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BIOCHEMICAL METHANE POTENTIAL OF PETROLEUM SLUDGE AND BUFFALO DUNG AT DIFFERENT BLENDING RATIOS.

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ABSTRACT

Petroleum Industry runs world but on the contrary produces Petroleum Sludge (PS) on large scale in which containing various amounts of wastes like chemical, oil and minerals etc. Which are harmful for the environment and difficult to process. The objective of this study is to perform co-digestion of Petroleum sludge and Buffalo Dung. This is achieved by blending PS and BD at different ratios and to determine optimum ratio to determine methane potential through batch digestion process. In Bio-Chemical Methane Potential (BMP) test PS and BD were subjected to anaerobic digestion for determination of methane potential at varying ratios 1:1, 1:0.5 and 0.5:1. The result indicates that the blending ratio of 1:1 gave maximum methane potential in PS and BD digestion process.

KEYWORDS: Bio-Chemical Methane Potential, Buffalo dung, Petroleum Sludge, Anaerobic Digestion, Batch Reactor, Biogas.

1. INTRODUCTION

Petroleum sludge (PS) is composed of wastewater, waste oil, chemicals, minerals and it is being produced by Petroleum industries on larger scale. There are different sources from which sludge is being created such as, drilling operations, refining of crude oil, production and processing of oil. Petroleum sludge is not only a waste product from Petroleum industry but also causing pollution for environment. (Islam et al., 2015) without required treatment drilling cuttings commingled with oil traces, chemicals, and heavy metals are increasing risk for living beings and environment. The contamination cannot be easily removed from petroleum Sludge by using the normal treatment such as heating microbiological deterioration, burring etc. (Guanghuan et al., 2016). Hence handling, treatment & disposal of Petroleum Sludge have become a serious harm for nature (Silva et al., 2017). To cope and alleviate the risk of hazardous waste strict policies are implemented by Environmental Protection Act and Hazardous Wastes Handling Rules. In USA Oil industries produce huge amount of Petroleum sludge approximately 2000g per ton of crude oil as waste, with yearly 4.5 million tons of production of oil waste is produced (Petroleum Sludge) (Aldemar et al., 2018). Biogas and bio solids are produced by anaerobic digestion (AD) of PS. The AD of 0.2 kg of PS in an anaerobic jar for a retention time of 16days take 10,5000m^3 per day Biogas its mean 1 gram of sludge could generate 525m^3 Biogas for a retention time of 16days (Effiong et al., 2018).Petroleum sludge subjected to anaerobic digestion results in the change of the biodegradable sludge to methane, carbon dioxide (CO_2) and microbial cells. Volatile suspended solids generated are quite low. Biological carbonaceous oxygen demand is destroyed. Biogas generated range from 50 to 80 % methane and 20 to 50% (CO_2) dependent on the chemical characteristics of the sludge digested. The biogas produced from this process is useful for power generation and heat (Sampson et al., 2018).

The typical composition of the biogas contains.

Methane (CH_4) - 55-75%

Carbon dioxide (CO_2) - 30- 45%

Hydrogen sulfide (H_2S)- 1-2%

Nitrogen (N_2) and Hydrogen (H2) - 0-1%

Oxygen (O_2) and Carbon monoxide (CO). (Igoni, 2008).

The organic substance can be processed using anaerobic digestion. The common available organic substance being used for generation of biogas are animal dungs, bird's faecal matter, the organic element of municipal solid waste/ trash/garbage, sewage sludge, agricultural crops & residues, industrial wastes and their byproducts, etc. (Sahito et al., 2014). Fresh buffalo manure comprises almost 10,000 anaerobic bacteria per gram, which can only continue under strict anaerobic conditions (Kalle et al., 1984), (Nanda et al., 2003) it is worth noted that 1000g fresh buffalo dung generates 0.037 m^3 of biogas and 1000 g Organic Total Solids from buffalo dung produces 0.105-0.468 m^3 of biogas while methane yield ranged between 0.069 to 0.284 m^3 (Abdel et al., 2008).

