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ORIGINAL PAPER

Anaerobic Digestion of Secondary Tannery Sludge: Optimisation of Initial pH and Temperature and Evaluation of Kinetics

A. B. Mpofu[1,2] · P. J. Welz[2] · O. O. Oyekola[1]

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Abstract

The feasibility of retrofitting and operating a low cost anaerobic mesophilic batch reactor for the reduction of secondary tannery sludge (STNS) produced in tannery wastewater treatment plants at varying initial reactor pH (pH_{in}) using acclimated inoculum was demonstrated using the bio-methane potential test protocol. Temperature had a significant effect on process indicators whilst the effect of pH_{in} was negated by the STNS' high alkalinity and its buffering capacity offered by ammonia/ammonium speciation, eliminating the need for pH control during digestion. Furthermore, there was an insignificant and significant variation in the biodegradability (B_o) and gas yields of STNS, respectively. This nullified the need for reactor heating if gas yields were not prioritised. Nonetheless, optimum conditions (35.5–37.0 °C and pH_{in} 6.5) yielded 200–217 mL biogas/gVS (≈55% CH_4), 108–118 mL CH_4/gVS and 69–74% VS, 54–57% TS and 47–48% COD reduction. Cumulative CH_4 generations were accurately modelled using the modified Gompertz, Logistic, First order, Cone ($0.828 \leq$ Adj $R^2 \leq 0.986$) and process kinetics were determined. However, the correlations between kinetics and process parameters were mostly non-monotonic. The positive effect of temperature on A ($r = 0.84$) coincided with a decrease in methanogenesis rate (k) and ratio of hydrolysis and methanogenesis (K/μ_m) at optimum pH_{in} signifying an inhibited steady state reactor condition.

Keywords Anaerobic digestion · Secondary tannery sludge · Optimisation · Temperature · Influent pH · Kinetics

Statement of Novelty

There are no comprehensive studies on optimisation, evaluation of kinetics and their correlation with initial pH, temperature and process efficiency during anaerobic digestion of secondary tannery sludge (waste activated tannery sludge).

Introduction

The tanning and leather finishing industry plays a prominent role in the global and national economy and in the reuse of skins/hides, by-products of the meat industry, particularly for developing countries that dominate both industries. Inexplicit environmental pollution standards, cheap labour and abundancy of skins/hides has led to the concentration of tanneries in the developing countries mainly focusing on the most polluting beam-house operations for the production of crusts, pickled skins and wet blue skins/hides that are mainly exported to the developed world for leather finishing [1]. However, only about 30% of the wet feed weight of skin/hides is tanned into a product and the remainder is hazardous solid wastes (fleshings, shavings, trimmings, and sludge) disposed of in landfills [2]. Most of the solid waste emanate from the beam house processes that generate about 80%, tanning 19%, and the rest 1% [3]. More than 50% of the wet feed weight of skins/hides ends up as sludge produced from the widely used activated sludge process (ASP) in the tannery wastewater treatment plants (TWWTP), exerting enormous pressure on the receiving environment [2]. According

✉ A. B. Mpofu
ashtonmpofu@gmail.com

P. J. Welz
welzp@cput.ac.za

O. O. Oyekola
oyekolas@cput.ac.za

[1] Department of Chemical Engineering, Cape Peninsula University of Technology, Bellville Campus, Symphony Way, Cape Town 7535, South Africa

[2] Institute of Biomedical and Microbial Biotechnology, Cape Peninsula University of Technology, Bellville Campus, Symphony Way, Cape Town 7535, South Africa

to [3] the lack of suitable (legalised) landfills in most developing countries, and the practice of open dumping without specific regulations and guidelines led to the pollution of the nearby rivers and land by Asian and African tanneries.

Anaerobic digestion (AD) has increasingly been realised as a cost-effective alternative, suitable for the reduction of organic waste for concurrent environmental protection and renewable energy generation in the developing world. However, its application in the treatment of nitrogenous waste such as manure, slaughterhouse, food and tannery waste has been limited by its susceptibility to ammonia (NH_3) inhibition [4, 5] and partly due to perception on related capital, process, and maintenance costs [1]. Even worse, TNS is complex and is typically laden with potentially inhibitory metal salts, sulphides/sulphate, long chain fatty acids (LCFA) and volatile fatty acids (VFA) [4]. Several studies have reported on strategies to alleviate NH_3 inhibition during AD of tannery wastes such as co-digestion, pre-treatment, microbial acclimation and bioaugmentation, optimisation of organic loading rate (OLR), solids/hydraulic retention time (S/HRT), carbon:nitrogen (C:N) and inoculum:substrate (ISR) ratio, and trace elements concentrations. These were correlated with NH_3/NH_4 levels and another factor, such as biogas/methane (CH_4) production, CH_4 quality, VFA accumulation, methanogenic pathway and activity (kinetics). Furthermore, they did not collectively take into account the interaction with other factors, such as operational temperature, pH, and mixing conditions as they were mostly maintained constant.

A number of studies have investigated the advantages of thermophilic (55 °C) over mesophilic (35–37 °C) AD. They have reported on the difficulty of operating at higher temperatures due to inhibition and process sensitivity regardless of improved kinetics [6]. The solubility dissociation constant (pKa) of most inhibitory unionised substances such as NH_3, H_2S, CO_2, H_2 and metal salts decreases with increasing temperature and with the exception of NH_3, follow Henry's law.

Conventionally, mesophilic AD (35–37 °C) at near neutral pH (6.5–7.2) offers more stable operation, reduces susceptibility to NH_3, VFA, and LCFA inhibition [7], provides more resilience to shock loads [8], has a low energy demand and promotes a more diverse microbial population [9]. These conditions support the fair distribution of the inhibitory species (NH_3 and H_2S) [5] and they often offer better or comparable gas yields, efficiencies and kinetics as compared to thermophilic AD [10]. Interestingly, lower mesophilic temperatures may achieve comparable results to the optimum (35–37 °C) [8, 11, 12]. However, the composition of NH_3 also increases with pH (Eq. 1) whereas H_2S, CO_2, H_2 and metal bioavailability decrease with increasing pH [4]. The NH_3/NH_4 species in anaerobic reactors treating nitrogenous waste provide a good buffering capacity, which helps to avoid digester souring (VFA accumulation) during inhibition leading to an inhibited steady state condition [12]. Thus, in practise initial reactor pH (pH_{in}) would be controlled instead of controlling the instantaneous reactor pH [13]. Optimal acetogenic and methanogenic pH and temperature conditions are shown in Table 1.

Therefore, the aim of this study was to optimise the reactor operating temperature (20–40 °C) and pH_{in} (6.0–9.0) during the AD of STNS using an acclimated inoculum in order to mitigate the envisaged NH_3, and/or H_2S and/or metal inhibition. Furthermore, the study aimed to investigate: (i) reactor performance (kinetics, gas yields and solids reduction efficiencies) and their dependence on pH_{in} and temperature, and (ii) the feasibility of operating an intermittently mixed (1 min day^{-1}) low cost (no heating, mixing and pH correction) ambient batch reactor at mesophilic temperatures suitable for a tannery in a developing world with a temperate climate. To the author's knowledge, there are no previous investigations reported in open literature, on the optimisation, evaluation and correlation of kinetics with pH_{in}, mesophilic temperatures and process performance during the mono AD of STNS for the alleviation of NH_3, and/or H_2S and/or metal inhibition.

