ANAEROBIC DIGESTION OF SECONDARY TANNERY SLUDGE: OPTIMISATION OF INITIAL pH AND TEMPERATURE AND EVALUATION OF KINETICS

A B Mpofu[1,2], PJ Welz[2], O O Oyekola[1]

[1]Department of Chemical Engineering, and [2]Institute of Biomedical and Microbial Biotechnology, Cape Peninsula University of Technology, Bellville campus, Symphony Way, Cape Town, South Africa, 7535

*Corresponding author Tel +27-21-953-8497; E-mail: ashtonmpofu@gmail.com

Co-author e-mail addresses: welzp@cput.ac.za; oyekolas@cput.ac.za

Keywords: Anaerobic digestion; Secondary tannery sludge; Optimisation; Temperature; Influent pH; Kinetics

Novelty Statement: 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.

1 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. 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]. 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]. Mpofu, (2018) reported that the lack of suitable (legalised) landfills in most developing countries, and 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].

Conventionally, mesophilic AD (35–37°C) and near neutral pH (6.5-7.2) offer more stable operations, reduce susceptibility to NH_3, VFA, and LCFA inhibition [7], more resilience to shock loads [8], has low energy demand and gives a more diverse microbial population [9]. 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 (Equation 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 such as tannery sludge provide a good buffering capacity, which helps to avoid digester souring (VFA accumulation), appropriating the control of initial reactor pH (pH_{in}) instead [13].

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 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 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.

2 MATERIALS AND METHODS

2.1 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.

2.2 Characterisation of secondary tannery sludge and inoculum

The inoculum and STNS samples were characterised for TS and VS concentrations following the loss on ignition standard methods using an oven at 105ºC and a furnace at 550ºC, respectively. A Merck Spectroquant Pharo® Spectrophotometer (Darmstadt, Germany) together with Merck cell tests or kits were used to determine COD, total volatile organic acids (VOA_t) as acetic acid (HAc), total organic carbon (TOC), total nitrogen (TN), total alkalinity as $CaCO_3$, total phosphorous (TP), total ammonia nitrogen as NH_3-N, SO_4, total sulphide as HS^-, and Cl^- 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.

2.3 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 Holliger et al. (2016). Optimisation of 2 numeric factors: operational reactor temperature (23-40°C) and pH_{in} (6.0-9.0) were studied on the maximisation of 2 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 5 levels for each factor. The experimental design matrix (Table 3) was generated using Design-Expert® Software Version 11 (Stat-Ease, Inc., Minneapolis, USA).

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 1L Tedlar bags, from which it was analysed. Experiments were terminated when the last reactor produced <1% of the cumulative biogas volume for 3 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.

RESULTS AND DISCUSSION

The following tables and figures illustrate the results obtained during this study. Equation 1-4 show the models fitted onto the response surface that were used for optimisation.

Table 1: 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 CaCO3)	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

Table 2: 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)	CH_4 Yield ($mLCH_4$/gVS)	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

