Cyanide degradation kinetics during anaerobic co-digestion of cassava pulp with pig manure

Naraporn Glanpracha, B. M. N. Basnayake, Eldon R. Rene, Piet N. L. Lens and Ajit P. Annachhatre

ABSTRACT

Anaerobic co-digestion of cassava pulp (CP) and pig manure (PM) under cyanide inhibition conditions was investigated and modeled. Batch experiments were performed with initial cyanide concentrations ranging from 1.5 to 10 mg/L. Cyanide acclimatized sludge from an anaerobic co-digester treating cyanide-containing CP and PM was used as the seed sludge (inoculum). Cyanide degradation during anaerobic digestion consisted of an initial lag phase, followed by a cyanide degradation phase. After a short sludge acclimatization period of less than 3 days, the anaerobic sludge was able to degrade cyanide, indicating that the sludge inhibition due to cyanide was reversible. Cyanide degradation during anaerobic co-digestion of CP and PM followed the first-order kinetics with a rate constant of 0.094 d^{-1}. Gas evolution during batch anaerobic degradation was modeled using the modified Monod-type kinetics to incorporate cyanide inhibition. The model predicted results yielded a satisfactory fit with the experimental data.

Key words | anaerobic co-digestion, cyanide degradation, cyanide inhibition, first-order kinetics, Monod-type kinetics

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INTRODUCTION

Cassava pulp (CP), a solid waste rich in organic carbon, is generated during the cassava starch production process. Approximately 0.33 tons of CP are produced per ton of cassava root processed (Sriroth *et al.* 2000; Chavalparit & Ongwandee 2009; Glanpracha & Annachhatre 2016). CP contains about 20–30% starch and 60–70% moisture on a wet weight basis. It also contains fibers, protein and cyanide in small proportions (Sriroth *et al.* 2000; Panichnumsin *et al.* 2010). A small portion of CP is sold as a low-cost animal feed material, while the remaining amount is often left untreated. Biodegradation of CP under uncontrolled anaerobic conditions in a disposal area results in extensive environmental pollution issues, thereby affecting the air, water, and soil quality. The presence of cyanide and the low protein content of CP are the major factors that limit its utilization as an animal feed. Cyanide detoxification processes, such as sun drying and ensiling, have been used for animal feed production. Fermentation using microorganisms such as *Saccharomyces cerevisiae* and *Aspergillus niger* to improve the protein content of CP has been reported for animal feed production (Chauynarong *et al.* 2009; Khempaka *et al.* 2014).

Anaerobic digestion (AD) is an alternative waste treatment option for CP because it contains a high starch and moisture content. The benefits of this process are organic waste stabilization and energy recovery in the form of biogas. The digestate from an anaerobic process can be applied as a fertilizer and soil conditioner. However, a low nitrogen content as well as the presence of residual cyanide in CP limits its utilization in the AD process. As reported in the literature, the anaerobic co-digestion (AcoD) of CP with a nitrogen rich co-substrate such as pig manure (PM), at a C/N ratio of 30–35, achieved almost three times higher specific methane yield as compared to mono-digestion (Panichnumsin *et al.* 2010; Ren *et al.* 2014).

The presence of residual cyanide is one of the factors limiting AD of CP. Free cyanide (sum of $HCN + CN^-$) has been reported to be toxic to methanogens. The toxicity of cyanide in AD is high as shown by its small value of the cyanide inhibition constant of 1.172×10^{-5} mg CN^-/L (Onukwugha & Ibeje 2013). Inhibition of AD by cyanide

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has been reported in the literature for the anaerobic treatment of synthetic wastewater containing starch and volatile fatty acids, residues from a flour and cassava meal industry and on the activity of anaerobic biogranules (Annachhatre & Amornkaew 2000; Gijzen *et al.* 2000; Paixão *et al.* 2000). In CP, cyanide exists mainly in two forms: (i) the cyanohydrins and (ii) the free hydrocyanic acid (HCN). Only a small amount of cyanogenic glucoside (linamarin) has been found in CP, because, during the process of cassava starch production, the cyanogenic glucoside is exposed to the extracellular enzyme linamarase and it undergoes hydrolysis to cyanohydrin and glucose, respectively. During the cassava starch production process, although a large amount of cyanide from the cassava tuber is removed, some residual cyanide still remains in the CP. The cyanide content in CP has been reported to be in the range of 45 to 154 mg CN^-_{eq}/kg CP.

According to Glanpracha & Annachhatre (2016), the cyanide concentration varies during the AD of CP. In that study, the authors observed that more than 90% of the bound cyanide (linamarin) in cassava is released as HCN, as evidenced by a nearly similar value of the total cyanide and free cyanide concentrations in a digester operating at pH 7.2–7.8, at which hydrolysis of cyanohydrins to HCN occurs. Despite its acute toxicity, the effects of cyanide on the AD process are temporary if a sufficiently long acclimatization period is allowed. The adaptation to cyanide can be explained by a population shift towards acetoclastic methanogens (Paixão *et al.* 2000; Zaher *et al.* 2006; Novak *et al.* 2013). By stepwise increasing the organic loading rate during the AD process, Glanpracha & Annachhatre (2016) reported that cyanide present in CP was successfully degraded and did not inhibit the AD process. Thus, under anaerobic conditions with sufficient time for acclimatization of anaerobic microorganisms to cyanide, AD systems can tolerate moderately high cyanide concentrations, eventually even degrading the cyanide.