The objective of this study is to carry out co-digestion of Petroleum sludge and Buffalo Dung. To optimize the blending ratio of petroleum sludge and buffalo dung for enhanced biogas production through batch digestion system. In order to find out optimum blending ratio of Petroleum Sludge and Buffalo Dung for biogas, Batch Digestion System can be carried out by biochemical methane Potential BMP Test. The BMP test is a conventional process which is commonly implemented at laboratory scale for measurement of biogas potential of bio-wastes, evaluating the efficiency of anaerobic digestion process and biodegradability of bio-wastes. The adequate and high-quality data cannot be achieved by conventional BMP (Shi et al., 2012) (Esposito et al., 2012).

2. METHODOLOGY

2.1. Sample Characterization

The Buffalo Dung was taken from the dairy farm situated nearby Mehran University of Engineering & Technology, Jamshoro, and Petroleum Sludge was taken from nearby oil/gas well drilling site. The MC (Moisture Content), VS (Volatile Solids), TS (Total Solids), VM (Volatile matter), FC (Fixed Carbon), AC (Ash Content),Alkalinity, pH, VF Volatile Fatty Acid, Volatile matter were determined according to the Standard Methods. (APHA et al., 1998).

Table 1: Sample Characterization using Standard Methods.

Parameters	**Equipment**	**Formula**
Proximate Analysis (American Public Health Association 2018)		
MC	Oven Dry	MC% = [(a – b)/a] x 100
TS	Oven Dry	TS% = 100 – MC%
VS	Muffle Furnace	VS% = [(b – c)/b] x 100
VM	Muffle Furnace	VM %=[(b-c)/b] x 100
AC	Muffle Furnace	AC% = (d/b) x 100
FC		FC%=TS-(VM+AC)
Ultimate Analysis		
CC, HC and SC		CC%= 0.460VM+0.635FC − 0.095ASH HC% = 0.060VM+0.059FC + 0.010ASH SC%=(A x R x DF)/Mass of sample
OC		OC% = 0.469VM+ 0.340FC − 0.023ASH
Volatile Fatty Acids (VFA)	Distillation Assembly	VFA = b*n*60000 / ml of sample

Power of hydrogen (pH)	Portable pH meter	
Alkalinity	Titration apparatus	TA = a*n*50000 / ml of sample
Where, MC = Moisture content, TS = Total solids, VS = Volatile solids, AC = Ash contents, CC = Carbon contents, HC = Hydrogen contents, SC = Sulphur contents, NC = Nitrogen contents and OC = Oxygen contents, VM= Volatile Matter, FC=Fixed Carbon, A=Sulphur, R= Total Volume of sample , DF=Dilution Factor		

2.2. Preparation of Batch Reactor

BMP Test was conducted by using Automatic Methane Potential Test System (AMPTS) providing favorable conditions for laboratory. AMPTS [fig.1] is equipped with reactor bottles having controlled inlet and outlet valves for collection of biogas. The reactor has total capacity 500ML. 100ML is left for accumulation of gas phase; rest of volume is filled with different ratios of PS: BD (1:1, 1.5:0.5, and 0.5:1.5). To provide anaerobic condition oxygen contained in bottle is required to be purged by displacing with nitrogen prior to test (Korai et al., 2018) and favorable temperature is to be provided to carry out BMP Test effectively.