Table 3: 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

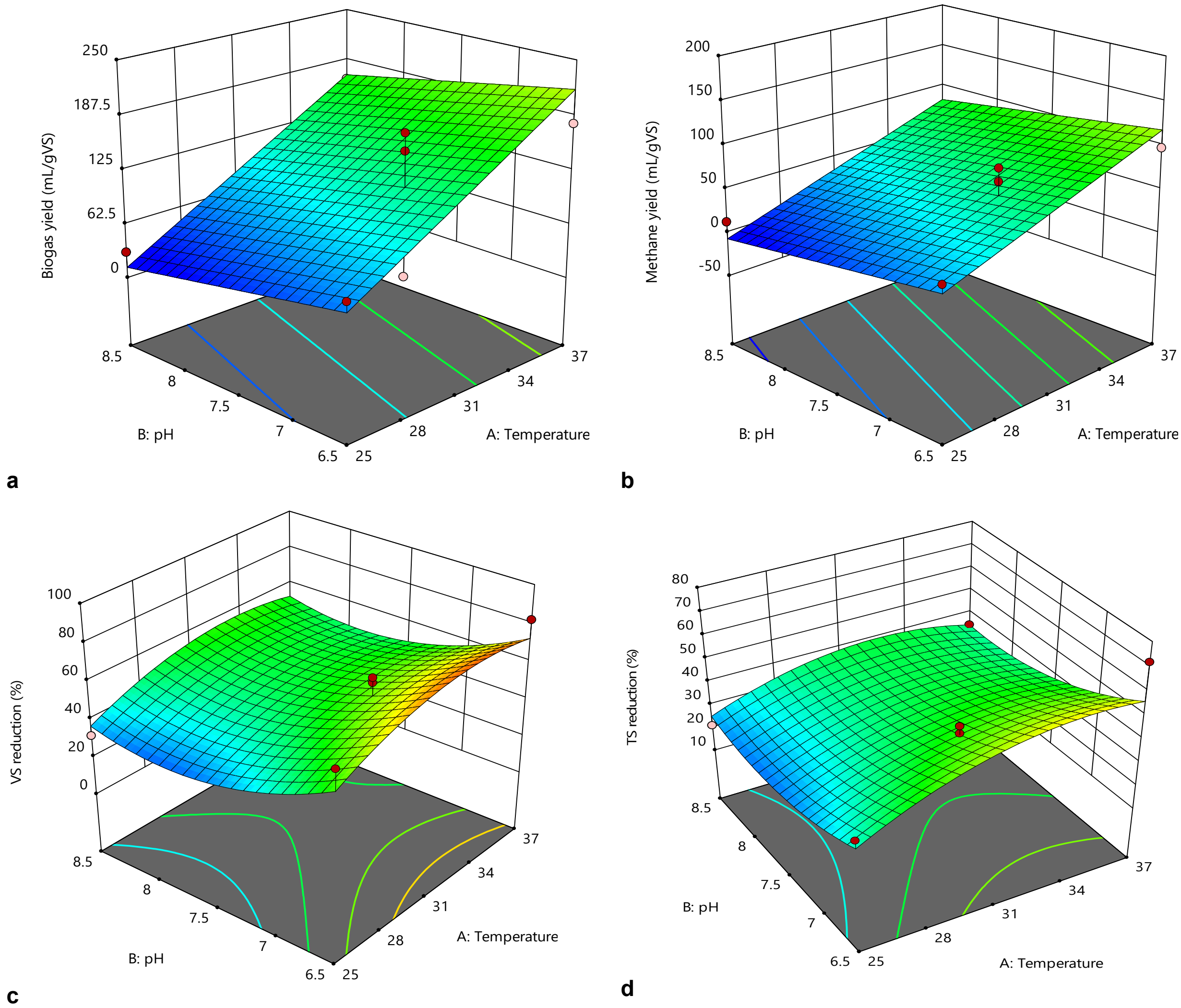
$$\boldsymbol{Biogas\ yield = 13.1(temp) - 24.2(pH_{in}) - 109} \quad \textbf{Equation 1}$$

$$\boldsymbol{CH_4\ yield = 7.48(temp) - 17.6(pH_{in}) - 44.1} \quad \textbf{Equation 2}$$

$$\%\ \boldsymbol{VS_{red} = 13.4({pH_{in}}^2) - 0.279(temp^2) - 0.002(temp \times pH_{in}) - 211(pH_{in}) + 18.6(temp) + 570} \quad \textbf{Equation 3}$$

$$\% \, TS_{reduction} = 7.10(pH_{in}{}^{2}) - 0.26(temp^{2}) - 0.587(temp \times pH_{in}) - 95.4(pH_{in}) + 21.9(temp) + 64 \quad \textbf{Equation 4}$$

$$\% \, COD_{reduction} = 0.486(temp) - 4.52(pH_{in}) + 59.1 \quad \textbf{Equation 5}$$



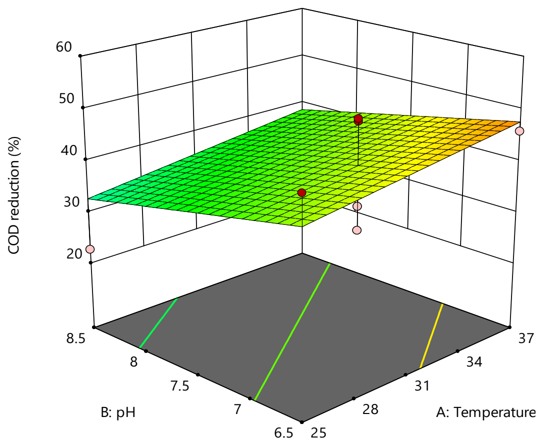


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Figure 1: Effect of temperature and pH_{in} on a-biogas yield; b-cumulative methane yield; c-volatile solids reduction; d-total solids reduction; and e-COD reduction during anaerobic digestion of tannery sludge

Table 4: 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 & 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

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 d^{-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/μ_m~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.

