 1994). Samsooni et al. (1987, 1991) also speculated that granulation was much dependent on hydrogenotrophic bacteria. Thus, butyrate may become a preferable substrate compared with acetate for anaerobic sludge to form granules, since the hydrogen formed via degradation can be further utilized by hydrogenotrophic bacteria.

Debate exists whether wastewater treatment plants emit a significant quantity of greenhouse gas (Monteith et al., 2005; Sahely et al., 2006). Comprehensive work is needed to accurately estimate carbon balances for treatment facilities. This study aims at exploring the use of carbon mass balance analysis as a tool to investigate biomass and biogas yields from the anaerobic sludge enriched by acetate and butyrate. Carbon credit thus gained will be estimated.

2. Experimental

Two translucent plastic cylinders with 55 cm height and 14 cm diameter and a total working volume of 2.5 l were used as the UASB reactors. Synthetic substrate was fed to the bottom of reactor by Masterflex pump. To maintain the operating temperature of the reactor at 35 °C, a closed circulation system was used. Biogas produced by the reactor was recorded daily by gas chromatography (Shimadzu GC-9A) equipped with a thermal conductivity detector and a column packed with molecular sieve 5A 80/100 mesh. The oven temperature was set at 70 °C and helium was used as the carrier gas at a flow rate of 30 ml/min. The biogas after passing through a gas–solid–liquid separator and water trap was collected by the water displacement method and sampled for gas composition from a port between the reactor and the water trap.

Synthetic VFA-based wastewater containing acetate or butyrate at 20 g COD l⁻¹ was used as feed. Composition of the feed was set as follows (in mg l⁻¹): CaCl₂, 200; MgCl₂ · 6H₂O, 200; FeCl₂ · 4H₂O, 50; NH₄Cl, 1000; KH₂PO₄, 500; Na₂S, 250; L-cysteine, 250; ZnCl₂, 0.5; CuCl₂, 0.5; NiCl₂ · 6H₂O, 1; MnSO₄ · H₂O, 1; H₃BO₃, 0.5; (NH₄)₆Mo₇ · 4H₂O, 0.5; CoCl₂ · 6H₂O, 0.5; AlCl₃, 0.5; Na₂SeO₃ · 5H₂O, 0.5; EDTA, 4; Resazurin, 0.5.

Aerobic seed sludge was obtained from the wastewater treatment plant of the Uni-President Oven Bakery Corp., Taoyuan, Taiwan. The sludge was stored for one month under anaerobic condition before seeding. Each digester was filled with the seed and substrate, resulting in a total sludge bed volume of 1 l composing 59% of volatile suspension solid (VSS) and the VSS concentration was 4 g l⁻¹.

Two UASB reactors were started up simultaneously. Initially, both reactors were fed with synthetic wastewater with mixed VFAs at 20 g COD l⁻¹ (acetate:propionate:butyrate = 1:0.88:1.25 in COD ratio). The pH of the feed was adjusted by sodium hydroxide to 6.5. The reactors were operated at an OLR of 0.82 g COD l⁻¹ day⁻¹, corresponding to a COD concentration of 20 g COD l⁻¹ and a hydraulic retention time (HRT) of 24.4 day. On day 36, 67, and 93, the OLR of both reactors was step-increased to 3.84, 5.2, and 10.4 g COD l⁻¹ day⁻¹, respectively. Subsequently, the carbon source of the reactor was changed to pure acetate and pure butyrate respectively at a same COD concentration of 20 g COD l⁻¹. Gas production and composition was recorded at intervals of 5 h. The reactors were operated until a steady-state performance was reached as marked by consistent gas production and effluent COD concentration.

Total organic carbon (TOC) and total inorganic carbon (TIC) was analyzed by the OI Analytical Aurora Model 1030 TOC analyzer.

Suspended solids concentrations were determined in accordance to procedures described in the standard methods (APHA et al., 1998) Section 2540D and 2540E. COD measurements were carried out according to the standard methods (APHA et al., 1998) Section 5220D. pH was measured by a WTW pH 315 meter. Gas composition was calibrated by standard gas (methane, nitrogen, and carbon dioxide) and calculated according to the area recorded on the chromatographic integrator (Shimadzu C-R3A). Compositions of VFAs were determined using a high performance liquid chromatograph system (Ecom LCP 4100 pump, LCD 2083 detector) with auto sampler (hta HT3000L). Detector wavelength was set at 210 nm and the mobile phase was 25 mM phosphate buffer at pH 2.5. Each sample was tested in triplicate.