A large amount of the information available in the literature originates from the biodegradation of cyanide by pure cultures (Dursun & Aksu 2000; Akcil *et al.* 2003; Dash *et al.* 2006; Naveen *et al.* 2011). However, no information is available on the cyanide degradation kinetics using mixed bacterial cultures in the AD process. In this study, AcoD of CP and PM with cyanide addition was carried out in batch experiments using seed sludge from an anaerobic digester treating CP and PM, and the kinetics of cyanide degradation were investigated.

METHODS

Substrates and the seed sludge

The seed sludge was obtained from an anaerobic co-digester treating CP and PM on day 420 of reactor operation under variable organic loading conditions (Glanpracha & Annachhatre 2016). The mixed feedstock of CP and PM, in a proportion of 80:20 (volatile solids basis), corresponding to a C/N ratio of 35, was used as feed throughout this study. The characteristics of CP, PM and the mixed feedstock of CP and PM are presented in Table 1.

Experimental setup

The degradation of cyanide was investigated by analyzing the CN^- concentration in the digestate of three replicate batch experiments, at different cyanide concentrations. Batch tests were performed in 50 mL serum bottles capped with a septum and an aluminum cap. All bottles were filled with 20 mL of sludge and 0.75 g of mixed feedstock. Thereafter, cyanide was added to the desired final concentrations of 0, 1.5, 3, 5, 8 and 10 mg/L, respectively. The initial pH of the sludge and mixed feedstock was adjusted

Table 1 | Characteristics of the cassava pulp, pig manure and mixed feedstock used in this study

Characteristics	Unit	CP	PM	Mixed feedstock[a]
Moisture content	% wet weight	78.9 ± 0.7	78.5 ± 1.2	78.9 ± 0.9
Total solids	% wet weight	20.9 ± 0.9	20.6 ± 1.0	20.8 ± 0.8
Volatile solids	% wet weight	19.6 ± 0.8	13.1 ± 0.9	18.2 ± 0.6
Total organic carbon	% dry weight	52.1 ± 3.2	27.8 ± 0.8	47.6 ± 0.3
Total nitrogen	% dry weight	0.3 ± 0.1	4.4 ± 0.6	1.3 ± 0.1
C/N	–	176.4 ± 3.1	6.3 ± 0.6	35.0 ± 1.1

[a]Mixture of CP and PM 80:20 (volatile solids basis); CP, cassava pulp; PM, pig manure.

to about 7.2–7.5 by adding a sodium bicarbonate solution. Anaerobic conditions were maintained by flushing nitrogen gas through the headspace of the bottle. All bottles were incubated at 31 (±1) °C, for 30 days.

Sampling

Forty-five bottles (15 bottles × 3 replicates) were prepared for each cyanide concentration and the bottles at each concentration were sampled once every 2 days to analyze the residual cyanide concentration. Daily biogas production was measured using an air-tight syringe. During the incubation period, biogas composition and CN^- concentration were monitored periodically.

Analytical

The biogas composition was determined using gas chromatography (Agilent 7800: Perkin-Elmer), fitted with a steel column, packed with WG-100 packing material, and a thermal conductivity detector. The analysis of cyanide in the digestate included extraction and transformation of cyanogenic compounds to free cyanide (CN^-) as per the procedure given by Cooke (1978) and Essers *et al.* (1993). Free cyanide concentration was measured using the calorimetric method procedure described in standard methods (APHA 2005).

Kinetic study

Cyanide degradation was modeled using first-order reaction kinetics (Equations (1) and (2)):

$$\frac{dCN}{dt} = -kCN \tag{1}$$

$$CN_{(t)} = CN_{(0)}e^{-k(t-\lambda)} \tag{2}$$

where $CN_{(0)}$ is the cyanide concentration (mg/L) at time $t = 0$; $CN_{(t)}$ is the cyanide concentration (mg/L) at time t; k is the rate constant (d^{-1}); λ is the lag time (d) and t is the time (d).

Gas generation under the influence of cyanide inhibition was modeled as follows.

This model comprises two parts, i.e. the first is a Monod-type equation for gas generation, while the second includes the inhibitory effects due to cyanide (Equation (3)).

$$G_{(t)} = \frac{G_{(\infty)}t}{K_t + t}\left(1 - \frac{CN_t}{CN_L}\right)^n \tag{3}$$

where $G_{(t)}$ is the cumulative biogas production (mL); $G_{(\infty)}$ is the cumulative biogas production at time infinity (mL); K_t is the half-velocity constant (d); CN_t is the cyanide concentration at time t (mg/L); CN_L is the limiting cyanide concentration beyond which no methanogenic activity is observed (mg/L); t is the time (d); and n is the exponent term and the value of n depends on the acclimatization or degradation stages.

Statistical analysis

Statistical significance between the experimental results and model predicted values was obtained using the paired t-test analysis.

