

# Biomethanation of tannery sludge: Optimisation of initial pH and temperature and evaluation of kinetics

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# 1. INTRODUCTION AND BACKGROUND

- Global trade value of ~US\$100 billion per year
- Potentially a major environmental polluter, discharges ~27-57m<sup>3</sup> of effluent and ~700kg solids (~500kg sludge) laden with toxic metal salts, organics, and inorganic substances for every tonne (Buljan & Král, 2015)
- Treatment and landfill disposal of tannery sludge accounts for 30-40% of capital cost and ~60% of the total cost of a TWWTP (Akyol et al., 2014)
- Inefficiency of versatile activated sludge process (ASP) + physico-chemical methods in sludge reduction ~20% (Buljan & Kral, 2011)
- AD is limited due to inhibition by ammonia (low C:N) and sulfide (inhibitory species are a function of pH and temperature) and partly due to perception on the related capital, process, and maintenance costs

# 1. INTRODUCTION AND BACKGROUND

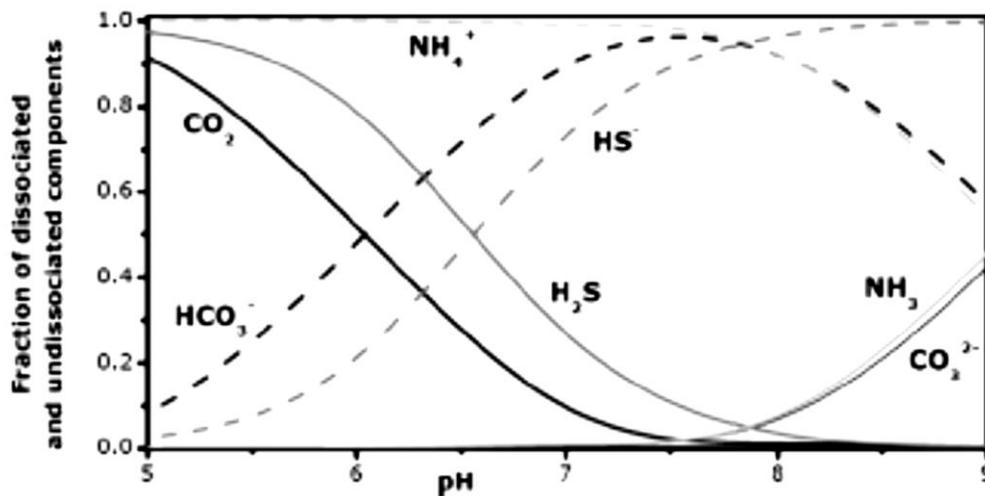


Figure 1: Fraction of dissociated and un-dissociated ammonia, hydrogen sulphide and carbon dioxide depending on the pH value