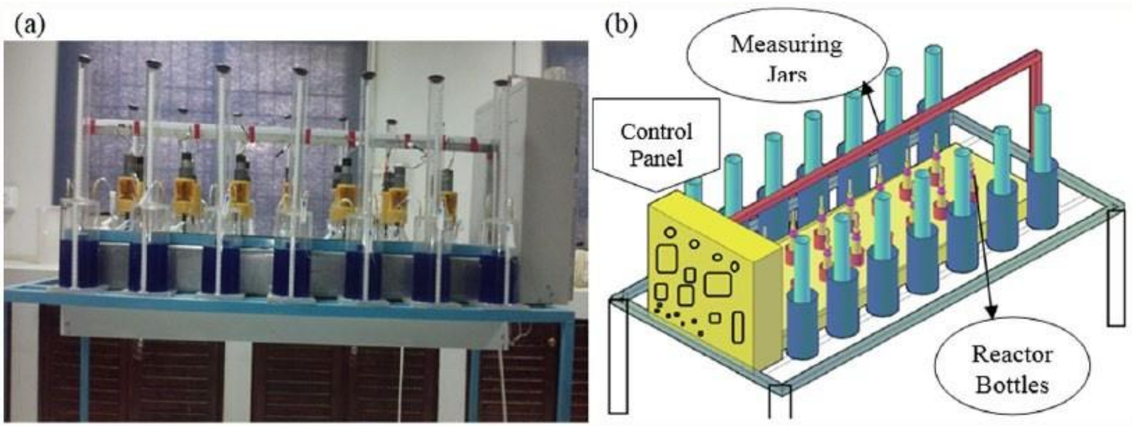

Figure 1: Semi-Automatic Methane Potential Test System SAMPTS.[14]

Theoretical Biochemical Methane Potential (TBMP) can be obtained by Buswell formula (2) Experimental Bio-chemical Methane Potential (EBMP) can be determined by equation (3) and Methane Based Degradability (MBD) can be found by dividing EMBP with TMBP (4) (HF et al., 1952) (Oran et al., 2011) (Zhou et al., 2011) (Sahito et al., 2014)

2.3.Equations

$$TBMP = C_aH_bO_cN_d + \frac{4a-b-2c+3d}{4}H_2O \rightarrow \frac{4a-b-2c-3d}{8}CH_4 + \frac{4a-b+2c+3d}{8}CO_2 + dNH_3 + \quad (1)$$

$$TBMP = \frac{2790 \times H + 930 \times C + 350 \times O - 600 \times N - 175 - S}{C+H+O+N+S} \quad (2)$$

$$MBD\ (\%) = \frac{EMBP}{TBMP}\ X\ 100 \tag{3}$$

The reactor was loaded with sample by filling different ratios of PS: BD (R=1:1, R=1.5:0.5, R=0.5:1.5) and 100ML was left for accumulation of gas phase. The inoculum was taken from running Dome Anaerobic Digester (AD) at Masri Sheikh Village Hyderabad.

3. RESULTS AND DISCUSSION

3.1.Characteristics of substrate and inoculum

Characterization of substrate and inoculum (biodegradable waste) are very significant for carrying out the anaerobic digestion because efficacy of the process is affected by them. Substrate and inoculum samples were analyzed, and its characteristics are listed in Table 1.

Table 2: Characteristics of substrates and inoculum.

Parameters		Substrate					Inoculum
		PS	BD	PS:BD 1:1	PS:BD 1.5:0.5	PS:BD 0.5:1.5	I
MC (%)	Range	55.93-54.47	84.24-84.08	68.54-68.97	64.20-63.91	72.24-72.56	94.42-94.00
	Avg	55.21	84.17	68.76	64.09	72.41	94.22
	SD	1.03	0.11	0.30	0.15	0.23	0.30
TS (%)	Range	44.06-45.52	15.75-15.91	31.45-31.02	35.79-36.01	27.75-27.43	5.57-5.99
	Avg	44.79	15.83	31.24	35.91	27.59	5.78
	SD	1.03	0.11	0.30	0.15	0.23	0.30
VS (%)	Range	25-25.19	71.09-71.67	44.32-46.47	30.35-31.23	46.24-48.75	80.46-79.66
	Avg	25.10	71.39	45.35	30.80	47.50	80.07
	SD	0.14	0.41	1.59	0.62	1.77	0.57
VM (%)	Range	28.19-28.45	80.07-79.56	42.00-38.78	41.08-49.73	53.84-53.57	80.37-79.27
	Avg	28.31	79.82	40.39	40.40	53.70	79.82
	SD	0.523	56.208	26.007	6.116	0.191	0.778
AC (%)	Range	33.04-34.05	4.55-4.50	17.54-16.60	24.93-24.76	14.91-14.05	1.08-1.21
	Avg	33.55	4.53	17.07	24.85	14.49	1.15
	SD	0.71	0.03	0.66	0.12	0.61	0.09
C (%)	-	9.44	39.22	15.96	16.39	22.76	37.38
H (%)	-	2.79	5.51	3.37	3.42	3.97	5.29
O (%)	-	13.24	39.17	19.08	19.31	25.35	38.26
N (%)	-	0.08 a	1.32 b	0.7	0.39	0.99	3.95 c
S (%)	-	0.6	0.15	0.67	0.7	0.46	0.14
C/N	-	118	29.90	26.62	30.02	24.27	9.68
Where, a= (Janajreh et al., 2020), b= (Sahito et al., 2014), c= (Korai et al., 2018).							

