Journal of Inventive Engineering and Technology (JIET) **March/April 2024**
Journal of Inventive Engineering and Technology (JIET)
ISSN: 2705-3865
Volume-5, Issue-2, pp-36-47
www.jiengtech.com
Research Paper Open Access

An Investigation of Corrosion and Its Effects on Mild Steel Biodigester Materials by Electrochemical Corrosion Method

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ABSTRACT : *An investigation of corrosion and its effects on mild steel biodigester materials was carried out using electrochemical corrosion method. Animal wastes (cattle and pig) and mild steel (AISI 1020) were used as the study materials. The corrosion experiments on cattle and pig slurries were conducted in 14, 28, 42, 56, 70, 84 and 98 days respectively. The corrosion potentials (E_{corr}) measured in cattle slurry after 98 days was -734 mV_{SCE} with a corrosion current density ($I_{corr.}$) of 194.52 $\mu A/cm^2$. After 98 days of experimentation, the results show a stronger tendency for general and pitting corrosion compared to pig waste slurry (-628 mV_{SCE} with $I_{corr.}$ of 148.023 $\mu A/cm^2$). At the end of the experiment, $I_{corr.}$ of samples in cattle slurry increases in the order of C7 < C5 < C6 < C1 < C3 < C4 < C2 whereas $E_{corr.}$ increases in the order of C6 < C7 < C5 < C1 < C3 < C2 < C4. Similarly, the E_{corr} of samples in pig slurry increases in the order of P6 < P5 < P7 < P1 < P3 < P2 < P4 whereas $I_{corr.}$ increases in the order of P3 < P7 < P6 < P5 < P1 < P2 < P4. The findings demonstrated that the corroded samples exhibited pitting and generalized corrosion characteristics together with widely distributed cracks. The cattle waste with 5.70% protein was found to be the most aggressive medium of the media and the pig waste, which contained 6.13% protein was the less corrosive medium.*

KEYWORDS: *Corrosion resistance, corrosion rate, animal waste, anaerobic digestion, mild steel, biodigester*.

Date of Submission: 11-04-2024 Date of acceptance: 14-04-2024

I. INTRODUCTION

The anaerobic digestion (AD) of biomass for the production of biomass is a complex chemical process that results to degradation of mild steel biodigesters. The wear rate of the metal is determined by the nature and composition of the waste slurry produced after the removal of biogas generated. Although, substantial research on biogas production from different biodegradable wastes have been carried out (Okoroigwe, Iloeje, Enibe, & Eze, 2006) (Okoroigwe, Ibeto, & Okpara, Comparative Study of Potential of Dog Waste for Biogas Production, 2010) (Okoroigwe, Ibe, & Ezema, Experimental Study of Anaerobic Digestion of Dog Waste, 2014) (Oparaku, Ofomatah, & Okoroigwe, 2013) but the synergy between biodigester material and corrosion effects of AD slurry has not been fully explored. Mild steel biodigesters are widely employed in commercial agricultural production and institutions where large amounts of biomass (animal and biodegradable plant) wastes are generated (Elliot, Foister, Johnson, & Wood, 1983; Akdogan & Eker, 2000). The oxidative effect of the slurry and the stored biogas on the metallic biodigester material is evident when the biodigester walls erode, resulting in the metal biodigester system's eventual collapse and failure. Mild steel's availability, low cost, and mechanical properties (such as weldability, fabricability, and formability) (Wensley, Materials for Fabrication and Repair of Batch Digesters, 1997; Wensley, Moskal, & Wilton, "Materials Selection for Batch Digesters," , 1997; Wensley & Dykstra, Corrosion of Batch Digesters, 1997; Pfeiffer, Scheil, & Schmidt, 1955) set it apart from other steel materials for use in biodigester construction.

Despite its safety and effectiveness, the MS biodigester's longevity is restricted by corrosion attacks from the various chemical and biological components in waste during the AD processes (Akdogan & Eker, 2000). The degree of corrosion is mostly determined by the chemical composition of the metal (Parker, 1955), the type of waste and digestive environment (Furhman, 1949; Ungar & Caywood, 1954). In addition, impurities and microorganisms in the waste contribute to the corrosion of MS biodigester materials (Elliot, Foister, Johnson, & Wood, 1983; Hassler, 1995; Robert & Anders, 2017). Several research have looked into the impact of AD slurry on biodigester materials. The corrosion behavior of MS and stainless steel (SS) was investigated in sewage sludge (Englert & Muller, 1996). The electrochemical tests and corrosion experiments were performed in a CH_4/CO_2 mixture (3:7) at 1 atm pressure and $CH_4/CO_2/N_2$ (3:7:13) at 7 atm pressure. Their finding demonstrated that MS suffered generalized corrosion at pressures of 1 and 7 atm, respectively. A non-protective corrosion film, containing sulfides, was identified on the samples as well as pits which were associated with the activation of $E_{corr.}$