RESULTS AND DISCUSSION

Effect of initial cyanide concentration and the degradation of cyanide

Figure 1 shows the variation of the cyanide concentration as a function of time during batch anaerobic degradation by the cyanide acclimatized sludge. As seen from this figure, the variation of the cyanide concentration follows two distinct phases. The first one was a lag phase during which no cyanide degradation occurred as evidenced by the near constant cyanide concentration. During this state, negligible biogas production was observed (Figure 2(a) and 2(b)). The

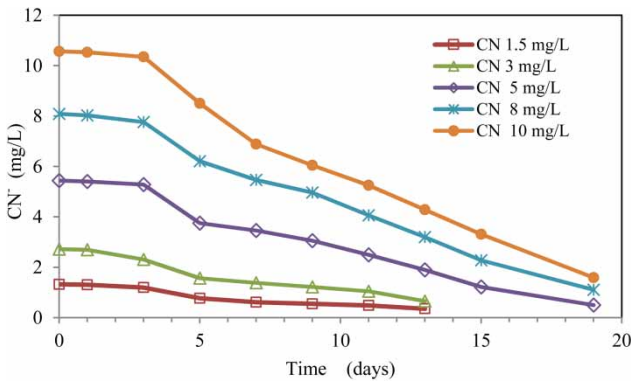

Figure 1 | Variation of cyanide concentration with time during the batch anaerobic degradation by CN^- acclimatized sludge.

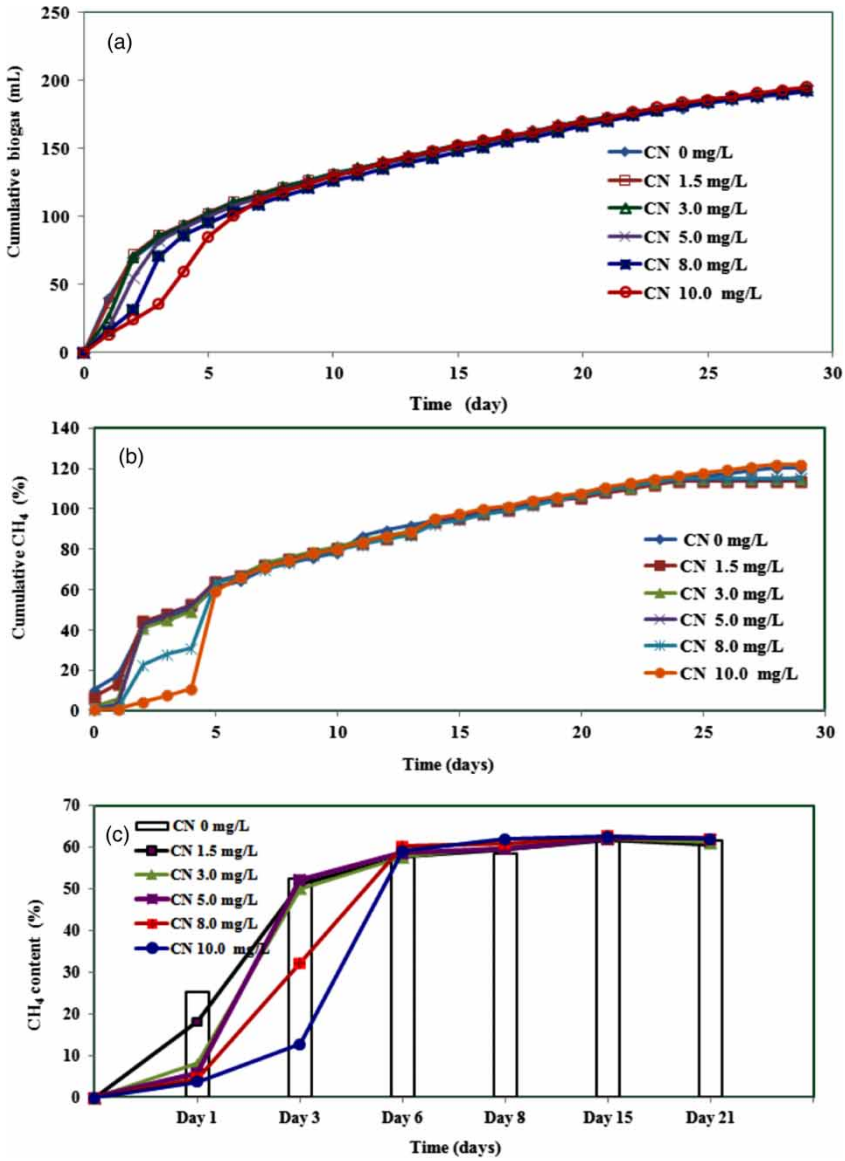

Figure 2 | Variation of (a) cumulative biogas, (b) cumulative CH_4 and (c) CH_4 content at different cyanide concentrations in the batch experiments.

duration of lag phase depended on the initial cyanide concentration, i.e. with increasing initial cyanide concentration yielding increased lag phase times. Anaerobic degradation with substantial biogas production occurred in the second phase. From day 3 onwards, the cyanide concentration gradually decreased with the incubation time, indicating that the sludge had acclimatized to cyanide present in the system (Figure 1). Thereafter, the cyanide acclimatized sludge could degrade cyanide in the system, leading to stabilized reactor operation, as evidenced by the steady values of biogas production with 60% methane production (Figure 2(c)). A short initial lag period of less than 3 days was observed since the seed sludge used in the batch experiments was already acclimatized to free cyanide due to the fact that it was obtained from an anaerobic co-digester treating cyanide-containing CP and PM for over 420 days (Glanpracha & Annachhatre 2016).