3. Results and discussion

3.1. UASB reactor performance

Biogas production dropped drastically in the first 200 h when pure acetate was fed into UASB reactor instead of mixed VFA (Fig. 1). After the biogas production rebounded to a high value of approximately 18,000 ml day⁻¹, it converged to about 9600 ml day⁻¹. The biogas contained 90% methane, with the remaining 10% of carbon dioxide. The overall result showed that the COD removal decreased from 85% (20,000–3000 mg l⁻¹) to 78.5% (20,000–4300 mg l⁻¹) after the feed changed to pure acetate. The pH increased gradually from 8.2 to 8.6 after operating for 550 h.

Compared with the reactor fed with pure butyrate, biogas production from acetate-fed reactor decreased more severely in the

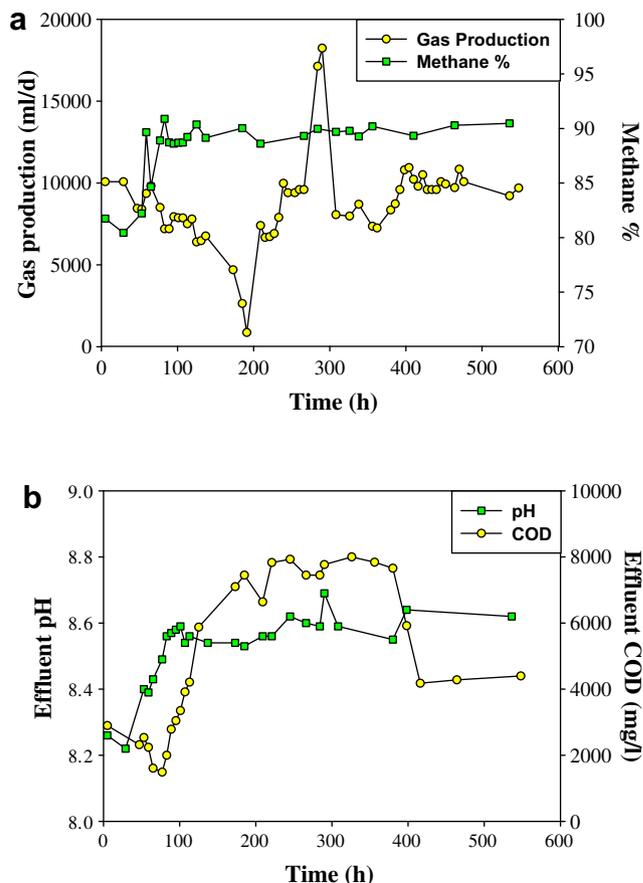


Fig. 1. (a) Gas production, methane fraction, (b) effluent pH and COD for UASB reactor with substrate changing from mixed acid to pure acetate (at $t = 0$).

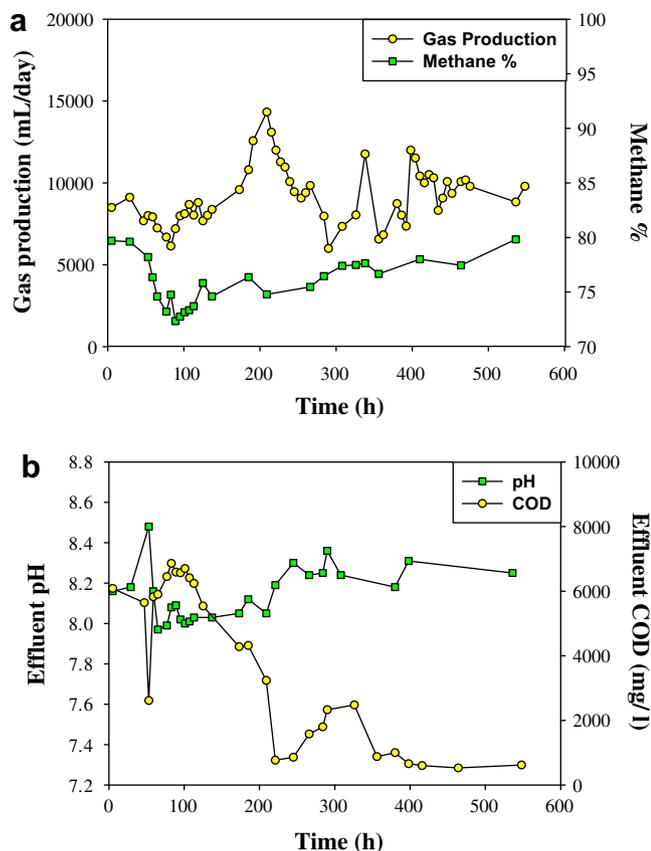


Fig. 2. (a) Gas production, methane fraction, (b) effluent pH and COD for UASB reactor with substrate changing from mixed acid to pure butyrate (at $t = 0$).