Materials and Methods

Secondary Tannery Sludge and Inoculum Source

The fresh STNS and inoculum used in this study were sampled from a secondary clarifier of a South African TWWTP and a laboratory anaerobic batch reactor treating STNS, respectively. The TWWTP is equipped with a conventional ASP preceded by the pre-treatment and primary treatment units consisting of screens, an equalisation basin, and a primary clarifier. The STNS and inoculum composite samples were obtained by grab sampling with plastic scoops and collected in separate polyurethane airtight storage containers. Similarly, aliquots were obtained for experimental set up and characterisation.

Characterisation of Secondary Tannery Sludge and Inoculum

The inoculum and STNS samples were characterised for total solids (TS) and volatile solids (VS) concentrations following the loss on ignition standard methods using an oven at 105 °C and a furnace at 550 °C, respectively. A Merck Spectroquant Pharo® Spectrophotometer (Darmstadt, Germany) together with Merck cell tests or kits were used to determine the chemical oxygen demand (COD) (cat no: 14555), total volatile organic acids (VOA_t) as acetic acid (HAc) (cat no: 01763), total organic carbon (TOC) (cat no: 14879), total nitrogen (TN) (cat no: 14537), total

Table 1 Optimum temperature and pH conditions for some acetogenic and methanogenic bacteria Adapted from [3, 41]

Substrate	Product	Typical species	Temperature °C	pH
Acetogenic bacteria				
H_2/CO_2	HAc	*Clostridium aceticum*	30–37	NG
HPr	H_2/CO_2, HCO_2	*Syntrophomonas wolfei*	35–40	NG
	HBu, HAc	*P. schinkii*	32–37	NG
		Smithella propionica	35–40	NG
HBu	HAc	*Syntrophobacter wolinii*	35–40	NG
	H_2/CO_2, HCO_2	*S. fumaroxidans*	35–40	NG
Methanogenic bacteria				
HCO_2, H_2/CO_2	CH_4, CO_2	*Methanocorpusculum*	35–37	NG
		Methanoplanus limicola	40	7.0
		M. ruminantium	37–39	7.0
		M. maripaludis	35–40	6.5–8.0
		Methanobrevibacter smithii	37–39	7.0
		M. deltae	37	NG
		M. marisnigri	20–25	6.8–7.3
		Methanogenium cariaci	20–25	6.2–6.6
		Methanobacterium formicicum	37–45	6.6–7.8
		Methanococcus voltae	35–40	6.5–8.0
		M. bourgense	35–42	6.3–6.8
		M. tatii	37–40	7.0
		M. olentangyi	37	NG
		Methanomicrobium mobile	40	6.1–6.9
H_2/CO_2	CH_4	*Methanolacinia paynteri*	40	6.6–7.2
		Methanoplanus endosymbiosus	40	6.6–7.2
		Methanobrevibacter arboriphilus	30–37	7.8–8.0
		M. olentangyi	30–40	NG
		Methanobacterium bryantii	37–39	6.9–7.2
		Methanospirillum hungatei	30–37	NG
		M. alcaliphilum	37	8.1–9.1
HAc	CH_4/CO_2	*Methanosarcina acetivorans*	35–40	6.5–7.5
		Methanosaeta concilii	35–40	7.1–7.5
		Methanothrix soehngenii	35–40	7.4–7.8
HAc, CH_3OH CH_5N	CH_4/CO_2	*Methanosarcina mazeii*	30–40	6.0–7.0
		Methanosarcina barkeri	35–40	5.0–7.0

NG not given

alkalinity as $CaCO_3$ (cat no: 101758), total phosphorous (TP) (cat no: 14729), total ammonia nitrogen as NH_3–N (cat no: 00683), SO_4 (cat no: 14791), total sulphide as HS^- (cat no: 14779), and Cl^- (cat no: 14789) concentrations according to manufacturers' instructions. Metal concentrations (Al, Cd, Cr, Fe, Ni, Pb, and Zn) and earth elements (Ca, K, Mg, and Na) were extracted using Ethylenediaminetetraacetic acid (EDTA) and ammonium acetate, respectively and analysed at Bemlab (Somerset West, South Africa) using a Varian® MPX (Agilent Technologies, Palo Alto, USA) inductively coupled optical emission (ICP-OES) spectrophotometer. Where filtration and dilution were necessary to avoid interferences, 0.45 µm Millipore membrane filters (Darmstadt, Germany) and deionised water were used, respectively.

The Eutech instrument (Ayer Rajar, Singapore) was used for the measurement of pH following the prescribed standard procedure of operation. CH_4, CO_2, H_2S, and O_2 content of the biogas from BMP tests was analysed using a Geotech biogas 5000 analyser (Warwickshire, England). Density (p) was determined by measuring mass of a known volume of sample.

$$C_{NH_3} = \frac{TAN \times pK_a}{C_H \times \left(\frac{pK_a}{pH} + 1\right)} \quad (1)$$

where TAN is in mg/L, pKa is the temperature dependent dissociation constant (0.564×10^{-9} at 25 °C, 1.097×10^{-9} at

35 °C and 3.77×10^{-9} at 55 °C), and C_H is the concentration of hydrogen ions [14].

Anaerobic Digestion Optimisation Experiments

Standard mesophilic bio-methane (BMP) tests were carried out in 500 mL (effective volume) glass screw-cap bottles following the procedure described by [15]. Optimisation of two numeric factors: operational reactor temperature (23–40 °C) and pH_{in} (6.0–9.0) were studied on the maximisation of two response variables: CH_4 yield ($mLCH_4/gVS$) and anaerobic biodegradability (%TS, %VS and %COD reduction), using response surface methodology (RSM) based on full factorial central composite (CCD) experimental design with 13 runs and five levels for each factor. The experimental design matrix (Table 3) was generated using Design-Expert® Software Version 11 (Stat-Ease, Inc., Minneapolis, USA). Each experimental reactor was set up to an inoculum to substrate ratio (ISR = 4) based on the conclusions of BMP experiments by [3] except for the controls contained an equivalent volume of inoculum only. The final volume of the reactors was made up to 500 mL using sterile deionised water and the pH_{in} was adjusted accordingly using 1M HCl and NaOH solutions. The reactors were purged with N_2 to ensure anaerobic conditions.

Daily biogas production was measured using displacement of saturated NaCl solution (prevented the dissolution of biogas constituents) in inverted burettes and the bioreactors were subsequently mixed by gently agitation for 1 min. A 100 mL gas tight syringe was used for collecting and transferring biogas from the burettes to separate 1 L Tedlar bags, from which it was analysed. Experiments were terminated when the last reactor produced < 1% of the cumulative biogas volume for three consecutive days. After digestion, each reactor pH was measured and the digestate sampled for analyses of VS, TS, VFAs, COD, sulphide and total ammonia nitrogen (TAN) in order to determine process stability and efficiency. Equation 2 was used to calculate B_o in terms of %VS and %TS [16].

$$TS \text{ or } VS\ (\%) = \frac{(F+I) \times a - I \times b}{F} \times 100\% \tag{2}$$

where F is total TS or VS of sludge added to reactor (g); I is total TS or VS of inoculum added to reactor (g); a is the calculated TS or VS reduction of sludge plus inoculum based on total initial and final mass of TS or VS after AD (%); b is calculated TS or VS reduction from inoculum in blank controls (%) [17].