3.2. Characterization of sample before BMPT

In order to checked the consistency of anaerobic method there are several parameters such as TA, VFA and pH are used by way of indicator. Accumulation of VFA can is result of Low pH, which causes low methane yield due to inhibition of digestion process. Another important indicator is VFA/TA Ratio. Three levels of VFA/alkalinity ratio are suggested in literature (Callaghan et al., 2002) Stable if VFA/TA ratio is less than 0.4, if the ratio result between 0.4 and 0.8 it indicates some variability, while ratio greater than 0.8 results variability in digestion method. Shows the similar behavior as pH is observed decreased VFA Value is increasing similarly increasing VFA/TA Ratios.

Table 4: Characteristics of sample before BMPT.

Parameters		**Sample**		
		R1 (1:1)	**R2 (1.5:0.5)**	**R3 (0.5:1.5)**
MC (%)	Range	90.89-90.36	86.33-85.96	92.81-92.86
	Avg	90.625	86.145	92.835
	SD	0.375	0.262	0.035
TS (%)	Range	9.10-9.63	13.66-14.03	7.18-7.13
	Avg	9.365	13.845	7.155
	SD	0.375	0.262	0.035
VS (%)	Range	61.78-58.85	46.30-49.53	42.20-40.74
	Avg	60.315	47.915	41.47
	SD	2.07	2.28	1.03
VM (%)	Range	59.82-60.29	51.87-52.00	55.48-57.13
	Avg	59.82	51.94	56.30
	SD	0.332	0.092	1.167
TA (mg/L)	Range	850-900	1100-1150	700-800
	Avg	875	1125	750
	SD	35.36	35.36	70.71
pH	Range	10.3-10.4	10.6-10.5	10-9.8
	Avg	10.35	10.55	9.9
	SD	0.071	0.071	0.141
VFA (mg/L)	Range	360-365	480-490	240-245
	Avg	362.5	485	242.5
	SD	3.54	7.07	3.54
VFA/TA	Range	0.423-0.405	0.436-0.426	0.343-0.306
	Avg	0.41	0.43	0.32
	SD	0.01	0.01	0.03

3.3. Bio -methane yield and Methane- based degradability

Figure 2 and 3 shows methane flow rate and cumulative methane yield of PS, BD and inoculum after 60 days of BMPT at different Substrate/Inoculum ratios R1, R2 and R3. The initial spike in curves seen in R3 on Day 11 R1 on Day 20 putrescible phenomenon of substrate and then the curve shifted downward because of inhibition. However putrescible effect has been observed delayed in R2 and immediate increase after slight decreasing trend. Figure 3 shows S-shaped curves R1 and R2 which represent the inhibition of digestion process and resulted in lower methane production on given ratio. Methane Potential estimated from Figure 3 as R1 with PS: BD 1:1=504.3 Nml / gVS, R2 with PS: BD=1.5:0.5= 345 Nml / gVS, and R3 with PS: BD=0.5:1.5=496.65 Nml / gVS. This shows with higher ratios of PS in substrate decreases the Methane Yield.