first 100 h (Fig. 2). The biogas production rate showed oscillatory behavior, gradually converged to a steady-state production rate of 9750 ml day^{-1} . Such an observation may be attributable to the two different stages involved that induce nonlinear system dynamics (Chua et al., 1997). The methane composition decreased initially to 72% at the first 100 h of operation, it then increased gradually to 80% after 500 h of operation. Compared with reactor fed with pure butyrate feed, the biogas produced in acetate-fed reactor showed relatively high methane content. The COD removal efficiency increased from 70% ($20,000\text{--}6000 \text{ mg l}^{-1}$) to 95% ($20,000\text{--}600 \text{ mg l}^{-1}$) after the feed had changed from the mixed VFA to pure butyrate ($t = 550 \text{ h}$).

Table 1 shows the overall performance of the reactors. The steady-state biogas production rates for acetate- and butyrate-fed UASB reactors were 9940 and 9740 ml day^{-1} , respectively. The methane percentages were 90% and 77.5%. Reactor fed by pure acetate showed the highest methane composition while the methane composition of pure butyrate-fed reactor was similar to the result fed with mixed acid before.

Table 1
Steady-state result of acetate- and butyrate-fed reactors

	Acetate-fed reactor	Butyrate-fed reactor
Biogas production (ml day^{-1})	9940	9740
Methane%	90	77.5
Carbon dioxide%	10	22.5
Effluent pH	8.6	8.2
Effluent COD (g COD l^{-1})	4.3	0.6
Effluent TIC (g l^{-1})	12.4	7.9
Effluent TOC (g l^{-1})	1.6	0.2
Effluent biomass (g VSS l^{-1})	0.7	0.2

Another reason is the overall Gibbs free energy change of acetate degradation was higher (-36 kJ/mol) than butyrate degradation (-88 kJ/mol). Energetically, acetate is a poor substrate (Zehnder et al., 1982); this might result in the energy required for acetate uptake at very low concentrations exceeding the energy gained from acetate metabolism, thereby limiting the acetate removal in the overall digester performance (Ahring and Westermann, 1988).

3.2. Carbon balance of acetate and butyrate-fed reactors

Carbon in the substrate was converted into methane and carbon dioxide in the biogas, TOC, TIC in the effluent and biomass (Fig. 3). The total feed carbon was calculated from the carbon fraction of acetate or butyrate feeding per day, whereas this carbon released daily in the biogas, effluent TOC and TIC were calculated according to these data shown in Table 1. The TIC in the effluent was attributed to the sums of HCO_3^- and CO_3^{2-} . The biomass generated may be washed out in the effluent daily or accumulated in the reactor. The biomass washout was measured VSS. The accumulated biomass was calculated by the subtraction of total outlet carbon from inlet carbon. The carbon content in the biomass was calculated by the commonly adopted formula of microbial cell $\text{C}_5\text{H}_7\text{O}_2\text{N}$, in which 1 g VSS contains 0.53 g carbon (Postgate, 1967).

Table 2 shows daily carbon flow and its relative percentage in both reactors. Total carbon and substrate in acetate- and butyrate-fed reactors were 9.7 g C day^{-1} , $24.3 \text{ g acetate day}^{-1}$ and 7.8 g C day^{-1} , $14.3 \text{ g butyrate day}^{-1}$, respectively. Although both reactors were fed by substrates in the same COD concentration, more carbon and substrate was fed into acetate-fed reactor as carbon fraction of acetate ($0.38 \text{ g C/g acetate COD}$) was higher than that of butyrate ($0.3 \text{ g C/g butyrate COD}$). As both feeds were adjusted by sodium hydroxide to pH 6.5 before entering the reactors, higher amount of sodium ions presented in acetate substrate than butyrate substrate as the result of charge balance. After the anions in the substrate (acetate or butyrate) were converted to methane and carbon dioxide, the only anions that remained to balance with sodium ions were bicarbonate ions. Thus, it was expected that more carbon dioxide was presented as TIC (32.5%) in the effluent than that of butyrate-fed reactor (25.8%) but less carbon dioxide presented in gas form in acetate-fed reactor (3.1%) than that of butyrate-fed reactor (13.5%). Based on the same reason, this also explained both the effluent pH and methane compositions of acetate-fed reactor (8.6 and 90%) were higher than that of butyrate-fed digester (8.2 and 77.5%).