Acclimatization of anaerobic bacteria to cyanide has been well documented in the literature (Gijzen *et al.* 2000; Paixão *et al.* 2000; Zaher *et al.* 2006; Novak *et al.* 2013). This can be due to a population shift in acetoclastic methanogens. Zaher *et al.* (2006) observed that the gradually increased cyanide concentration in the influent led to a gradually decreased sensitivity and less tolerant acetoclastic

methanogenic population. *Methanosaeta* and *Methanosarcina*, which use acetate to produce methane and carbon dioxide, have a different acetate affinity threshold and different tolerances to cyanide. As reported in a previous study, *Methanosarcina* was dominant at increasing cyanide concentrations in an AD system due to its more tolerant nature to toxic compounds such as cyanide (Novak *et al.* 2013). Therefore, *Methanosarcina* sp. is an important microbial group involved in cyanide degradation.

The inhibitory effects and acclimatization to cyanide in AD reported in the literature are summarized in Table 2. The data in Table 2 show that the inhibitory effects of cyanide in the AD process are temporary and reversible if a sufficiently long acclimatization period is allowed. Therefore, the anaerobic conditions with sufficient time for acclimatization of anaerobic microorganisms to cyanide allows the system to tolerate high concentrations of cyanide, eventually leading to cyanide degradation. As shown in Table 2, different acclimatization periods (from 21 days up to 6 months) have been reported in AD of cyanide-containing substrates, depending on the type of substrate, feed composition, influent cyanide concentration, digester configuration and operating conditions. The tolerated cyanide concentrations fall within the range of 6 mg/L up to 240 mg/L. In bioreactors, anaerobic sludge could be adapted to high cyanide concentrations by gradually increasing the cyanide concentration in the influent (Gijzen *et al.* 2000). In upflow anaerobic sludge blanket reactors treating cassava starch wastewater, it was reported that the population shift in acetoclastic methanogens depended on the cyanide concentrations in the influent (Zaher *et al.* 2006). As seen from Table 2, cyanide can be biodegraded by cyanide-adapted anaerobic sludge in different bioreactor configurations, with removal efficiencies exceeding 80%.

The degradation pathway of cyanide is illustrated in Figure 3 (Zaher *et al.* 2006). Accordingly, cyanohydrin in CP is hydrolyzed to free HCN under neutral conditions in AD systems. After an acclimatization period, adapted acetoclastic methanogens (e.g. *Methanosarcina* sp.) are an important

Table 2 | Literature reports on cyanide acclimatization period and removal efficiency of AD for cyanide-containing wastes

Substrate	Influent CN^- concentration	Digester configuration	Acclimatization period	Threshold concentration	CN removal efficiency (%)	References
Cassava peel	840 mg/2 days	Plug flow semi-continuous	NR	6 mg/L	>90	Cuzin & Labat (1992)
Synthetic starch wastewater	NR	Fixed-bed continuous	6 months (includes start-up)	240 mg/L 75 mg/(L·d)	90	Siller & Winter (1998)
Synthetic starch wastewater	5–125 mg/L	UASB continuous	21–28 days	250 mg/(L·d)	95	Gijzen *et al.* (2000)
Synthetic starch wastewater	1–100 mg/L	Batch	NR	NR	91–93	Annachhatre & Amornkaew (2000)
Cassava wastewater	5–25 mg/L	UASB continuous	80 days	25 mg/L	>90	Zaher *et al.* (2006)
Synthetic starch wastewater	NR	Two stage CSTR UASB + fixed-bed continuous	NR	NR	90	Paixão *et al.* (2000)
Cassava and brewery wastewater	1–8.5 mg/L	Batch	22 days	8.5 mg/L	NR	Novak *et al.* (2013)
Cassava pulp with pig manure	6.5 mg/L	Single stage semi-CSTR	40 days	6.5 mg/L	92	Glanpracha & Annachhatre (2016)
Cassava pulp with pig manure	1.5–10 mg/L	Batch	3 days	10 mg/L	80–85	This study

NR, not reported; UASB, upflow anaerobic sludge blanket; CSTR, continuous stirred tank reactor.