Modelling and Statistical Analysis

Design-Expert® Software allowed the fitting of linear and quadratic empirical models (Eqs. 8–12) containing known constants onto the experimental data using multiple regression analysis. The software performed multiple regression analysis including ANOVA at 95% confidence interval (CI) to evaluate the interactions between process variables and the responses. The fitted models only included significant terms ($p < 0.05$) except when maintenance of the hierarchal structure was required. Using the proposed best fitting model equation, optimisation analysis was performed to find combinations of process variables that would maximise CH_4 yield and B_o. Similarly, nonlinear regression using Microsoft Excel Software® was performed to fit known kinetic models (Eqs. 3–6) [18–20] onto the experimental cumulative methane yield data and to estimate the kinetic parameters.

Logistic

$$\boldsymbol{P} = \frac{\boldsymbol{A}}{\boldsymbol{1}+\boldsymbol{e}^{\left[\left(\frac{\boldsymbol{4}\boldsymbol{\mu}_{\boldsymbol{m}}}{\boldsymbol{A}}\right)(\boldsymbol{\lambda}-\boldsymbol{t})+\boldsymbol{2}\right]}} \tag{3}$$

Modified Gompertz

$$\boldsymbol{P} = \boldsymbol{A}\boldsymbol{e}^{\left[-\boldsymbol{e}^{\left(\frac{\boldsymbol{\mu}_{\boldsymbol{m}}\boldsymbol{e}}{\boldsymbol{A}}(\boldsymbol{\lambda}-\boldsymbol{t})+\boldsymbol{1}\right)}\right]} \tag{4}$$

Cone

$$P = \frac{A}{1 + (kt)^{-n}} \tag{5}$$

First order

$$P = A\left[1 - e^{(kt)}\right] \tag{6}$$

where P ($mLCH_4/gVS$) is the cumulative CH_4 yield at retention time t (day) over the AD period; A ($mLCH_4/gVS$) is the CH_4 potential of a substrate; μ_m ($mLCH_4/gVS/d$) is the maximum CH_4 production rate (specific microorganisms growing speed); K (day^{-1}) is the specific rate constant; λ (day) is the lag phase; n (dimension less) is the shape factor constant.

Selection of the best model fit was determined through the adjusted coefficient of determination (adj R^2), root mean square error (RMSE), Akaike's information criterion (AIC) and F Test at 95% CI. Pearson's correlation coefficient (r) was used to test for linear relationships between factors and/or responses and/or kinetics.

Results and Discussion

Characteristics of Inoculum and Secondary Tannery Sludge

The STNS and inoculum used in this study were comprehensively analysed and the results (Table 2) were interpreted to determine their potential for AD. The inoculum exhibited ideal characteristics except for high concentrations of $VFA_t > 1$ g/L AAE [15]. Such high concentrations of VFAs are known to inhibit microbes, particularly HPr which is

Table 2 Characteristics of the inoculum and secondary tannery used in this study

Parameter	Inoculum	STNS
pH	7.51	7.21
Density (g/L)	1.01	0.97
Alk (g/L $CaCO_3$)	9.85	2.38
TS (g/L)	98.4	179
TVS (g/L)	51.6	144
COD (g/L)	81.4	94.7
TOC (g/L)	7.88	6.23
TVOA/TVFA (g/L)	2.15	2.88
TN (g/L)	6.30	1.78
TP (mg/L)	395	74.1
Cl (g/L)	5.43	23.9
S_2t (mg/L)	7.01	11.0
SO_4 (mg/L)	580	1202
TAN (mg/L)	1185	262
Na (g/L)	0.56	6.36
Fe (mg/L)	475	241
Mg (mg/L)	77.4	183
Zn (mg/L)	67.4	4.34
K (mg/L)	53.1	21.3
Cd (µg/L)	< 0.005	< 0.005
Ni (mg/L)	2.46	0.62
Cr (mg/L)	261	145
Pb (mg/L)	0.63	0.22
VS:TS	0.52	0.80
C:N	6.20	5.75
VFA:Alk	0.22	1.21
$COD:SO_4$	140	78.8
C:N:P:S	39:31:2:1	15:4.3:0.2:1

reported as the most toxic to methanogens [21]. The methanogenic inhibitory rates are in the order HPr > HBu > HAc. Most metal concentrations of the inoculum and STNS fell within the optimal range except for Ni and Cd (below optimum), whereas Na, Fe, Zn, and Cr were above the optimum, and possibly inhibitory [3]. The inoculum contained high concentrations of alkalinity and phosphate (314 and 434% higher than the STNS), which were likely to mitigate the adverse effects caused by high STNS' VFA:Alkalinity ratio and lack of phosphate.

The STNS had a TS content (> 15 wt%/vol%) and an ideal VS:TS ratio (= 0.8), suitable for an efficient dry/solids AD and a high CH_4 yield [5]. The high $COD:SO_4$ ratios of the STNS (78.8) and inoculum (140) indicated the unlikelihood of sulphidogenesis superseding methanogenesis [22]. Conversely, it demonstrated low COD:VS and C:N, high VFA:Alkalinity and imbalanced C:N:P:S ratios (Table 2), likely to lead to NH_3 inhibition, significant reactor instability, low B_o and low CH_4 yields. Furthermore, the STNS total sulphide and TAN concentrations were likely to lead to inhibitory concentrations of H_2S and NH_3, depending on the reactor operating pH and temperature. Nonetheless, S/TNS with 'non-ideal' organic and inorganic characteristics were successfully digested in previous studies [3, 23–25].

Cumulative Methane Generation and Process Inhibition

The generated experimental design matrix (Table 3) shows the experimental reactor (R1–R13) operating conditions (temperature and pH_{in}), CH_4 yield and B_o results from the AD of STNS. The cumulative biogas and CH_4 yields were 25–303 mL/gVS and 12.5–176 mL/gVS, respectively, with a

Table 3 Experimental design matrix showing the CH_4 yield and biodegradability results for the mono anaerobic digestion of secondary tannery sludge

Reactor	Temperature (°C)	pH_{in}	Biogas yield (mL/gVS_{added})	CH_4 yield ($mLCH_4/gVS_{added}$)	Biogas quality ($\%CH_4$)	Biodegradability indicators (% reduction)		
						VS	TS	COD
R1	37	8.5	164	65.4	40	47.5	34.9	35.0
R2	31	7.0	124	62.0	50	52.3	37.5	30.2
R3	31	7.0	113	59.0	52	66.4	48.4	34.8
R4	23	7.0	26.2	13.0	50	25.4	14.2	35.2
R5	31	6.0	135	70.3	52	78.7	53.1	51.7
R6	25	8.5	30.3	12.7	42	32.0	21.3	22.7
R7	31	7.0	25.1	12.5	50	69.0	48.3	42.4
R8	40	7.0	303	176	58	47.5	30.1	44.6
R9	31	7.0	167	80.2	48	55.6	43.2	50.7
R10	25	6.5	72.5	38.4	53	67.5	3.6	47.6
R11	31	9.0	55.7	21.2	38	74.5	47.9	47.1
R12	31	7.0	187	95.4	51	56.0	45.3	51.2
R13	37	6.5	179	98.2	55	76.9	66.4	45.9