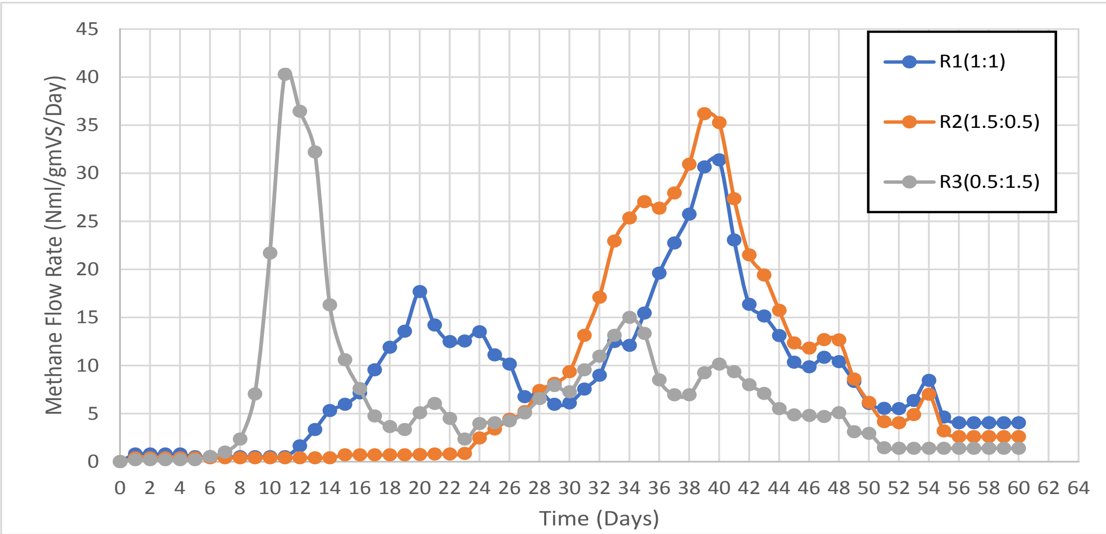

Figure 2: Methane flow rate of substrates at different Substrate/Inoculum ratios.

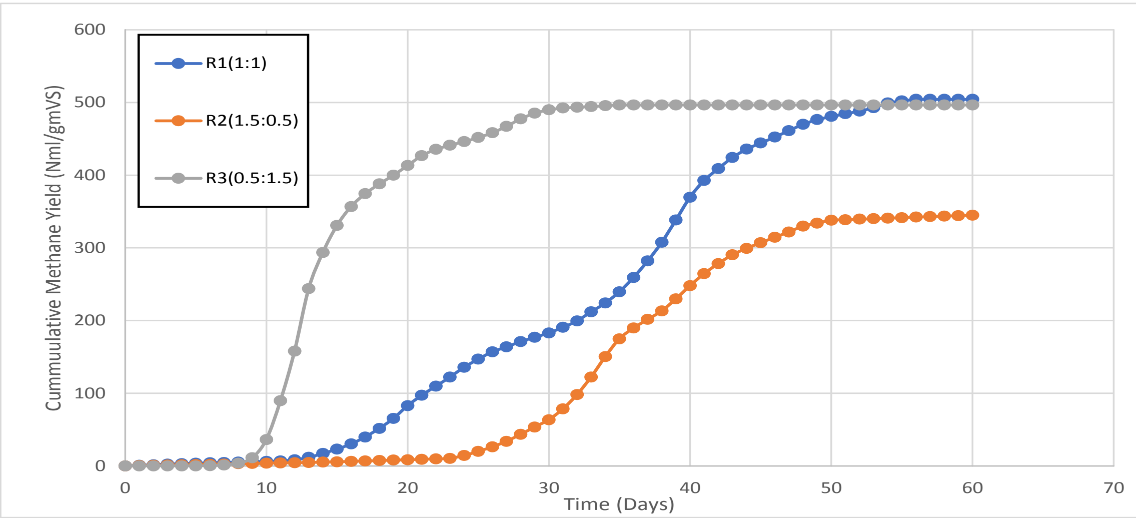

Figure 3: Cumulative methane yield of substrates at different Substrate/Inoculum ratios