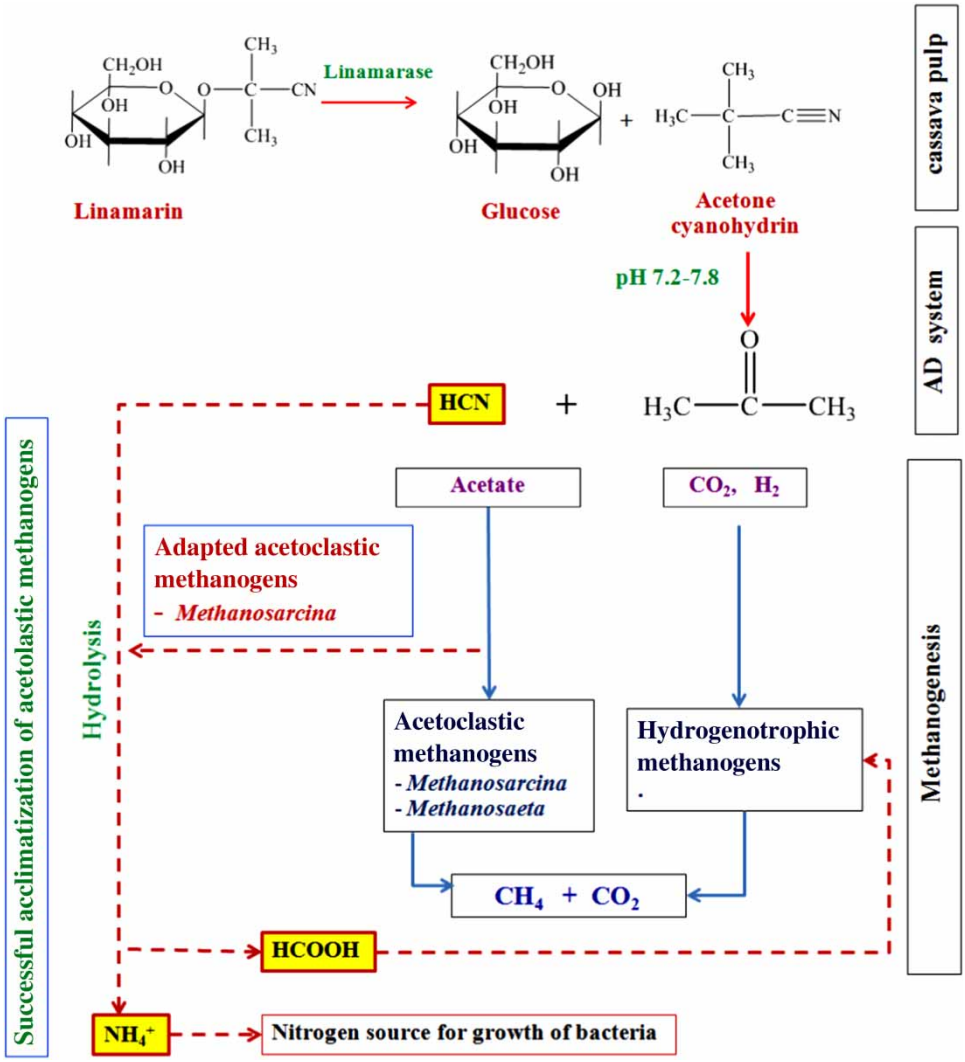

Figure 3 | Fate of cyanide during the AD of CP (adapted from Zaher *et al.* 2006). Dashed line represents the cyanide degradation pathway with adapted acetoclastic methanogens.

microbial group for cyanide degradation. The HCN degradation pathway in anaerobic processes is a hydrolytic reaction. HCOOH and NH_4^+ are produced as the products during the hydrolysis of cyanide. NH_4^+ can be used as a

Table 3 | Lag time at different initial cyanide concentrations

Initial cyanide (mg/L)	Lag time, λ (d)	
	Calculated values	Observed values
1.5	1.0	1
3.0	1.4	1
5.0	1.8	2
8.0	2.2	2
10.0	2.5	3

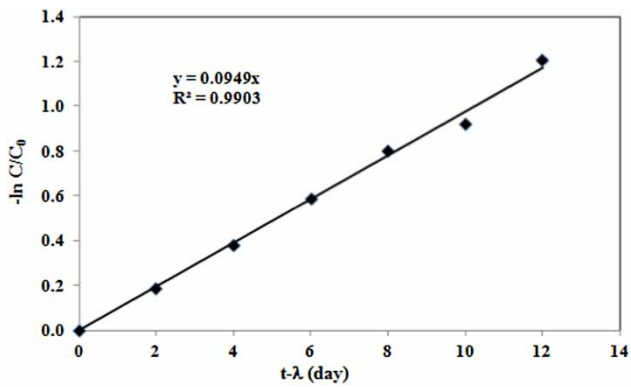

Figure 4 | Determination of rate constant by plotting $-\ln (C/C_0)$ against time minus lag time ($t-\lambda$) from batch experiment performed at a cyanide concentration of 1.5 mg/L.

Table 4 | Rate constant (k) at different cyanide concentrations according to the first-order kinetic reaction

CN^- concentration (mg/L)	Rate constant (k) (d^{-1})	R^2
1.5	0.0949	0.9903
3	0.0940	0.9799
5	0.0939	0.8804
8	0.0938	0.9581
10	0.0931	0.9696
Average	0.0939 ± 0.0006	0.9557 ± 0.0083

source of nitrogen for bacterial growth, while formate can be used as a substrate for the metabolism of hydrogenotrophic methanogens. Methane and carbon dioxide are thus the final products of the reaction (Zaher *et al.* 2006).