R reactor, *TS* total solids, *VS* volatile solids, *COD* chemical oxygen demand

biogas %CH_4 content range of 40–58% (Table 3). The reactors experienced lag phases of approximately 20–83 days (Fig. 1). There was severe discrete reversible inhibition of CH_4 generation in R2, R3, R4, R5, and R6 (for ≈60 days), R10 and R11 (for ≈80 days). The inhibition of CH_4 generation in these reactors was reversed 2–6 times during the 108 days of AD, with each inhibition phase lasting between 3 and 52 days. The cumulative CH_4 generation in R2, R3, R4, R5, and R10 exhibited short exponential rises over the first 5 days followed by discrete stationary phases, whereas R6 and R11 initially experienced lag phases for about 20 and 70 days, respectively (Fig. 1). The rest of the reactors experienced relatively shorter reversible inhibition periods (≈20–44 days), as they operated at 31–40 °C and at a neutral pH_{in} of 6.5 or 7. However, R1 operating at an inhibitory pH_{in} 8.5 and 37 °C underwent 64 days of inhibition.

The results suggested that the low reactor operating temperatures of below 31 °C and/or non-neutral pH_{in} (not in the range of 6.5–7.0) acted as the primary inhibitors as they reduced microbial growth and activity (Table 1). Theoretically, slow microbial activity and low reaction rates in R4 (22.5 °C), R6 (25 °C), and R10 (25 °C) led to the low gas yields and solids reduction efficiencies (Table 3). However, R10 with a pH_{in} (=6.5) achieved a higher CH_4 yield (200%) than R6, as the latter operated at an above optimal pH_{in} (=8.5) for most microbes (Table 1). The final reactor pH was near neutral with a range of 0.66 (7.0–7.66) regardless of the pH_{in}. Similar observations were reported by [12, 13, 26]. This minimised the inhibitory NH_3 (Eq. 1) and H_2S concentrations and negated the influence of pH_{in} in AD. It was hypothesised that the high initial TAN (≈807 mg/L) and alkalinity concentrations (≈9.85 g/L $CaCO_3$) controlled the reactor pH and must have maintained it near neutral [12].

Theoretically, at digester pH < 7.0, almost all the TAN should be present as NH_4^+, thereby increasing pH by releasing hydroxyl ions (OH^-). Conversely, at pH > 6.5 pH should be reduced due to the release of hydrogen ions (H^+) from higher concentrations of FAN. Similarly, at 4 < pH < 13 CO_2 should be present in both molecular and ionic forms (CO_2–HCO_3^-–CO_3^{2-}) with pH reduction via H^+ release (Eq. 7). However, the high H_2 partial pressures (> 10^{-4} atm) are known for inhibiting HPr, HBu and ethanol (EtOH) degrading acetogens. Thus, it was concluded that the positive effect of temperature (within the range applied in this study) on methane yields, surpassed its adverse effect in promoting dissociation of toxicants (H_2S, NH_3, and H_2) and precipitation of metals, particularly Ni and Cd (reduced bioavailability) [7]. reported the doubling of rate constant (methanogenesis) due to a 10 °C temperature increase overshadowed the inhibition effects of increased NH_3 concentration (from 100 to 250 mg/L). Nonetheless, many authors have reported that the effect of temperature increase during AD does not follow the Arrhenius principle [27–29].

Although the final reactor concentrations of FAN (8.9–42 mg/L) and H_2S (6.0–11 mg/L) were slightly below the inhibitory range (53–1450 mg/L NH_3 and H_2S IC_{50} = 14–125 mg/L), the observed reversible inhibitions were possibly caused by intermittent inhibitory concentrations reached during the RT and the adaptability of the microorganisms. The concentrations of NH_3 and VFAs may have possibly reached inhibitory levels due to increased formation from protein hydrolysis, and acidogenesis, respectively vs rate limiting methanogenesis. Similarly, metal concentrations (Na, Fe, Zn, and Cr) may have fallen within the inhibitory range, particularly for reactors operating at lower temperatures and pH conditions that promoted metal bioavailability. The sub-optimal concentrations of Ni and Cd were hypothesised to have limited microbial growth and activity. Ni has been reported to promote the dominance of NH_3 resilient *Methanosarcina* methanogens [30]. Nonetheless, mesophilic reactors have highly diverse and complex methanogenic communities, which enhance their

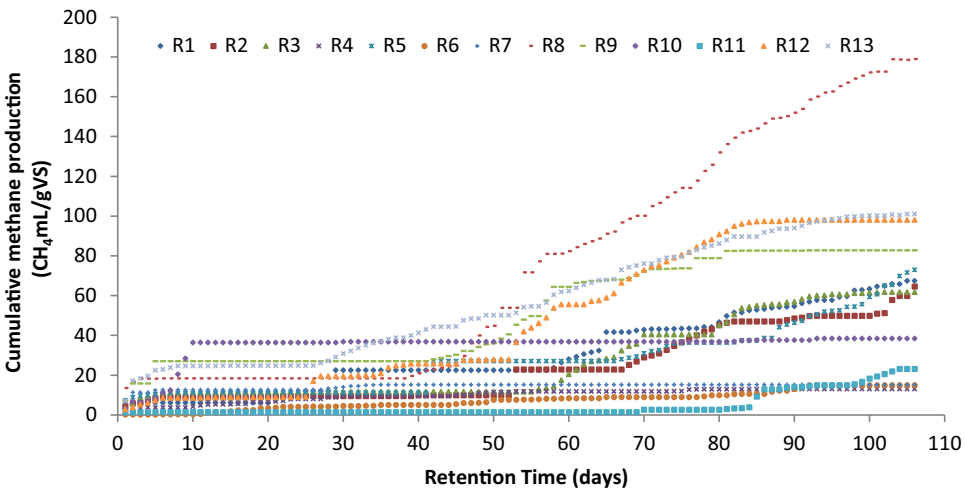

Fig. 1 Cumulative methane yields of reactors operating at different temperatures and initial pH

adaptability, inhibition resistance, and resilience, leading to their operation at inhibited steady state conditions [8, 9].

It was postulated that the presence of micro-niches at the bottom of the reactor strata may have protected microbes against high levels of inhibitory substances in the bulk of the reactor. Sedimentation in the reactors may have provided closer microbial consortia proximity (juxtapositioning), essential in syntrophic microorganisms such as syntrophic acetate oxidising bacteria (SAOB) and hydrogenotrophic methanogens (HMs) [31]. Furthermore, microbes may have protected themselves against high metal concentrations through excretion of soluble microbial products (SMPs) and extracellular polymeric substances (EPS) [23–25].