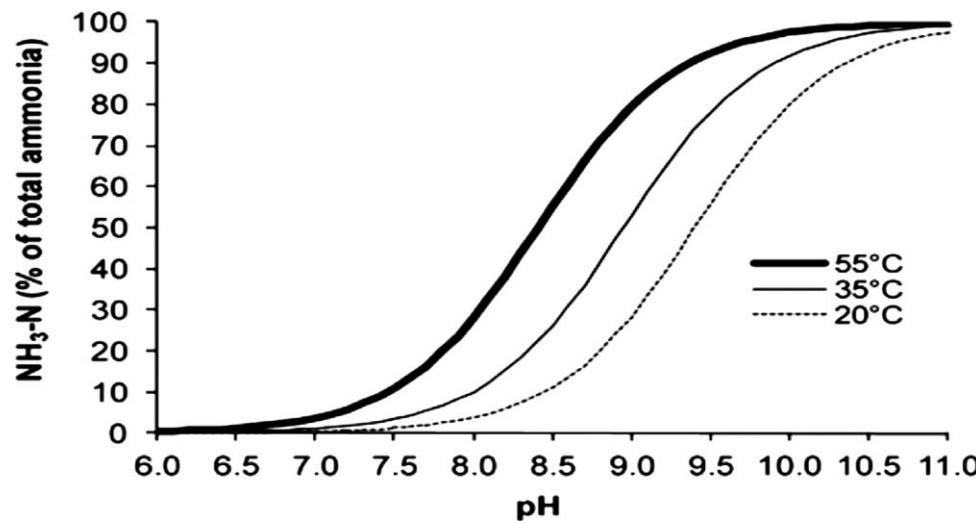


Figure 2: Ammonia-ammonium nitrogen equilibrium behaviour with pH and temperature (Zhang et al., 2014)

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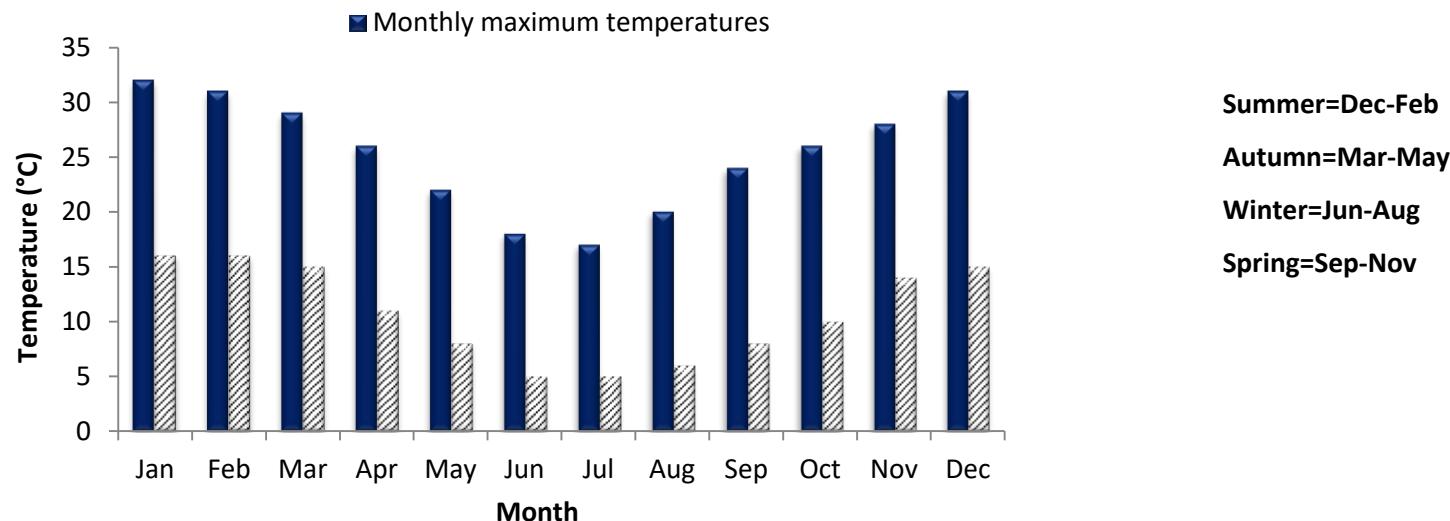


Figure 3: Monthly maximum and minimum temperatures over the sampling period (adapted from [www.weather-and-climate.com](http://www.weather-and-climate.com))