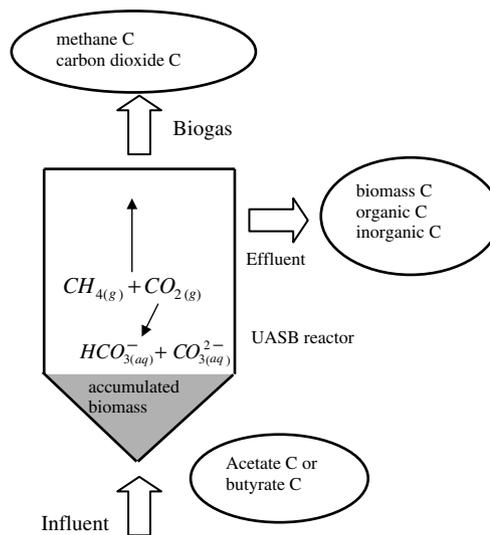


Fig. 3. Schematic diagram of carbon mass balance in the UASB reactor.

Table 2
Carbon balance of acetate- and butyrate-fed reactors

	Acetate-fed digester		Butyrate-fed reactor	
	g C/day	Percentage	g C/day	Percentage
Influent	9.72		7.79	
CH _{4(g)}	4.43	45.6	3.62	46.5
CO _{2(g)}	0.3	3.1	1.05	13.5
Effluent TIC	3.16	32.5	2.01	25.8
Effluent TOC	2.08	21.4	0.25	3.2
Effluent biomass	0.38	3.9	0.12	1.5
Carbon recovery		106		90.5
Estimated accumulated biomass	0	0	0.74	9.5

Carbon recovery from the acetate-fed reactor and butyrate-fed reactor are 106% and 90.5%, respectively. Carbon recovery of acetate-fed reactor exceeded 100% which may be due to some of the biomass in the reactor being converted to methane once the feed had changed from mixed VFA to pure acetate. This was possible as the acetogenic bacteria cultivated by mixed VFA previously may decay to form biogas after the substrate changed to pure acetate (Hatamoto et al., 2007). The total sludge in acetate-fed reactor and butyrate-fed reactor were 18.7 and 31.7 g VSS respectively after both reactors reached steady-state lasted for two months. Higher fraction of biomass carbon washout daily (3.9%) in acetate-fed reactor caused severe decrease in the amount of sludge compared with that of butyrate-fed reactor (1.5%). At steady-state condition, the sludge bed height and solid content in the acetate-fed reactor were invariant, thus the biomass washout can be treated as the net yield of sludge. On the other hand, biomass maintained well in the butyrate-fed reactor and the sludge granulation was also observed. Sludge particle size distribution (Fig. 4) also showed that there is higher fraction of large particle size (>1 mm) sludge in butyrate-fed sludge. Thus, by the subtraction of inlet carbon from outlet carbon overall the reactor, about 9.5% carbon was estimated to be converted to biomass accumulated in the reactor.

3.3. Estimation of net sludge yield of acetogenic and methanogenic bacteria

Degradation of butyrate involved acetogenesis, aceticlastic methanogenesis and hydrogenotrophic methanogenesis, as shown in reaction 1, 2, and 3 but degradation of acetate only involved in reaction 2. By using the mass balance result shown above, the net sludge yield of each type of bacteria involved in the reaction thus can be estimated.

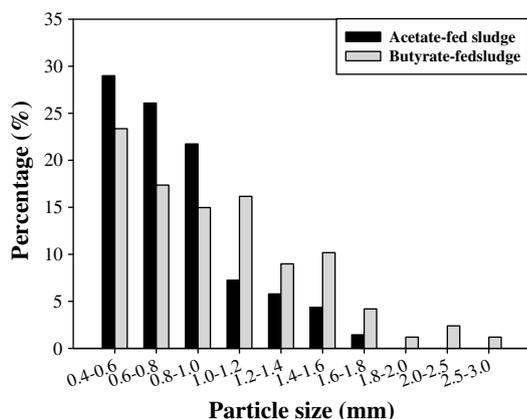


Fig. 4. Size distribution of acetate-fed and butyrate-fed reactor sludge.