Curriculum Vitae of Ashton Busani Mpofu

(UPDATED 14/09/2018)

PERSONAL DETAILS

Name:	Ashton Busani Mpofu (Mr)
Mobile:	+2778 724 6455 and +2781 541 0811
Address:	39 Excelsior Street, Highbury, Kuils River, 7580
Driver's License:	Code 08
e-Mail:	ashtonmpofu@gmail.com or ashton.mpofu@yahoo.com

PROFILE SUMMARY

- 3 years' experience in chemical engineering, consultancy, engineering sales, research and development
- Expertise in process and plant design, optimisation, trouble shooting and audits, consultancy and engineering sales
- Successfully audited, trouble shot, optimised and developed plant processes for big mining and food companies, while at Magnetech working alongside Gravmax
- Academic Profile: MEng - Chemical Engineering and certificates – IP Law
- Held numerous leadership roles throughout my education and spearheaded the founding of voluntary organisations to assist high school and university students' with their academics, and career guidance

EDUCATION

Tertiary Education **CPUT** 2015 - 2018
MEng (Chemical Engineering)
Outcome: Cum laude
Thesis, 3 journal articles, 5 presentations at local and international conferences

ND and BTech. (Chemical Engineering) **CPUT** 2011 - 2014
Outcome: Degree Average: 70%

Secondary Education **Matopo High School** 2008 - 2009
Advanced Level Certificate
Outcome: Mathematics "D", Physics "D", Biology "B"
2009 Academic Honours Award *
2010 Presidential Scholarship Award *

Ordinary Level Certificate **John Tallach Mission** 2004 - 2007
Outcome: 5"A"s, 1 "B" & 3 "C"s (Core Sciences)
2005, 2006 and 2007 Academic Honours Award*

CAREER DEVELOPMENT

Cape Peninsula University of Technology
Part time lecturer June 2017 – June 2018
Lectured Mathematics, Chemical Process Industries and Computer Applications
- Achieved an average of 94% and 85% respectively
- Managed to motivate, simplify the subject matter, promote student engagement and class attendance

Research assistant May 2015 –May 2017
Worked on a project funded by the Water Research Commission alongside Chris Swartz Water Utilization Engineers, International School of Tanning Technology, Tannery Environmental Consulting Services and various tanneries country wide:
- Conducted a national survey and reported on the use and management of water and energy, and waste generation and management

- Performed a through rigorous root cause analysis, identified and streamlined the key areas in order to improve the use/generation and management of water, energy and waste for the reduction of the tanneries' environmental foot print and increase in profitability
- Investigated and recommended the adoption of anaerobic digestion process for the treatment of tannery sludge in order to reduce the pollution load, generate renewable energy in the form of methane and other resources
- Successfully came up with a novel and sustainably approach that enhanced the anaerobic treatment of tannery sludge and supported the identified and recommended cleaner production techniques
- Engaged in: wastewater treatment plant troubleshooting, optimisation, consultancy, presentation (seminars symposiums and conferences) and publication (reports, posters and journals) of the R&D outcomes.

Magnetech
Technician and then Graduate process engineer January 2013 – Dec 2014 – April 2015
Worked alongside Gravmax:

- Plant process development and design for the recovery of minerals from tailings for local and international firms (BASF, IFM, Kumba Iron Ore, Tugela mining, Petra diamonds, and etc)
- Troubleshot, audited, optimised and provided turn and key solutions for the local mining, food, plastic and paper process plants (Pioneer foods, Tiger brands, Afgri, Lafarge, Illovo, and etc). This sustainably improved process efficiency and productivity
- Involved in the design, calibration and commissioning of magnetic and electrostatic separating equipment
- Handled engineering sales, customer technical support and consultancy on magnetic and electrostatic separating equipment
- Engaged in: Business opportunity identification, market penetration strateies, laboratory analysis and team coaching

NOTABLE ACHIEVEMENTS

- 2018 National vice chairperson– Young Water Professionals SA and Outstanding reviewer - Elsevier Journal of Hazardous materials
- 2017 Associate Member - IChemE (100081375), SAIChE (007370) and WISA (38418)
- 2015 Member - ECSA Candidate Engineering Technologist (201580285)
- 2015 Member – IAENG (157339)
- 2011 Founding Member – Christian campus network
- 2009 Head boy, President Environmental Club and Treasurer Scripture Union - (Matopo High)
- 2007 Senior school Prefect - (John Tallach Mission)

SKILLS AND PROFICIENCE

- Team player and adaptability
- Autonomous working
- Problem solving and critical thinking
- Operations improvement and optimisation
- Interpersonal skills and effective communication
- Strong analysis background
- Proficient in MS tools, Aspen- Plus, Inventor, Auto Cad, Solid Works, Design Expert, and PLMCC

REFERENCES

Available on request