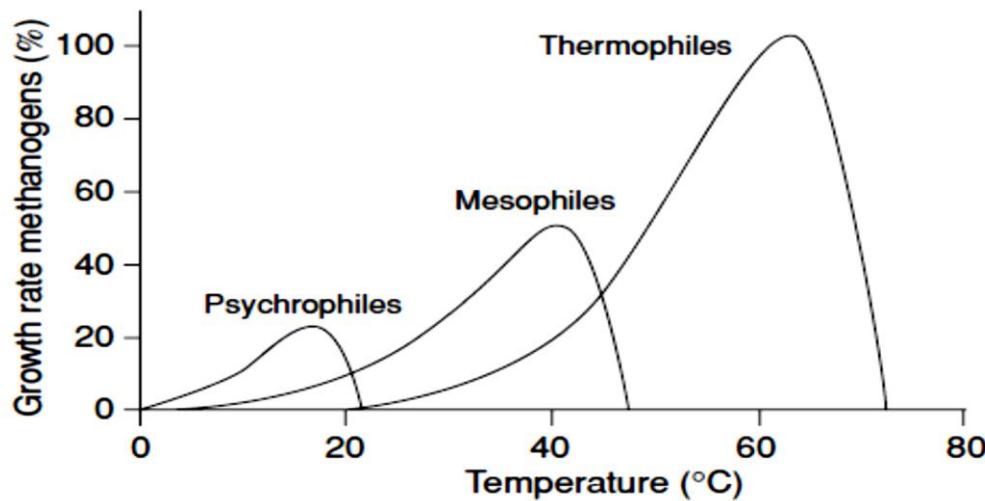


Figure 4: Effect of Temperature on growth rate of methanogens (Lettinga et al., 2001)



**Table 1: Optimum temperature and pH conditions for some acetogenic and methanogenic bacteria adapted from [3,14]**

Substrate	Product	Typical species	Temperature °C	pH
<b>Acetogenic bacteria</b>				
H <sub>2</sub> /CO <sub>2</sub>	HAc	<i>Clostridium aceticum</i>	30–37	NG
HPr	H <sub>2</sub> /CO <sub>2</sub> , HCO <sub>2</sub>	<i>Syntrophomonas wolfei</i>	35–40	NG
		<i>P. schinkii</i>	32–37	NG
HBu	HBu, HAc	<i>Smithella propionica</i>	35–40	NG
	HAc	<i>Syntrophobacter wolinii</i>	35–40	NG
	H <sub>2</sub> /CO <sub>2</sub> , HCO <sub>2</sub>	<i>S. fumaroxidans</i>	35–40	NG
<b>Methanogenic bacteria</b>				
HCO <sub>2</sub> , H <sub>2</sub> /CO <sub>2</sub>	CH <sub>4</sub> , CO <sub>2</sub>	<i>Methanocorpusculum</i>	35–37	NG
		<i>Methanoplanus limicola</i>	40	7.0
		<i>M. ruminantium</i>	37–39	7.0
		<i>M. maripaludis</i>	35–40	6.5–8.0
		<i>Methanobrevibacter smithii</i>	37–39	7.0
		<i>M. deltae</i>	37	NG
		<i>M. marisnigri</i>	20–25	6.8–7.3
		<i>Methanogenium cariaci</i>	20–25	6.2–6.6
		<i>Methanobacterium formicicum</i>	37–45	6.6–7.8
		<i>Methanococcus voltae</i>	35–40	6.5–8.0
		<i>M. bourgense</i>	35–42	6.3–6.8
		<i>M. tatii</i>	37–40	7.0
		<i>M. olentangyi</i>	37	NG
		<i>Methanomicrobium mobile</i>	40	6.1–6.9
H <sub>2</sub> /CO <sub>2</sub>	CH <sub>4</sub>	<i>Methanolacinia paynteri</i>	40	6.6–7.2
		<i>Methanoplanus endosymbiosus</i>	40	6.6–7.2
		<i>Methanobrevibacter arboriphilus</i>	30–37	7.8–8.0
		<i>M. olentangyi</i>	30–40	NG
		<i>Methanobacterium bryantii</i>	37–39	6.9–7.2
		<i>Methanospirillum hungatei</i>	30–37	NG
		<i>M. alcaliphilum</i>	37	8.1–9.1
HAc	CH <sub>4</sub> /CO <sub>2</sub>	<i>Methanosarcina acetivorans</i>	35–40	6.5–7.5
		<i>Methanosaeta concilii</i>	35–40	7.1–7.5
		<i>Methanotherrix soehngenii</i>	35–40	7.4–7.8
HAc, CH <sub>3</sub> OH CH <sub>5</sub> N	CH <sub>4</sub> /CO <sub>2</sub>	<i>Methanosarcina mazeii</i>	30–40	6.0–7.0
		<i>Methanosarcina barkeri</i>	35–40	5.0–7.0