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \quad (7)$$

Optimisation of Cumulative Methane Yield, and Anaerobic Biodegradability

A general quadratic polynomial with up to second-degree interaction terms, and linear equations were used to model B_o (%VS and %TS reduction) and experimental gas (biogas/CH_4) yields, respectively (Fig. 2). The fraction design space (FDS) (0.95) and the adequate precision (8.52–10.8) (Table 4) of the models (except %COD reduction) were > 0.8 and > 4 respectively, as desired (Stat-Ease, Inc., Minneapolis, USA). The fitted models (besides COD) were significant ($p < 0.05$) and there was only 0.14–2.7% chance that the relationship between the response and the terms might have existed due to noise (Table 3). The models (Table 3) had an insignificant lack of fit (LOF $p > 0.05$) except for %TS reduction, R^2 (0.72–0.80) and adj R^2 (0.63–0.68) suggesting moderate to good predictability of the actual gas yields and B_o (%VS, and %TS). Nevertheless, the adeq prec of the %TS reduction model was desirable (desirability > 4), with an $R^2 = 0.78$ and an adj $R^2 = 0.63$ (Table 3) proving that it could be used to predict the %TS reduction. Although all the B_o indicators had negative predicted R^2 values that suggested that the overall mean might have been a better predictor, the models (Eq. 8–11) in terms of actual factors were used to navigate the design space and to optimise the cumulative biogas and CH_4 yield, %VS, and %TS (Fig. 2). The suggested %COD reduction model (Eq. 12) and its terms were not significant ($p > 0.05$) and indicated (i) a lack of relationship between the response and the terms, and (ii) lack of effect of the terms on the response. Although the LOF was insignificant ($p > 0.05$), the model did not fit the experimental data as indicated by the low R^2 ($= 0.259$), adj R^2 ($= 0.111$), pred R^2 ($= -0.426$) and adeq prec (< 4) (Table 3) and could not be used to navigate the design space (Fig. 2). There was 22.1% probability that the lack of relationship between %COD reduction and the investigated factors may have been caused by experimental error and the promotion of solids degradation in all the reactors by operating at a long retention time.

The results of the F test suggested that temperature was the only significant factor ($p < 0.05$) for gas yields (biogas and CH_4) and %TS reduction, whereas both temperature, and pH_{in} affected %VS reduction (Eq. 8–11). The effect of pH_{in} was only on %VS reduction as the distribution of ionised and unionised (volatiles) species is directly affected by pH level. However, in some cases, temperature and pH_{in} were slightly over the significance level with $p = 0.069$ for temperature on %VS reduction, $p = 0.077$ and $p = 0.057$ for pH_{in} on CH_4 yield and %TS reduction, respectively. Nonetheless, these factors had a weak effect on the responses and were included in the models.

$$\text{Biogas yield} = 13.1(\text{temp}) - 24.2\left(\text{pH}_{\text{in}}\right) - 109 \quad (8)$$

$$CH_4 \text{ yield} = 7.48(\text{temp}) - 17.6\left(\text{pH}_{\text{in}}\right) - 44.1 \quad (9)$$

$$\%\text{VS}_{red} = 13.4\left(\text{pH}_{\text{in}}^2\right) - 0.279\left(\text{temp}^2\right) - 0.002\left(\text{temp} \times \text{pH}_{\text{in}}\right) - 211\left(\text{pH}_{\text{in}}\right) + 18.6(\text{temp}) + 570 \quad (10)$$

$$\%TS_{\text{reduction}} = 7.10\left(\text{pH}_{\text{in}}^2\right) - 0.26\left(\text{temp}^2\right) - 0.587\left(\text{temp} \times \text{pH}_{\text{in}}\right) - 95.4\left(\text{pH}_{\text{in}}\right) + 21.9(\text{temp}) + 64 \quad (11)$$

$$\%COD_{\text{reduction}} = 0.486(\text{temp}) - 4.52(\text{pH}_{\text{in}}) + 59.1 \quad (12)$$

The ANOVA results indicated that there was a significant ($p < 0.05$) variation in the outcomes (gas yields and B_o) of the reactors. However, ANOVA in B_o was statistically insignificant ($p > 0.05$), indicating that the performance of individual reactors in reducing TS and/or VS and/or COD were relatively similar. This confirmed the observed negative pred R^2 values that suggested that their overall means were better estimators than the chosen models. Conversely, ANOVA in gas yields indicated a significant variation ($p < 0.05$) and as expected, high gas yields were achieved at 37–40 °C, with optimal yields at 40 °C (R8). Therefore, during operation the optimum conditions and retention time will have to be determined depending on whether solids reduction and/or biogas yield is prioritised. Operating conditions that would favour lower retention time would be selected if solids reduction was prioritised. Nonetheless, the specific optimal conditions that favoured both maximum gas yields and B_o had to be identified. As expected the AD of STNS achieved optimal performance ($p > 0.05$) with a desirability of 0.73–0.75 at temperatures ($= 35.5$–37 °C) and pH_{in} ($= 6.5$–6.6). These conditions favour the activity of most acetogens and methanogens (Table 1) and are comparable to the results reported by [13, 32].