The effects of corrosion and prevention measures on steel biodigesters in corrosive settings were researched (Robert & Anders, 2017), and the literature show that coating and maintaining steel biodigesters offer improved long term corrosion resistance ($R^1_{corr.}$). It alleviates the need for maintenance, repairs, or replacement in biodigester management. The impacts of biodegradable waste on various MS compositions were examined, and MS was discovered to exhibit active and passive corrosion behavior (Wensley & Dykstra, Corrosion of Batch Digesters, 1997) (Wensley, Corrosion of Batch and Continuous Digesters, 1998) (Wensley, Corrosion of Carbon Steel and Stainless Steel in Digesters, 2000). The results demonstrated that MS exhibited active $R_{corr.}$ at $E_{corr.}$ below -50 mV_{Mo} with $R_{corr.}$ of 2.4 mm/y (95 m/y) and passivation at $E_{corr.}$ above -50 mV_{Mo} with $R_{corr.}$ of 7.3 mm/y (288 m/y). Based on the current research, it appears that research on the corrosive effects of AD on MS biodigesters is quite limited but warrants more investigation. This serves as the foundation for conducting corrosion research on MS biodigesters employing animal waste, and to accomplish this objective, a biodigesters will be designed and built.

II. MATERIALS AND METHODS

The biodigester test facility was designed and constructed with MS sheet with metallurgical composition as shown in Table 1.

Table 1: Biogas production prospects of some common wastes (Okeke, 2001)

Type of waste	Biogas yield per kg of waste input (m^3/kg)	Quantity of waste per day (kg/day)	Population (million)	Fresh waste production per day (kg/day/unit)	Feedstock production per day (million kg)	Biogas productio per day (millio m^3)
Cattle	0.025	1.080	12.10	9.00	108.90	3.27
Pig	0.045	0.600	1.30	4.00	5.20	0.26
Poultry	0.075	0.360	160.00	0.04	6.40	0.51
Human	0.025	1.080	115.00	0.18	20.70	0.62

A Experimental Procedures

To facilitate regular laboratory tests on the biodigester, the mild steel was mechanically press-cut into 10 × 10 mm squares with a thickness of 3mm. Fourteen samples were created and each was immersed in the slurry medium using a non-corrosive polymer rope fastened to it through a 2mm hole drilled at one end of each sample. To guarantee a uniform surface, the samples were hand filed. The study's material characterization includes chemical analysis of the metal test samples using EDS, surface morphology using SEM, and polarization curves obtained through electrochemical corrosion.

Table 2: Chemical compositions (wt. %) of the mild steel

Mild Steel	C	Cr	Ni	Mn	P	S	Si	Fe	Cu
AISI 1020	0.250	0.008	0.002	0.462	0.043	0.052	0.350	98.964	0.006

III. RESULTS/DISCUSSIONS

A. Preparation of Test Samples

Prior to immersion, samples were polished with a succession of silicon carbide (SiC) papers ranging from 150 220, 320, 400 and 600 to smooth the surfaces. The polishing process comprised rubbing the samples back and forth on SiC papers in directions roughly perpendicular to the scratches left by the previous paper. It involved removing fine scratches caused by cutting operations, which could have been potential causes of mistakes and inaccuracies in the studies, as well as smoothing and mirroring all samples prior to immersion. Cattle and pig waste slurry were utilized to create the AD medium by combining 4kg of waste with 12kg of water, which was then put into two separate biodigesters for each waste. Seven mild steel samples were independently submerged in each of the biodigesters for 98 days.

B. Preparation of Test Solutions

The corrosive solutions utilized were cattle and pig slurries, with chemical compositions shown in Table 3. For each experiment, glass beakers were filled with 20 ml of fresh trash. Waste excreted on each day of the experiment was collected and processed before to use. In two separate buckets, 4 kg of cattle and pig waste were mixed with 12 kilogram of water (1 kg of waste for every 3 kg of water). Each solution was then charged into the biodigesters after being well mixed with a wooden bar. Seven samples were immersed independently in each biodigester for 98 days.