Kinetics of cyanide degradation during the anaerobic co-digestion of CP and PM

The degradation of cyanide consists of two distinct phases, i.e. a lag phase followed by a degradation phase.

Lag phase

According to Figure 1, the duration of the lag phase depended on the initial cyanide concentration. The variation of lag time (λ) with respect to initial cyanide concentration was modeled using Equation (4).

$$\lambda^2 = \frac{CN_{(0)}}{1.6} \tag{4}$$

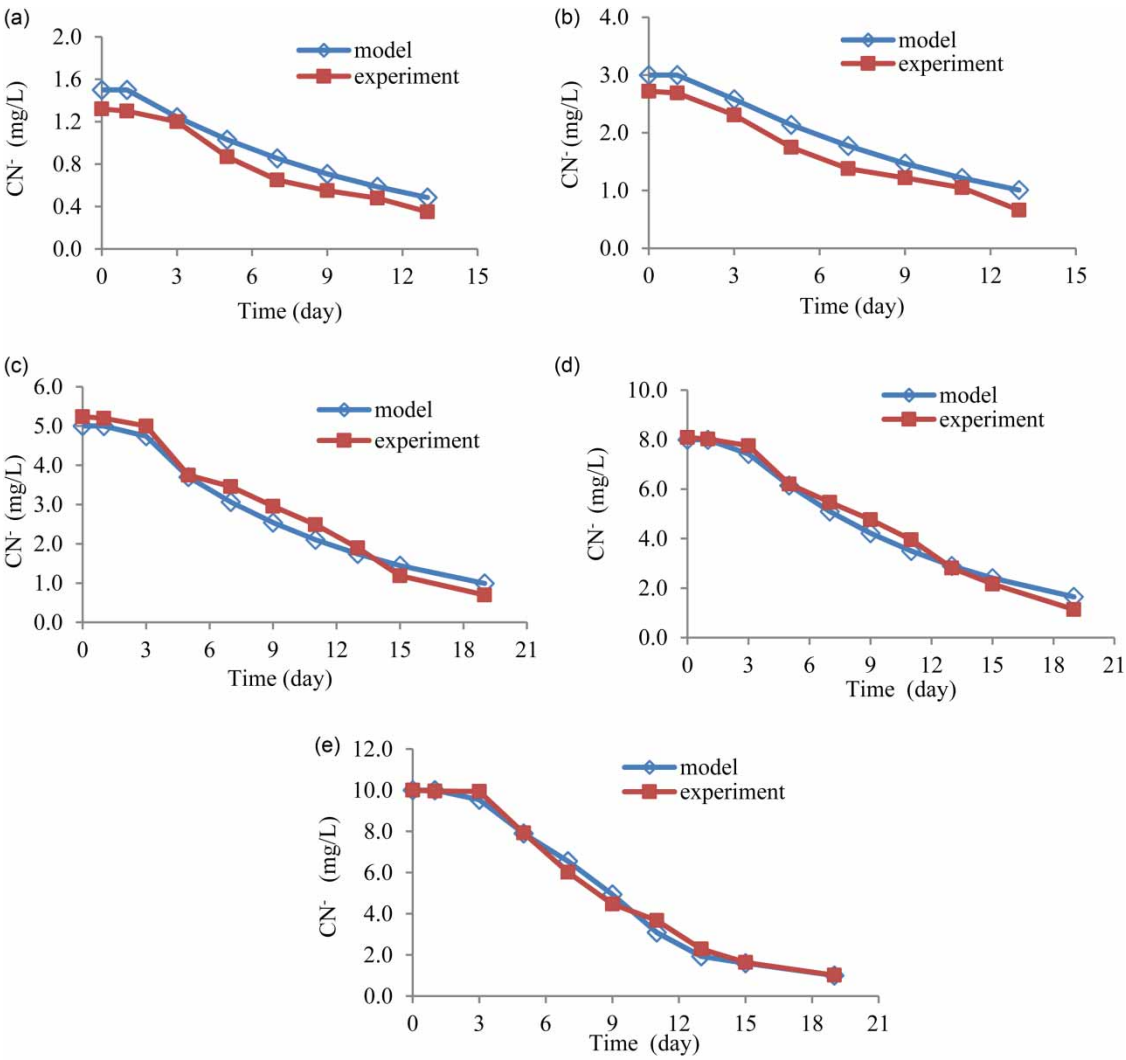

Figure 5 | Comparison of experimental and model predicted results during cyanide degradation under anaerobic condition. (a) 1.5 mg/L of CN^-, (b) 3.0 mg/L of CN^-, (c) 5.0 mg/L of CN^-, (d) 8.0 mg/L of CN^-, (e) 10.0 mg/L of CN^-.

where $CN_{(0)}$ is the initial cyanide concentration (mg/L) at time $t = 0$, and λ is the lag time (d^{-1}).

The observed and calculated lag times at different initial cyanide concentrations are presented in Table 3. It can be seen that increasing the initial cyanide concentration resulted in an increased lag time.