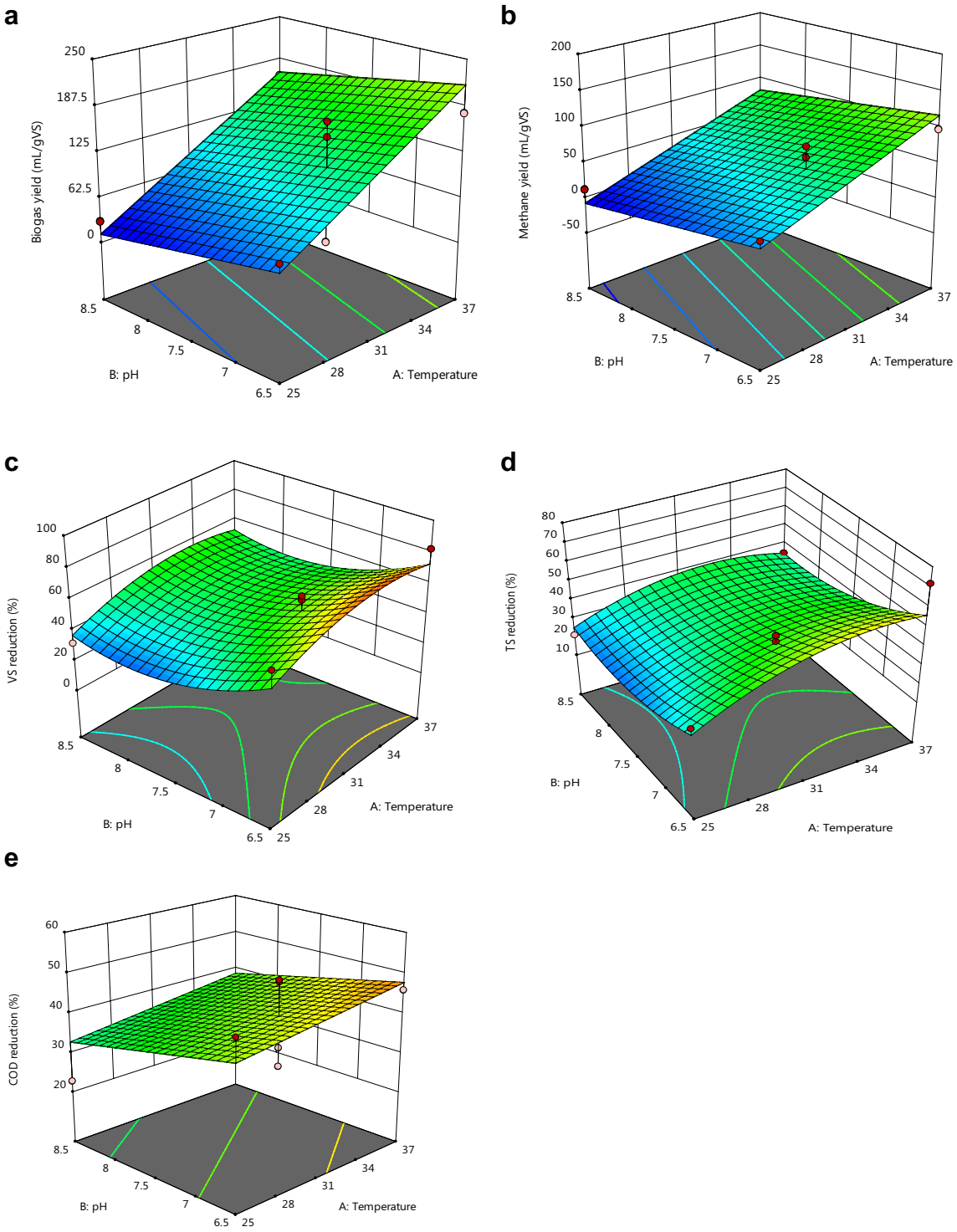

Fig. 2 Effect of temperature and pH_{in} on **a** biogas yield; **b** cumulative methane yield; **c** volatile solids reduction; **d** total solids reduction; and **e** COD reduction during anaerobic digestion of tannery sludge

According to the model predictions, operating at these conditions would result in biogas yields and CH_4 yield of about 200–217 (≈55% CH_4 content) and 108–118 mLCH_4/gVS, respectively, and B_o of 69.1–74.5% (VS), 53.7–57.3% (TS) and 47.1–47.7% (COD). These results are in agreement with those reported by [23] who achieved 89 mL/gVS (50% CH_4) although with lower %VS and %TS reduction (12–20% and 10–16%, respectively), [24] who

Table 4 Summary of the statistical results of the fitted models on anaerobic mono digestion

Models	Std dev	p value	F test (LOF) p value	R^2	Adj R^2	Pred R^2	Adeq Prec	AIC
Biogas linear	46.9	0.0017	0.93	0.72	0.66	0.58	10.3	142
CH_4 linear	26.8	0.0014	0.73	0.73	0.68	0.54	10.8	128
VS quadratic	10.1	0.0087	0.15	0.80	0.66	−0.08	9.23	115
TS quadratic	8.90	0.027	0.04	0.78	0.63	−0.18	8.52	112
COD linear	8.56	0.223	0.66	0.26	0.11	−0.43	3.62	98.0

Pred predicted, *Std dev* standard deviation, *TS* total solids reduction, *LOF* lack of fit, *AdeqPrec* adequate precision, *VS* volatile solids reduction, *Adj* adjusted, *AIC* Akaike's information criterion, *COD* chemical oxygen demand

achieved 50% VS reduction and the 55–70% CH_4 content reported by [25], besides the STNS' high concentrations of potential inhibitors. However, in the study by [24, 25] higher CH_4 yields of 216 mL/gVS and 617 mL/gVSS were reported, respectively. Therefore, the success of this study was hypothesised to have been due to the biological and physicochemical suitability of the inoculum and STNS. Theoretically, these process conditions supported the growth and activity of HPr and HBu degrading acetogens, resilient hydrogenotrophic methanogens, and the versatile *Methanosarcina* archaea (Table 1).

In terms of application, the results suggested that no pH correction measures are required and that energy requirements for heating could be reduced by operating the AD system at lower temperatures, which could be achieved under ambient conditions in some temperate regions. Generally, temperature fluctuations should not exceed ± 3 °C as this could result in significant reduced biogas production [25]. However, temperature fluctuations of up to 10 °C were reported to have caused an insignificant change in the reactor performance and microbial activity due to their acclimation particularly methanogens that are most sensitive [8, 12]. Furthermore, the long retention time is not economically as it will need to be compensated with a large reactor size (effective volume).

Correlative Analysis of Variables on Methane Yield and Anaerobic Biodegradability

Temperature had a strong positive linear relationship with biogas (r = 0.81) and CH_4 (r = 0.79) yield (Fig. 2), a moderate relationship with %TS reduction (r = 0.49), and a weak linear relationship (r = 0.27, r = 0.35 and r = 0.21) with %COD and %VS reduction and biogas $\%CH_4$, respectively. A number of authors have reported contradictory results on the relationship between temperature and gas yields or B_o or $\%CH_4$ during the anaerobic treatment of nitrogenous substrates. A study by [33] reported an insignificant increase in average $\%CH_4$ when temperature was decreased, whereas [12, 26] reported an increase with temperature and [11] reported no change. Temperature had nonlinear relationships with B_o and gas yields [8, 12, 32], whereas [34] reported a linear relationship. Conversely, weak negative linear relationships (r = − 0.26 to 0.43) existed between pH_{in} and the responses as its effect were negated due to the optimal reactor VFA:Alk ratios (< 0.4). These results are in accordance to the hypothesis testing for the statistical significance of variables on the responses ("Optimisation of Cumulative Methane Yield, and Anaerobic Biodegradability" section). Theoretically, dominance of inhibitory levels of H_2S (at pH < 8) and NH_3 (at pH > 8) was reduced through the stabilisation of the reactor pH at around 7.0–7.7. These pH conditions hypothetically reduced the availability of NH_3 (< 10%) and H_2S < 50% [5]. A strong negative correlation (r = − 0.89) existed with $\%CH_4$, as higher pH_{in} (in R1, R6 and R11) would theoretically have achieved NH_3 concentrations that reduced the CH_4 quality whereas low pH_{in} (in R2, R3, and R5) would theoretically have promoted sulphide (11 mg/L) dissociation, through the formation of H_2S. These results suggest that NH_3 had a greater impact than H_2S on $\%CH_4$ and CH_4 yield. The ANOVA showed that there was an insignificant variation (p > 0.05) in $\%CH_4$ quality of the reactors. Nevertheless, correlations involving pH_{in} were invalid due to its stabilisation at near neutral levels (pH 7.0–7.66).

Biogas $\%CH_4$ quality exhibited weak negative linear relationships with lag phase (r = − 0.39), and with the number of times that inhibition was reversed (r = − 0.32), as was expected. The final reactor pH showed a moderate positive correlation with temperature (r = 0.51) and with CH_4 yield (r = 0.52), a weak positive correlation with lag phase (r = 0.35) and no correlation with $\%CH_4$ (r = 0.01) and the number of times that inhibition was reversed (r = 0.28). As expected, moderate to strong positive linear relationships were established between %TS and %COD reduction (r = 0.55), %VS and %COD (r = 0.83) and %VS and %TS (r = 0.63). However, there was a weak positive linear relationships existed between gas yields and B_o (r = 0.11–0.38).