Table 3: Chemical compositions of the wastes used

Parameter	Protein (%)	Moisture (%)	NH_3 (%)	CO_2 (mg/kg)	$(NH_4)_2SO_4$ (%)	Mg mg/kg	Ca (mg/kg)	Na (mg/kg)	N (%)	K (mg/kg)
Cattle	5.70	62.20	2.25	24.04	6.63	4.80	12.00	19.47	0.92	30.18
Pig	6.13	39.75	1.12	18.03	4.34	26.40	16.00	8.23	0.98	37.18

C. pH – Measurement

Throughout the test period, the pH and temperature of the media were monitored and measured every 7 days. The experiment was conducted using a pH meter and a temperature instrument.

Table 4: Temperature (℃) and pH values of cattle and pig wastes used for the experiments

		Cattle waste		Pig waste	
S/N	Day	Temperature (^OC)	pH value	Temperature (^OC)	pH value
1	7	24.8	6.04	24.6	6.42
2	14	24.2	5.61	23.7	6.05
3	21	25.5	5.52	25.2	6.02
4	28	24.4	4.32	24.2	5.67
5	35	23.5	4.25	23.5	5.04
6	42	24.7	4.17	24.5	5.15
7	49	25.3	4.09	25.0	4.95
8	56	24.0	3.75	24.4	4.81
9	63	24.6	3.65	24.6	4.50
10	70	23.8	3.45	23.5	4.46
11	77	24.2	3.44	24.0	4.13
12	84	23.5	3.25	23.5	3.92
13	91	24.3	3.20	24.4	3.55
14	98	24.5	3.14	24.6	3.70

D. Electrochemical Measurements

To evaluate polarization, the test samples were immersed in two separate glass beakers containing 200 ml of waste slurry at 25°C. After each test, the samples' polarization (Tafel and OCP-T) was plotted. Tafel; plots of $E_{corr.}$ vs. $I_{corr.}$ and OCP-T; plots of $E_{corr.}$ vs. time were plotted. The measurements were done using an electrochemical analyzer with a scan rate of 0.01 V/s in the anodic direction and -0.01 V/s in the return cathodic, using a standard saturated calomel electrode (SCE). Measurements began in the anodic direction at $E_{corr.}$ of -1.5 V_{SCE} followed by a cathodic scan back to $E_{corr.}$ of 1.5 V_{SCE} with quiet and hold time of 2 and 0 seconds respectively, and a Tafel slope potential range of 0.06 V. A SCE was used as reference electrode and all $E_{corr.}$ in this work are referred to it. Corrosion tests were performed in three cylindrical arrangements with working electrode area of 1 cm^2, formula weight of 27.9225, electrons of 2 and density of 7.85 g/cm^3. A graphite rod was used as the counter electrode, standard Ag/AgCl electrode as reference electrode while the studied MS was used as working electrode. The polarization curves were examined at a scanning speed of 2 mV/s and a scanning range relative to E_{corr} of ±600 mV_{SCE} for the samples to determine the I_{corr} and E_{corr}.

E. SEM Micrograph of Samples in Cattle Slurry

Fig. 1 depicts a SEM micrograph of test materials in a cattle slurry environment across varied retention times. The data reveal that cattle slurry has varying degrees of corrosive effects on mild steel, which increase over time. The samples exhibited both general and localized rusting. Fig. 1a displays white and black patches in their original form, with no obvious corrosion products and just a small loss of shine on the sample. Fig. 1a and b showed consistent results, despite some local discolouration. Fig. 1a depicts a reasonably smooth surface, whereas 1b depicts fewer depositions of white and dark corrosion products with small pores, which may result in pitting. This result is attributed to the slurry and biogas produced on the fourteenth day of the experiment.

Fig. 1c appears homogenous, with fractures and pits indicating consistent corrosion features. The sample is covered in grey corrosion products, and fissures have spread over the surface as a result of slurry impacts. Corrosion layers of 1b and c appeared thicker and porous, increasing degradation and the diffusion of corrosive substances into the sample. Fig. 1d shows a definite boundary and longitudinal cracks, together with small pits spread on the surface, revealing cow slurry effects on mild steel. Long and shallow ditches with a definite direction were detected, indicating homogeneous corrosion, while appearing thinner and denser than Fig. 1b and c. Meanwhile, dense and thin corrosion layers provide better resistance to additional corrosion than thick and porous layers or surfaces.