## 2. AIM

- Optimise and determine the kinetics of AD of STNS at different temperatures (23-40° C) and pH<sub>in</sub> (6.0-9.0).

## 3. OBJECTIVES

- Sample STNS from a TWWTP in South Africa and inoculum
- Characterise the STNS and inoculum (solids, organic and inorganic substances)
- Perform AD optimisation experiments (standard biomethane potential tests) using RSM (Design-Expert® Software Version 11)
- Determine the optimum methane yield (mLCH<sub>4</sub>/gVS) and Bo (%COD, %TS & %VS reduction efficiency) of the STNS during AD
- Application of known kinetic models to determine the AD kinetics and correlate them with process conditions (pH<sub>in</sub> and temperature)



# 5. RESULTS AND DISCUSSION

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 <sub>3</sub> )	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 <sub>2</sub> t (mg/L)	7.01	11.0
SO <sub>4</sub> (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
Ni (mg/L)	2.46	0.62
Cr (mg/L)	261	145
Pb (mg/L)	0.63	0.22



# 5. RESULTS AND DISCUSSION

Table 3: Inoculum and secondary tannery sludge biodegradability indicators

Parameter	Inoculum	Secondary tannery sludge	Optimal
VS:TS	0.52	0.80	>0.8
C:N	6.20	5.75	20-30
VFA:Alk	0.22	1.21	<0.3-0.4
COD:SO <sub>4</sub>	140	78.8	>1-10
C:N:P:S	39:31:2:1	15:4.3:0.2:1	500-600:15:5:1

NG=Not given

# 5. RESULTS AND DISCUSSION

Table 4: Experimental design matrix showing the CH<sub>4</sub> yield and biodegradability results of anaerobic digestion of secondary tannery sludge

Reactor	Temperature (°C)	pH	Biogas yield (mL/gVS)	CH <sub>4</sub> Yield (mLCH <sub>4</sub> /gVS)	Biogas quality (%CH <sub>4</sub> )	Biodegradability indicators (%)		
						Reduction)	VS	TS
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