Degradation phase

The first-order kinetics (Equation (2)) was used to describe cyanide degradation during the degradation phase. The rate constant (k) was determined by plotting $-\ln(C/C_0)$ against $(t-\lambda)$ (Figure 4), where C_0 and C represent the cyanide concentration (mg/L) at time $t=0$ and time t minus lag time $(t-\lambda)$, respectively. A straight line was obtained with a slope equal to the rate constant, k (d^{-1}). According to Figure 4, the reaction followed the first-order kinetics with an R^2 value of 0.9903, for a CN^- concentration of 1.5 mg/L. The rate constant and coefficient (R^2) of different cyanide concentrations are summarized in Table 4. The average rate constant and R^2 values were 0.0939 and 0.9557, respectively.

From Table 4, it is evident that beyond the acclimatization period, the initial cyanide concentration did not have

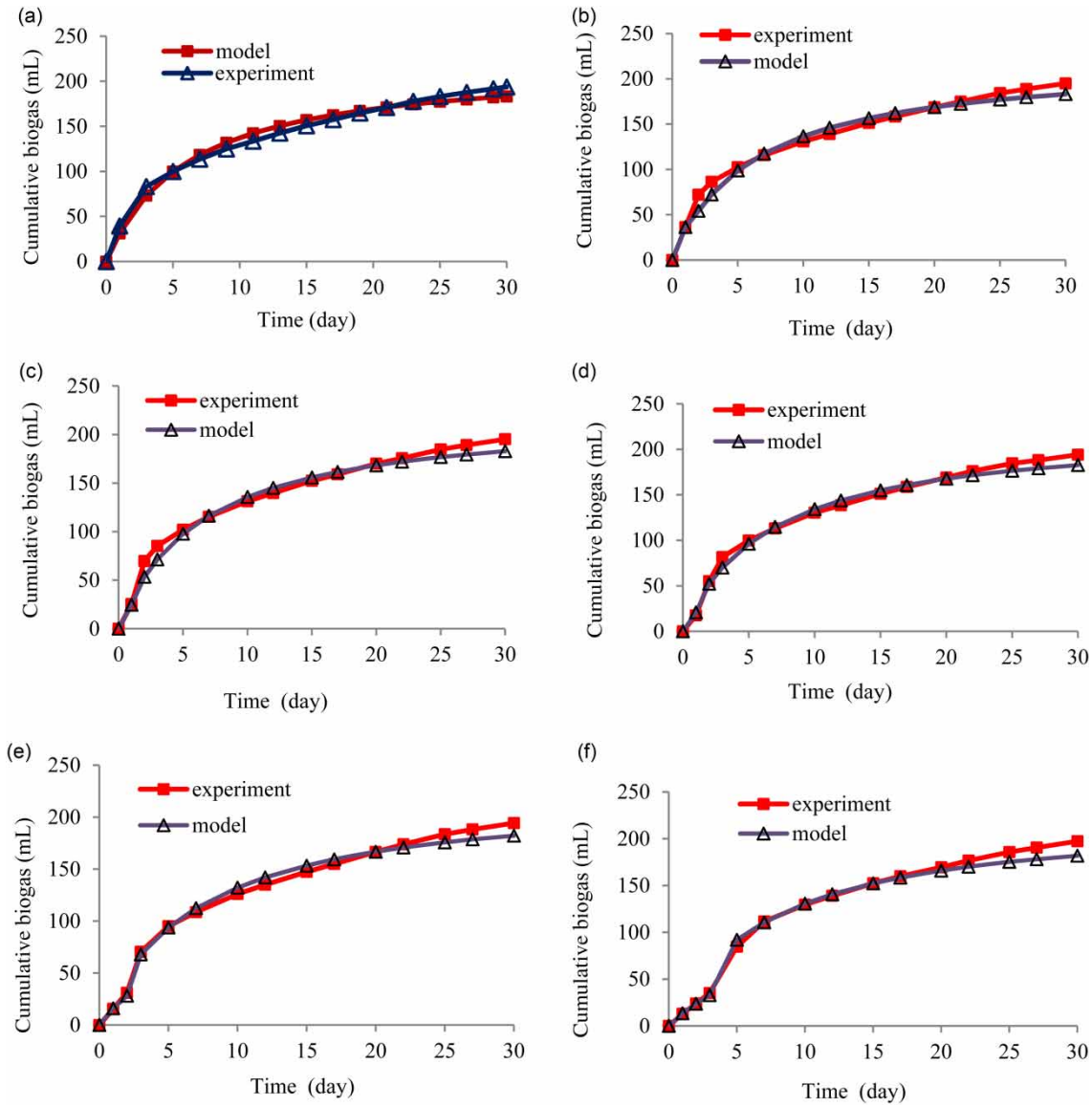

Figure 6 | Comparison of experimental and modified Monod's model prediction for biogas production under different CN^- concentration. (a) 0 mg/L of CN^-, (b) 1.5 mg/L of CN^{-1}, (c) 3.0 mg/L of CN^-, (d) 5.0 mg/L of CN^{-1}, (e) 8.0 mg/L of CN^-, (f) 10.0 mg/L of CN^{-1}.