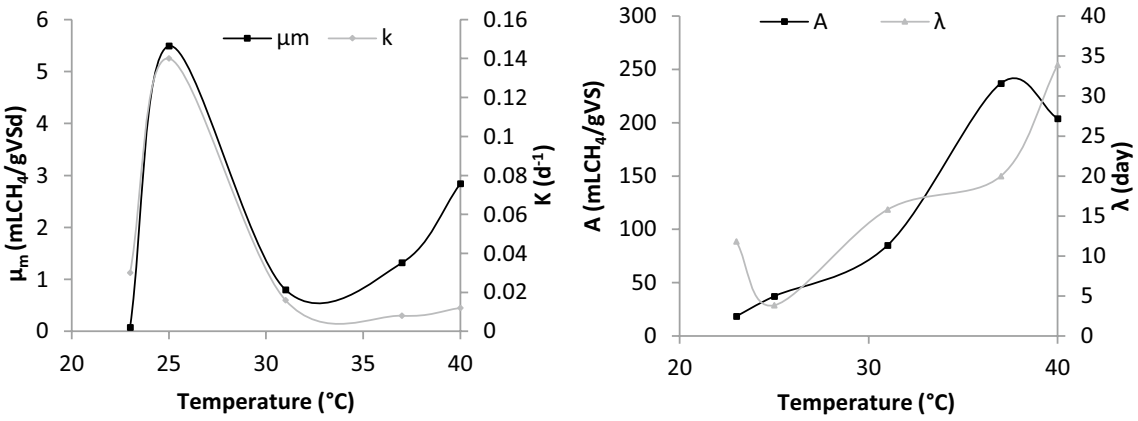

Fig. 3 Correlation between kinetic parameters with temperature for reactors operating at near/neutral (pH_{in} 6.5–7.0)

Kinetic Studies on the Anaerobic Digestion of Secondary Tannery Sludge

The anaerobic digestion kinetics of the reactors were determined by fitting the Cone, modified Gompertz, Logistic and first order models (Eq. 3–6) onto the cumulative CH_4 yields (Fig. 3). Statistical parameters (Table 5) showed that the latter was the worst performer in predicting the cumulative CH_4 yields of most reactors except for R6 (Adj $R^2 = 0.912$) and R13 (Adj $R^2 = 0.959$) where the model performed better than the modified Gompertz and Cone model, respectively. The first order model's statistical parameters had an insignificant variation ($p > 0.05$) when compared to other models simulating reactors with short lag phases. However, the exponential rise to a maximum curve portrayed by the first order model did not accurately fit the data for R8 (Adj $R^2 = 0.788$) and R11 (Adj $R^2 = 0.437$) due to their long lag phases of 34 and 69 days, respectively. The rest of the models fairly fitted ($p < 0.05$) the cumulative CH_4 yields of other reactors ($0.828 \leq$ Adj $R^2 \leq 0.986$) with high accuracy possibly owing to their sigmoidal shape curves which describe the lag, exponential and stationary phases. The modified Gompertz model significantly underestimated the ultimate cumulative CH_4 yield (A), and yielded the lowest kinetic values for maximum microbial specific growth rate (μ_m) and highest for the lag phase (λ). The Cone (Adj $R^2 = 0.83$–0.981) and Logistic (Adj $R^2 = 0.828$–0.985) models gave better estimations of the kinetic constants.

The kinetic constants obtained in this study: A, μ_m, and K were 18.4–237 $mLCH_4/gVS$, 0.08–5.49 $mLCH_4/gVSd$, and 0.008–0.14 day^{-1}, respectively. These results are comparable to those reported by [35] for μ_m (2.04–5.48 $mLCH_4/gVSd$) and K (0.0185–0.0239 day^{-1}) by [36, 37] during the co-digestion of tannery sludge and other tannery solid wastes. The influence of pH_{in} and temperature on the process kinetics was determined through the analysis of reactors operating at the same pH_{in} but different temperature or same temperature but different pH_{in}. The highest K and μ_m were found in reactors R10 and RC (R2; R3; R7; R9 and R12) operating at lower temperatures of 25 °C and 31 °C and pH_{in} of 6.5 and 7, respectively. An increase in temperature for reactors operating at constant pH_{in} led to a significant ($p < 0.05$) increase in A and μ_m, and an insignificant decrease ($p > 0.05$) in K. In contrast, a significant decrease of 316% in μ_m was observed at optimum pH_{in} (= 6.5) with an increase in temperature from 25 to 37 °C. These results did not display an Arrhenius relationship, as a 10 °C increase in temperature resulted in decreased reaction rates of about 15–1650%. However, a plot of the AD kinetics (K and μ_m) versus temperature (Fig. 3) for reactors operating at near/neutral pH_{in} (6.5 ± 0.5) showed that temperature increases from 23 to 25 °C, 25–31 °C and 31–40 °C led to an increase, decrease and increase in the kinetics, respectively. Authors [28, 29] observed similar trends in K whilst treating macroalgae and vegetable waste at 25–45 °C and 16–44 °C, respectively. However, A increased from 23 to 37 °C and decreased from 37 to 40 °C (Fig. 3).

Similarly, a decrease in A, μ_m and K was observed when pH_{in} increased beyond neutral ($6.5 + 0.5$) from 6.5 to 8.5 and from 7.0 to 9.0 regardless of operating temperature. Work by [38] reported a similar trend for μ_m of methanogens whilst investigating a pH range of 7.0–9.5. Inconsistency was also observed at the optimum temperature (= 37 °C) in which K increased by 63% with an increase in pH_{in} from 6.5 to 8.5. Furthermore, an increase in A, μ_m and K was observed when pH_{in} increased across optimum pH_{in} (= 6.5) from pH_{in} 6.0 (R5) to pH_{in} 7.0 (RC) whilst operating at 31 °C. A plot (Fig. 4) of the kinetics (A, μ_m and K) versus pH_{in} (6; 7 and 9) at 31 °C showed that kinetics were maximum at optimum pH_{in} (~ 6.5–7.0) as was observed by [39] for K (= 0.0633–0.0726 day^{-1}) during AD of food waste. The differences in μ_m and K values had an insignificant variation ($p > 0.05$). Overall, the relationship between kinetics and process parameters was non-monotonic and application