# 5. RESULTS AND DISCUSSION

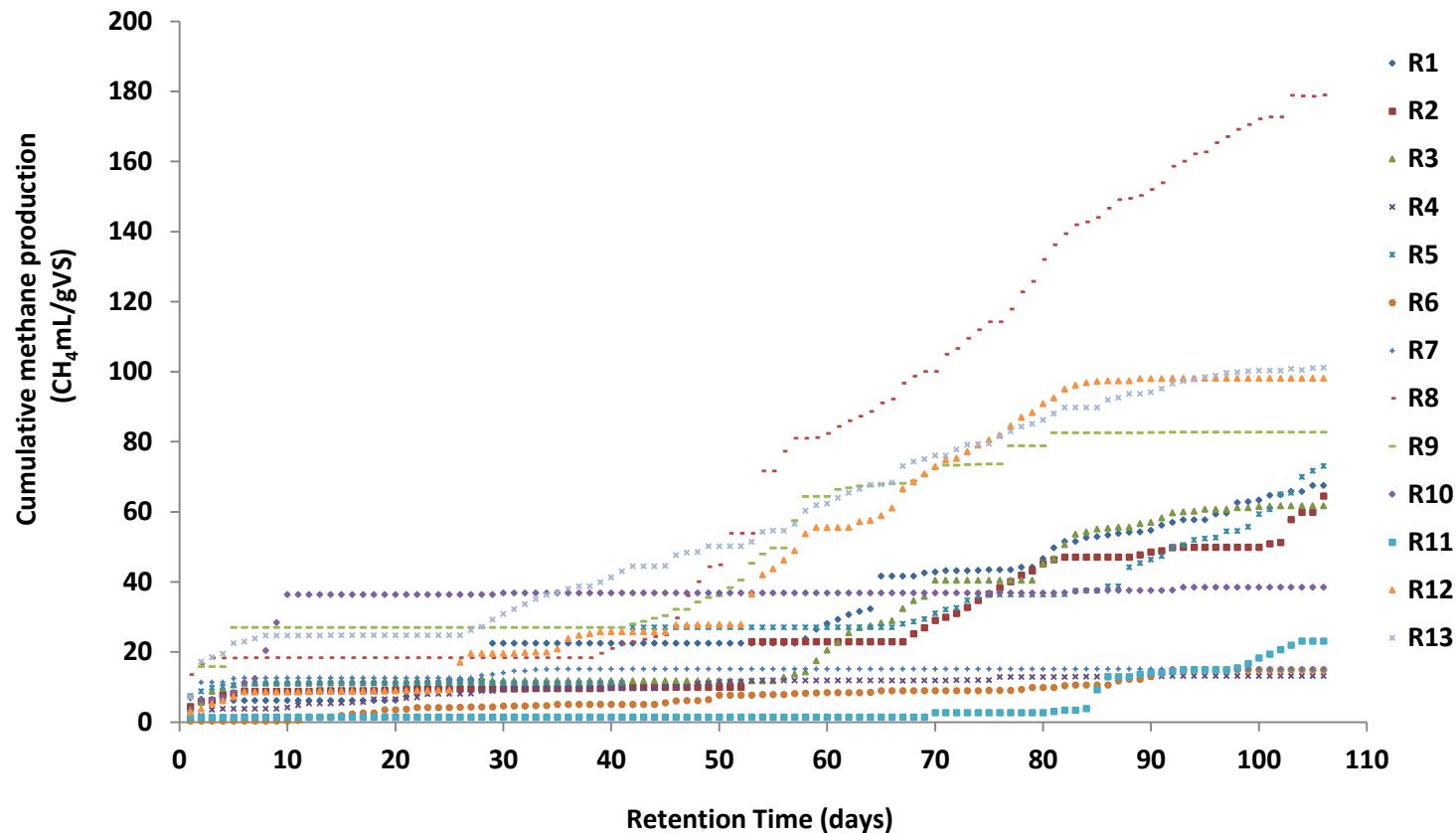


Figure 5: Cumulative methane yields of reactors operating at different temperatures and initial pH



# 5. RESULTS AND DISCUSSION

Table 5: Summary of the statistical results of the fitted models on anaerobic digestion of secondary tannery sludge

Models	Std dev	p-value	F test (LOF) p value	R <sup>2</sup>	Adj R <sup>2</sup>	Pred R <sup>2</sup>	Adeq Prec	AIC
Biogas Linear	46.9	0.0017	0.93	0.72	0.66	0.58	10.3	142
CH <sub>4</sub> 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

COD=chemical oxygen demand

Std dev=standard deviation

Adj=adjusted

TS=total solids

LOF=lack of fit

AdeqPrec=adequate precision

AIC= Akaike's information criterion

VS=volatile solids

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

$$\text{CH}_4 \text{ yield} = 7.48(\text{temp}) - 17.6(\text{pH}_{\text{in}}) - 44.1 \quad \text{Equation 9}$$