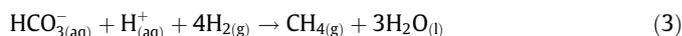
Butyrate acetogenesis



Aceticlastic methanogenesis



Hydrogenotrophic methanogenesis



Daily net sludge yield of acetate- and butyrate-fed reactor, which equal to the sums of effluent biomass and estimated accumulated biomass, were 45 mg VSS/g acetate COD and 85 mg VSS/g butyrate COD, respectively. The calculations were shown below:

Net sludge yield of acetate-fed reactor

$$: \frac{0.38 \text{ g C}}{20 \text{ g COD} \times 78.6\% \text{ removal}} \times \frac{\text{g VSS}}{0.53 \text{ g C}} = \frac{45 \text{ mg VSS}}{\text{g COD}}$$

Net sludge yield of butyrate-fed reactor

$$: \frac{0.86 \text{ g C}}{20 \text{ g COD} \times 95\% \text{ removal}} \times \frac{\text{g VSS}}{0.53 \text{ g C}} = \frac{85 \text{ mg VSS}}{\text{g COD}}$$

These values were comparable to the actual sludge yield of 49 mg VSS/g COD and 89 mg VSS/g COD in acetate-fed and butyrate-fed.

These values were comparable to the actual sludge yield of 49 mg VSS/g COD and 89 mg VSS/g COD in acetate-fed and butyrate-fed reactors. The products of butyrate degradation are 2 moles of acetate and hydrogen (Reaction 1). Based on COD balance, 1 g butyrate COD degraded to 0.8 g acetate COD and 0.2 g hydrogen COD. Since the net sludge yield of aceticlastic methanogenesis is 45 mg VSS/g acetate COD and the net yield for hydrogenotrophic methanogens (Reaction 3) is 46 mg VSS/g H₂ COD (Jia et al., 1996a), the net yield of butyrate-degrading acetogen was estimated as 40 mg VSS/g butyrate COD based on the mass balance and the stoichiometry of the reaction.

Table 3 summarizes the net yield values for various groups of methanogenic bacteria estimated from this study and corresponding values reported in literature. The net yields for acetogenesis of butyrate were reported as 20 mg VSS/g COD (Lin et al., 1989), 33 mg VSS/g COD (Jia et al., 1996b), 41 mg VSS/g COD (Furumai et al., 1991) and 40 mg VSS/g COD (this study). Generally, the net yield of acetate-fed sludge was comparable with those reported in literature. However, the net yield of butyrate-fed sludge was much higher. This could be due to the fact that the reactor was operated in granulation period and more substrate was utilized as microbial growth.

Table 3
Net yield of sludge for methane production

Substrate	Net yield of enriched sludge (mg VSS/g COD)	References
Acetate	45	This study
	61	Jia et al. (1996b)
	41	Lawrence and McCarty (1969)
	40	Smith and Mah (1978)
	50	Smith and Mah (1980)
	108	Chang et al. (1983)
	40	Frostell (1985)
	41	Furumai et al. (1991)
Butyrate	85	This study
	90	Jia et al. (1996b)
	47	Lawrence and McCarty (1969)
	16	Frostell (1985)
	37	Fang et al. (1995)

3.4. Carbon credit and emission trading

Emission trading is a regulatory program that allows firms the flexibility to select cost effective solutions to achieve established environmental goals, which are required to reduce worldwide greenhouse gas emissions by a collective average of 5% below 1990 levels of member countries. Emissions reduction can be achieved within a discrete emission unit, from another place within facility, and/or by purchase emission reductions from another facility. International treaties such as the Kyoto protocol set quotas on the amount of the greenhouse gases countries can produce over the commitment period from 2008 to 2012. Countries, in turn, set quotas on the emissions of businesses. Emissions trading, as set out by the Kyoto protocol (Lieferring et al., 2008), allows countries that have emission units to spare, namely emissions permitted to them but not used, may “bank” them for use later, or may sell them to countries that are over their quotas. Thus, a new commodity was produced in the form of certified emission reductions (CERs) or removals. Since carbon dioxide and methane are the principal greenhouse gases, emissions trading are simply of trading in carbon credits. For trading purposes, one carbon credit is considered equivalent to one tonne of carbon dioxide emissions. Carbon is now tracked and traded like any other commodity. In the “carbon market”, CERs can be exchanged between businesses or bought and sold in international markets at the prevailing market prices.