3.4. Characteristics of effluent at the end of BMPT

There are several parameters for example VFA alkalinity and pH which are used by way of indicators for examination stability of anaerobic method. Low pH results in accumulation of VFA because of which digestion method inhibits leading low methane yield (Lu et al., 2013). The VFA/TA ratio is also one significant parameter which determines the stability of digestion. Parameters like TA, VFA and pH of effluent at the end of BMPT were measured as shown in Table 5.

Table 5: Characteristics of effluent at the end of BMPT.

Parameters		Sample		
		R1(1:1)	R2(1.5:0.5)	R3 (0.5:1.5)
MC (%)	Range	92.399-93.138	90.804-90.394	94.060-93.078
	Avg	92.77	90.60	93.57
	SD	0.52	0.29	0.69
TS (%)	Range	7.6-6.8	9.60-9.19	5.93-6.92
	Avg	7.23	9.40	6.43
	SD	0.52	0.29	0.69
VS (%)	Range	43.97-40.20	37.93-36.68	42.66-32.91
	Avg	42.09	35.81	37.79
	SD	2.67	3.01	6.90
VM (%)	Range	49.73-48.65	46.53-44.87	48.26-47.24
	Avg	49.19	45.7	47.75
	SD	0.764	1.174	0.721
TA(mg/L)	Range	1550-1700	1650-1700	1250-1400
	Avg	1625.00	1675.00	1325.00
	SD	106.07	35.36	106.07
pH	Range	7.3-7.0	7.1-8.3	7.35-7.26
	Avg	7.15	7.70	7.31
	SD	0.21	0.85	0.06
VFA (mg/L)	Range	144-120	264-240	180-120
	Avg	132.00	252.00	150.00
	SD	16.97	16.97	42.43
VFA/TA	Range	0.093-0.071	0.160-0.141	0.144-0.086
	Avg	0.08	0.15	0.12
	SD	0.02	0.01	0.04

3.5. Theoretical biochemical methane potential (TBMP)

TBMP was calculated by using given formula (2) and Methane- based degradability (MBD) was determined by using formula (3) at different ratios of substrate and inoculum. Calculated values of TBMP and MBD for different ratios of Substrate and inoculum are given in Table 6. The results shows that value of methane potential is highest in 1:1 for PS and AD, while it decreases with reducing ratio of any of two.

Table 6: TBMP at different ratios of substrate and inoculum.

Ratios	Chemical formula with sulfur	Chemical Formula without sulfur	TBMP (NmL/g.VS)	EBMP (NmL/g.VS)	MBD (%)
R1	$C_7H_{218}O_{108}NS$	$C_7H_{218}O_{108}N$	680.8266	504.3	74.071
R2	$C_5H_{138}O_{68}NS$	$C_5H_{138}O_{68}N$	669.6845	345	54.503
R3	$C_4H_{238}O_{126}NS$	$C_4H_{238}O_{126}N$	654.375	496.65	75.89

4. CONCLUSION

PS being produced on large scale in Petroleum industries containing various amounts of waste chemical, oil and minerals causing it difficult to process as well as dangerous for the environment. The Study aims to use the same with BD to determine Biochemical methane potential and finding ways to make it beneficial. In this study different ratios of PS and BD were subjected to anaerobic digestion by BMP Test to generate methane and methane potential at varying ratios. The reactors were set for 60 days of time period at ratios 1:1, 1.5:0.5 and 0.5:1.5. The results show methane Potential 1:1 >0.5:1.5>1.5:0.5 during digestion.

5. RECOMMENDATIONS

The author suggests that petroleum refinery sludge can be used with animal dung to produce biogas.

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