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

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

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

# 5. RESULTS AND DISCUSSION

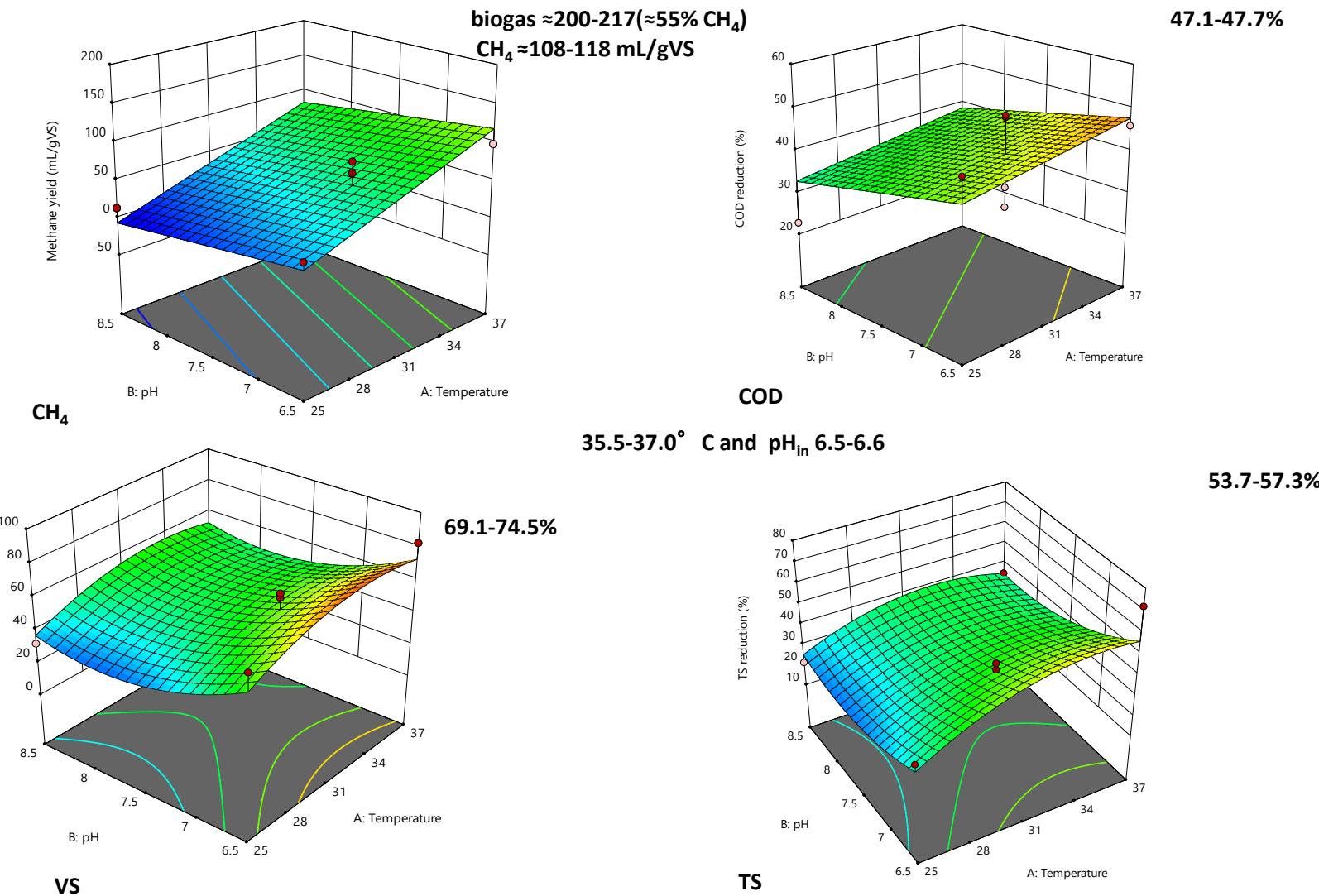


Figure 6: Effect of temperature and initial pH on A-cumulative methane yield; B-COD reduction; C-volatile solids reduction and D-total solids reduction



# 5. RESULTS AND DISCUSSION

Table 6: Anaerobic digestion kinetics of reactors operating at different temperatures and initial pH