It is also possible for developed countries within the trading scheme to sponsor carbon projects that provide a reduction in greenhouse gas emissions in other countries, as a way of generating CERs which can be applied to meeting their own emission targets. Kyoto protocol allows this through clean development mechanism (CDM) and Joint Implementation projects, in order to provide flexible mechanisms to aid regulated entities in meeting their compliance with their quotas. The recipient countries benefit from advanced technology transfer that allows their factories or plants to operate more efficiently, and hence at lower costs and higher profits. The atmosphere benefits because future emissions are lower than they would have been otherwise. The CDM will be overseen by an Executive Board that has already been established and has approved a series of methodologies for large-scale and small-scale projects.

Current median price in early 2008 for US carbon credits is around 6 US\$ per metric ton, with projected median and high percentile prices increase to 13 and 27 US\$ per metric ton, respectively by the end of 2012 when the current emission quota set by Kyoto protocol will be reviewed. Carbon emission trading has been steadily increasing in recent years. According to the World Bank's Carbon Finance Unit, 374 million metric tonnes of carbon dioxide equivalent were exchanged through projects in 2005, a 240% increase relative to 2004 at 110 million metric tonnes of carbon dioxide, which was itself a 41% increase relative to 2003 (78 million metric tonnes of carbon dioxide). A sharp rise in the number of transactions in the emissions trading market brought the value of trades to about \$64bn last year, says the World Bank in an annual review in 2008 (World Bank, 2008).

Looking at the prospects of carbon trading, it may not be an unreasonable expectation that, in the future, wastewater treatment will experience a global shift towards employment of highly efficient granular sludge-based anaerobic processes for energy production and greenhouse gas emission reductions.

3.5. Carbon credits estimation from the present study

CH₄ emissions from wastewater were calculated according to the IPCC guidelines as follows:

$$\text{CH}_4 \text{ emissions} = \text{Total COD}_{\text{baseline}} \times \text{Bo} \times \text{MCF}_{\text{baseline}} \left(\frac{\text{kg/year}}{\text{kg COD/year}} \right) \left(\frac{\text{kg CH}_4/\text{kg COD}}{\text{kg COD/year}} \right)$$

where, COD_{baseline} is the yearly chemical oxygen demand of effluent entering lagoons or directed to land application (measured); Bo is the maximum methane producing capacity; and MCF_{baseline} is the monthly methane conversion factor (fraction).

Based on the performance of UASB reactors achieved in the present study, the baseline CH₄ emission reduction could be calculated by calculating the difference of UASB reactors and open lagoon wastewater treatment systems. The total baseline CH₄ emissions can be further translated into CO₂ equivalent emissions by multiplying by its global warming potential (GWP) of 21 (Show and Lee, in press). As volatile fatty acids are intermediate products from anaerobic degradation of complex organics, the performances of mixed-VFA reactor can be used to estimate the total baseline CH₄ emission reduction. Based on the 2.5 l bench-scale UASB reactor fed with concentrated mixed-VFA substrate (20 g COD l⁻¹), the total baseline CH₄ emissions reduction was calculated as 29 kg CO₂/year at a HRT of 1.9 days. If the reactor is scaled up at 1,600,000 times to that of a typical full-scale anaerobic digester of 4000 m³ full-scale operating at same conditions, the total baseline CH₄ emissions reduction could be increased to 46,420 tons CO₂ reduction/year. The estimated carbon credits would amount to 278,500 US\$ per year by assuming a carbon price of 6 US\$ per metric ton CO₂ reduction. The credits are comparable with that calculated from similar full-scaled reactors treating pure acetate and butyrate at US\$273,000 and US\$338,000 per year, respectively.

4. Conclusions

This study employed carbon mass balance concept to examine the practical carbon flow over UASB reactors. The net yields of biomass were estimated from the conversion of butyrate and acetate to methane and carbon dioxide. The experimental results showed that butyrate degradation exhibited higher net yield of sludge compared with acetate degradation and also caused the sludge granulation. The observed granulation of butyrate-fed sludge may suppose that acetogen, hydrogenotrophic methanogen rather than microbial community may act important role on granulation. Based on scaling up of the laboratory-scale reactors and estimation of the carbon credits, it can be economically or financially attractive from the revenue generated from carbon credit. Looking at the prospects of carbon trading, it is reasonable to expect that, in the future, wastewater treatment will experience a shift towards employment of highly efficient granular anaerobic processes in maximising methane production and carbon credit.

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