Table 5 Kinetic parameters and goodness of fit obtained from evaluated models

Reactor	Model	Kinetic parameters					Statistical measures			
(°C/pH_{in})		*A	**μ_m	ʎ (d)	K	n	Adj R^2	p value Prob > F	AIC	RMSE
R1 (37/8.5)	Gompertz	61.9	0.30	98.2	ND	ND	0.973	0.43	564	3.25
	Logistic	92.7	0.82	21.8	ND	ND	0.972	0.44	565	3.27
	Cone	93.0	ND	ND	0.013	2.06	0.943	0.36	645	4.75
	First order	92.8	ND	ND	0.010	ND	0.883	0.01	719	6.70
R2; R3; R7; R9 and R12 (31/7)	Logistic	85.0	0.80	15.8	ND	ND	0.966	0.46	583	3.55
	Gompertz	58.9	0.28	92.0	ND	ND	0.957	0.48	609	4.02
	Cone	78.3	ND	ND	0.016	2.51	0.894	0.16	707	6.35
	First order	90.0	ND	ND	0.010	ND	0.855	0.03	739	7.37
R4 (23/7)	Gompertz	4.85	0.08	11.8	ND	ND	0.982	0.44	125	0.42
	Cone	18.4	ND	ND	0.030	0.88	0.981	0.49	134	0.44
	First order	13.3	ND	ND	0.036	ND	0.973	0.29	162	0.50
	Logistic	12.5	0.30	0.00	ND	ND	0.935	0.18	254	0.77
R5 (31/6)	Gompertz	75.2	0.30	123	ND	ND	0.930	0.45	635	4.53
	Cone	76.4	ND	ND	0.014	2.17	0.830	0.37	730	7.07
	Logistic	75.0	0.96	38.1	ND	ND	0.828	0.09	730	7.08
	First order	75.7	ND	ND	0.009	ND	0.782	0.01	757	8.01
R6 (25/8.5)	Logistic	21.2	0.17	15.4	ND	ND	0.954	0.33	298	0.94
	Cone	20.0	ND	ND	0.015	1.77	0.937	0.44	335	1.11
	First order	20.4	ND	ND	0.010	ND	0.912	0.02	369	1.31
	Gompertz	4.31	0.042	10.0	ND	ND	0.683	5.5E−12	508	2.50
R8 (40/7)	Logistic	204	2.84	33.9	ND	ND	0.985	0.43	734	7.21
	Gompertz	105	0.94	71.3	ND	ND	0.978	0.38	772	8.61
	Cone	273	ND	ND	0.012	2.88	0.976	0.29	784	9.09
	First order	250	ND	ND	0.008	ND	0.788	5.3E−05	1016	26.9
R10 (25/6.5)	Logistic	37.2	5.49	3.83	ND	ND	0.968	0.33	352	1.21
	Cone	37.2	ND	ND	0.14	4.99	0.959	0.16	397	1.49
	Gompertz	13.7	2.12	6.16	ND	ND	0.958	0.23	399	1.50
	First order	37.6	ND	ND	0.13	ND	0.849	0.03	517	2.61
R11 (31/9)	Logistic	28.2	0.79	75.3	ND	ND	0.943	0.311	401	1.52
	Cone	29.7	ND	ND	0.011	9.81	0.942	0.285	404	1.54
	Gompertz	13.6	0.27	92.5	ND	ND	0.940	0.276	407	1.56
	First order	38.0	ND	ND	0.003	ND	0.437	8.2E−14	648	4.81
R13 (37/6.5)	Gompertz	68.0	0.374	65.1	ND	ND	0.986	0.50	570	3.34
	Logistic	237	1.32	20.0	ND	ND	0.973	0.43	644	4.72
	First order	293	ND	ND	0.004	ND	0.959	0.30	686	5.75
	Cone	276	ND	ND	0.008	1.14	0.953	0.28	701	6.17

Adj adjusted, *RMSE* root mean square error, *AIC* Akaike's information criterion, *ND* no data

*mlCH_4/gVS, **mLCH_4/gVSd

of Pearson's correlations (r) showed that there was no significant linear correlation between kinetics and with pH_{in} or temperature, except for A with temperature (r = 0.838) and K with μ_m (r = 0.836) as observed by [27]. Nonetheless, A, μ_m and K were highest and/or lowest at pH_{in} (= 6.5) and temperature (= 37 °C) as these are optimum conditions for various acetogenic and methanogenetic bacteria (Table 1). These results suggested that lower K signify efficient AD as observed in natural AD sites such as ponds, wetlands, swamps, landfills and lagoons that steadily operate under slow reaction rates [27]. Such reactor systems cater for the large reactor volumes necessitated by the long retention times (20–180 days) which promote solids degradation and maximum biogas yield [25, 36, 40]. Therefore the optimum reactor (R13) operated under an inhibited steady state condition characterised by the five discrete lag phases caused by instantaneous inhibitory levels of NH_3, H_2S and VFAs.

Process disturbances are generally caused by imbalances between metabolic rates of acidogenesis and methanogenesis and/or sulphidogenesis leading to accumulation of inhibitory

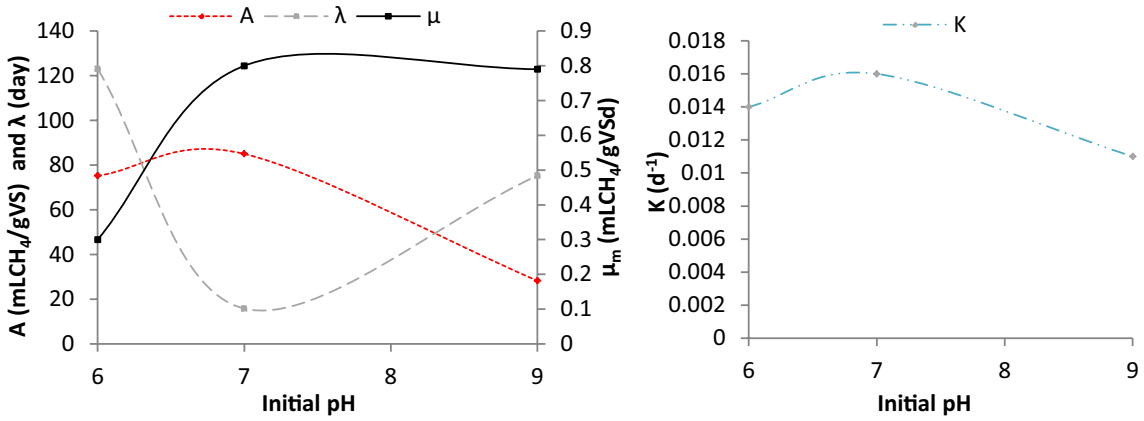

Fig. 4 Correlation between kinetic parameters with pH_{in} for reactors operating at 31 °C

substances such as VFAs, and/or NH_3, and/or H_2S. Thus, studying the relationship between K and μ_m was paramount in understanding the balance between hydrolysis and methanogenesis [27]. The units of μ_m were converted to day^{-1} using the relationship that 1 gCOD produces 350 $mLCH_4$ and the substrates' gCOD/gVS ratio of 0.66 (Table 2). The K/μ_m ratio was ≥ 1.0 in all reactors, demonstrating a balance between hydrolysis and methanogenesis rate in R8 (pH_{in} 7.0 and 40 °C) and strongly suggesting that methanogenesis was the rate limiting step for the rest of the reactors. The ratio K/μ_m decreased with increasing temperature regardless of pH_{in} ($r = -0.63$), whilst it showed a nonlinear decreasing trend with an increase pH_{in} when operating at constant a temperature. Thus, the closer the reactors were operated to optimum conditions, the better the balance between methanogenesis and hydrolysis leading to high CH_4 yields (A).

Conclusion

This study demonstrated the feasibility of operating an ambient anaerobic batch reactor for the purpose of reducing the amount of sludge, at varying pH_{in} (6.0–9.0) and minimal mixing (1 min day^{-1}) suitable for tanneries in the developing world with temperate climates. Such a system will provide a low cost solids reduction alternative as it eliminates the heating energy, pH correction and mixing costs. If the recovery of biogas/methane is also desired (maximum A) the reactor must be operated at optimum conditions (35.5–37 °C and pH_{in} 6.5–6.6). At optimum/near optimum conditions the kinetics (k and k/μ') were minimal suggesting that the reactors operated at an inhibited steady state condition, with methanogenesis balanced/closely balanced ($K/\mu_m \sim 1.0$) with hydrolysis rate. Nonetheless, nonlinear correlations mainly existed between process parameters, kinetics, and performance indicators except for correlations involving gas yields or A with temperature; K with μ_m; and pH_{in} with $\%CH_4$/VS.

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