Reactor	R4	R10	R6	R5	RC	R11	R13	R1	R8
Temperature °C	23	25	25	31	31	31	37	37	40
pH <sub>in</sub>	7	6.5	8.5	6	7	9	6.5	8.5	7
A	18.4	37.2	21.2	75.2	85	28.2	237	92.7	204
μ	0.08	5.49	0.17	0.3	0.8	0.79	1.32	0.82	2.84
λ	11.8	3.83	15.4	123	15.8	75.3	20	21.8	33.9
K	0.03	0.14	0.015	0.014	0.016	0.011	0.008	0.013	0.012
μ' (d <sup>-1</sup> )	3.48E-04	2.39E-02	7.39E-04	1.30E-03	3.48E-03	3.43E-03	5.74E-03	3.56E-03	1.23E-02
K/μ'	86.3	5.87	20.3	10.7	4.60	3.20	1.39	3.6	0.97

Table 7: Correlation of anaerobic digestion kinetics and process parameters

	Temperature	pHin	A	μ	λ	K	μ'	K/μ'
Temperature	1							
pHin	-0.007	1						
A	0.838	-0.370	1					
μ	0.029	-0.327	0.153	1				
λ	0.167	-0.108	-0.056	-0.324	1			
K	-0.476	-0.308	-0.320	0.836	-0.341	1		
μ'	0.029	-0.327	0.153	1.00	-0.324	0.836	1	
K/μ'	-0.627	-0.076	-0.444	-0.347	-0.207	0.011	-0.347	1

$$\mu' = \mu \text{ (d}^{-1}\text{)}$$

# 5. RESULTS AND DISCUSSION

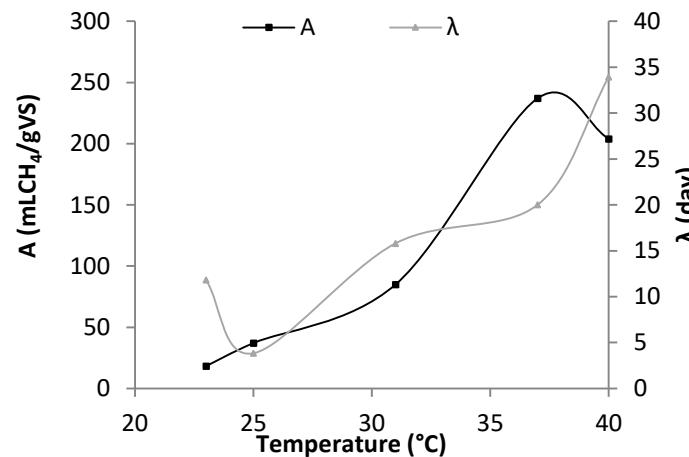
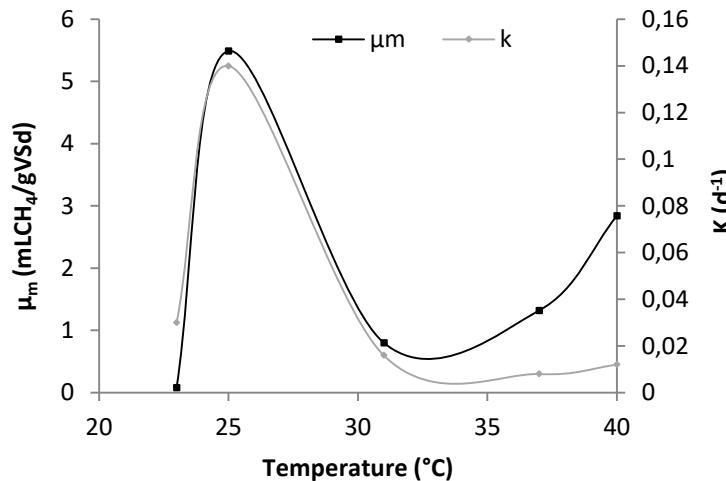