Table 5 | Degradation kinetics of cyanide reported in the literature

Substrates	Influent CN^- concentration	Condition	Reactor configuration	CN^- degradation		Kinetics of degradation	Rate constant (k)	References
				Biological	Chemical			
Ferro cyanide solution	100 mg/L	Aerobic	Packed bed column (operated under different flow rates)	*Pseudomonas fluorescens*		First-order	1.43×10^3–2.56×10^3 (L/(g dried cell·h^{-1}))	Dursun & Aksu (2000)
Synthetic wastewater	3.85–2.5 mM	Aerobic	Semi-batch		Alkali hydrolysis at high T and P	First-order	6.63×10^3 (s^{-1})	Oulego *et al.* (2012)
Synthetic cyanide-containing wastewater	NR	Aerobic	Batch		Photocatalytic - Using TiO_2-SiO_2 aero gel - Using V_2O_5-SiO_2 and ozone	 First-order First-order	 0.045 min^{-1} 0.0075 min^{-1}	Ibrahim *et al.* (2003)
Sodium cyanide solution	0.5 g/L	Aerobic	Batch		Oxidative using activated carbon as the catalyst	First-order	0.0512 h^{-1}	Adams (1990)
Cassava starch wastewater	5–14 mg/L	Anaerobic	Continuous	Mixed culture anaerobic sludge		Second-order	0.6 d^{-1}	Zaher *et al.* (2006)
Cassava pulp and pig manure	1.5–10 mg/L	Anaerobic	Batch	Mixed culture anaerobic sludge		First-order	0.0939 d^{-1}	This study

NR, not reported.

any influence on the cyanide degradation rate under the tested concentrations (~10 mg/L), since the rate constant values are nearly similar for all the concentrations. This observation is in agreement with the conclusions derived from the research of Kojima *et al.* (2005) and Oulego *et al.* (2012). These authors concluded that cyanide degradation was not affected by the initial cyanide concentration, indicating that the degradation pathway is a non-radical pathway. In radical systems, the initial concentration affects the generation of radicals and this influences the degradation rate. Nevertheless, when the initial pollutant concentration is higher, more free radicals are generated and reaction times are usually shorter. According to Oulego *et al.* (2012), the cyanide degradation pathway was hydrolytic, and ammonia and formate were produced as reaction products.

Model development for cyanide degradation

Figures 1 and 2 show that the presence of cyanide results in a lag phase (phase 1) with negligible cyanide degradation and biogas production. The lag phase was followed by a first-order cyanide degradation phase (phase 2) in which significant biogas production was observed. Biogas production in phase 2 could be modeled by incorporating a correction factor. The modified Monod's equation was developed (Equation (3)) by introducing the correction factor of $(1 - (CN/CN_L)^n)$ in order to predict biogas production in the presence of cyanide in the system.

Figure 5 compares the experimental results and the model predictions during batch AD. From the experimental data presented in Figure 2, $G_{(\infty)}$ had a value of 220 mL. This represents the biogas production after a sufficiently long batch incubation time when anaerobic degradation of all the substrate was completed. The half-velocity constant was then estimated as 6 days, representing the time duration of the batch at which half of the maximum cumulative gas production was obtained. On the other hand, a CN_L of 100 mg/L was selected as the limiting cyanide concentration at which anaerobic activity is completely inhibited. Moreover, since the methanogenic activity during the inhibition phase (phase 1) was negligible during the degradation phase (phase 2), the value of the exponent term n was set at 8 and 1 for the inhibition and degradation phases, respectively. The comparison of experimental values and calculated values from the modified Monod-type equation for biogas production under different cyanide concentrations is presented in Figure 6. The model statistical significance determined by paired t-test analysis yielded satisfactory data comparison.

The kinetics of cyanide degradation reported in the literature are summarized in Table 5. As seen from this table, most of the degradation kinetics for cyanide available in the literature were investigated under aerobic conditions. In contrast, the existing information on the cyanide degradation kinetics under anaerobic conditions is rather limited. Furthermore, Table 5 shows that the biological and chemical cyanide degradation followed the first-order kinetics with different rate constant values depending on the digester configuration and operating conditions. For biodegradation, a lower rate constant has been reported in this study as compared to the rate constant of aerobic biodegradation of cyanide reported in the study of Dursun & Aksu (2000). The results from this study showed that anaerobic biodegradation of cyanide is much slower than aerobic biodegradation, since anaerobic bacteria have a cyanide inhibitory level of only 2 mg/L, compared to ~200 mg/L for aerobic bacteria (Naveen *et al.* 2011).

CONCLUSIONS

Batch biodegradation experiments were conducted to evaluate the effect of cyanide inhibition on the anaerobic co-digestion of CP and PM using cyanide acclimatized anaerobic sludge. It can be concluded that:

- the presence of cyanide during AD inhibited the methanogenic activity; however, this cyanide inhibition was temporary and reversible by nature;
- cyanide degradation during AD consisted of an initial lag phase, followed by a cyanide degradation phase;
- an acclimatization period of ~3 days was required for the onset of cyanide biodegradation in the concentration range of 1.5 to 10 mg/L;
- the degradation of cyanide followed the first-order kinetics with a rate constant (k) value of 0.0939 d^{-1};
- a modified Monod-type equation with a cyanide inhibition correction factor was used to model the gas evolution during batch methanogenesis.

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