Figure 8: Correlation between kinetic parameters with temperature for reactors operating at near/neutral ( $\text{pH}_{\text{in}}=6.5-7.0$ )

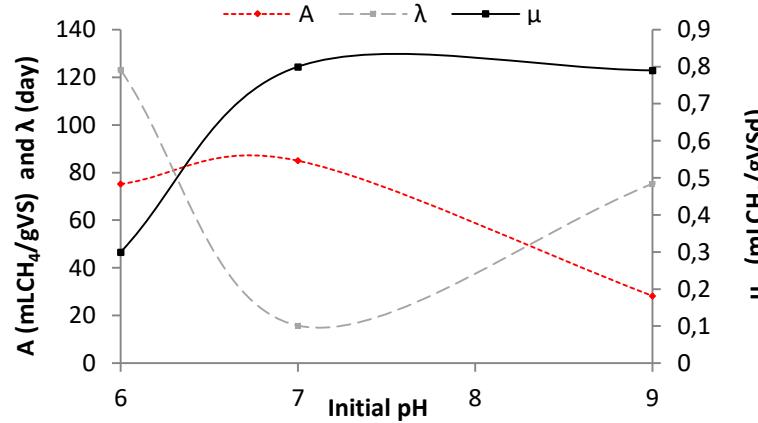
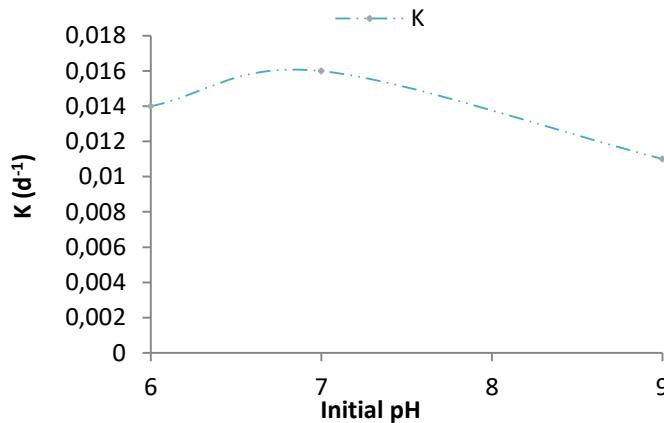


Figure 7: Correlation between kinetic parameters with  $\text{pH}_{\text{in}}$  for reactors operating at  $31^{\circ}\text{C}$



## 6. CONCLUSIONS

- Temperature - gas yields and %TS reduction and both factors on %VS
- The optimum conditions were  $35.6\text{-}37.0^\circ\text{ C}$  and  $\text{pH}_{\text{in}} 6.5\text{-}6.6$  ( $200\text{-}217\text{mL/gVS} \approx 55\%$  average  $\text{CH}_4$  content,  $\text{CH}_4$  yield of  $108\text{-}118\text{ mLCH}_4/\text{gVS}$ , and Bo of  $69.1\text{-}74.5\%$  (VS),  $53.7\text{-}57.3\%$  (TS) and  $47.1\text{-}47.7\%$  (COD))
- Insignificant variation in Bo (regardless of  $\text{pH}_{\text{in}}$  and Temp)
- Heating can be reduced by operating the AD system at lower temperatures, which can be achieved under ambient conditions in most temperate regions
- $A$ ,  $\mu_m$  and  $K$  decreased when  $\text{pH}_{\text{in}}$  increased beyond neutral ( $6.5 \pm 0.5$ ) regardless of operating temperature and were low as in ponds, lakes and wet lands
- $K$  and  $\mu_m$  increased ( $23\text{-}25^\circ\text{ C}$ ), decreased ( $25\text{-}31^\circ\text{ C}$ ) and increased ( $31\text{-}40^\circ\text{ C}$ ) for reactors operating at near/neutral  $\text{pH}_{\text{in}}$  ( $6.5 \pm 0.5$ )

# THANKS TO.....

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