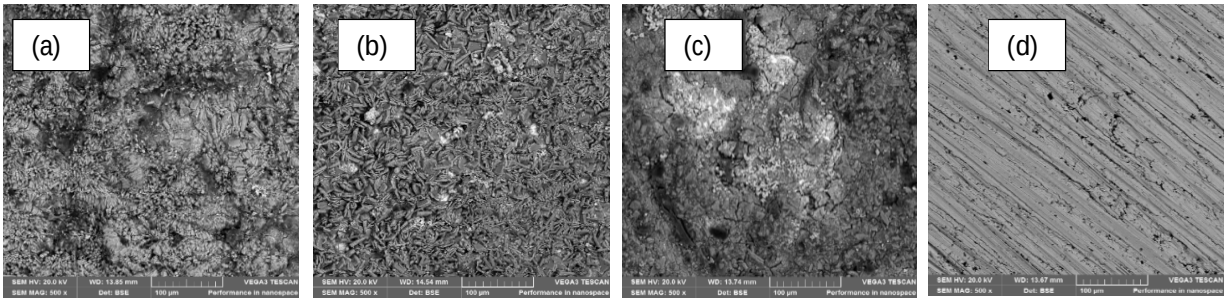


Fig. 1: SEM micrograph of MS samples in cattle slurry. (a) Control sample, (b) sample in slurry for 14 days (C1), (c) sample in slurry for 56 days (C4), (d) sample in slurry for 98 days (C7)

F. SEM Micrographs of Samples in Pig Slurry

The sample in Fig. 2a was partially covered with fractures and corrosion products, such as white deposits, which indicate corrosion but are unevenly distributed when compared to Fig. 2b, which was almost completely coated with white deposits. Fig. 2b illustrates fissures and white corrosion products caused by the dissolution of hardened slurry and particle diffusion via anodic and cathodic processes, respectively. The test sample's surface is dense and homogenous, which reduces corrosivity by decreasing slurry permeability.

Fig. 2c clearly demonstrates severe localized corrosion pits, cracks, and the deposition of white and dark grey corrosion products, in contrast to 4d, which shows highly uniform corrosion features. Fig. 4c is evidently much more pronounced as pits and dark corrosion products are bigger than Fig. 2a and b. Specifically, less corrosion products were developed in the white sections, while more were produced in the dark grey parts, which were primarily made of Fe and O, connected with

FeOOH, FeO, and Fe_2O_3 (known as rust when hydrated). Furthermore, a study of the corrosion products revealed the presence of FeS.

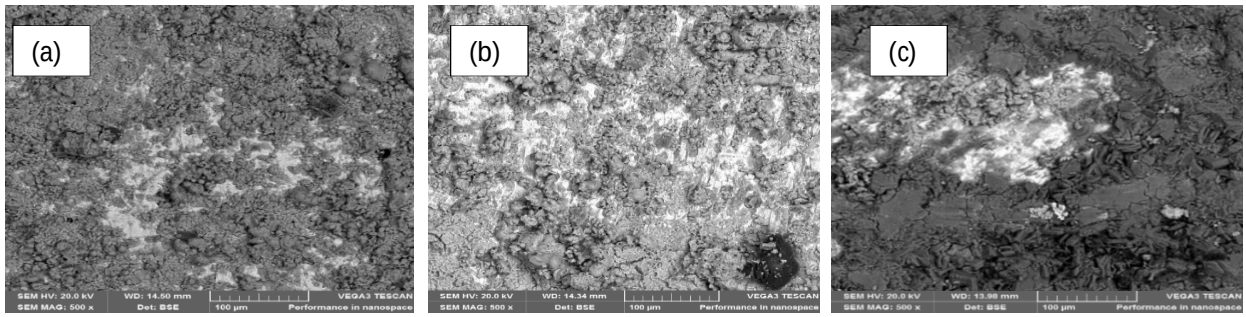


Fig. 2: SEM micrograph of MS samples in pig slurry. (a) Sample in slurry for 14 days (P1), (b) Sample in slurry for 56 days (P4), (c) Sample in slurry for P7 98 days (P7)

G. Polarization Tests of the Samples

a. Tafel Polarization Measurements

Fig. 3a to j depict Tafel curves of samples at various retention times. In Fig. 3a, $E_{corr.}$ and $I_{corr.}$ of CC (control sample in cattle slurry) are -57 mV_{SCE} and 3,024 $\mu A/cm^2$ respectively while for CP (control sample in pig slurry), $E_{corr.}$ and $I_{corr.}$ are -56 mV_{SCE} and 5,353 $\mu A/cm^2$ respectively. The shift of $E_{corr.}$ in both samples to negative indicates that polarization happened in the cathodic area, and R_{corr} is cathodically controlled.

In Fig. 3b, C1 with $E_{corr.}$ of -137 mV_{SCE} and $I_{corr.}$ of 1,052 $\mu A/cm^2$ possesses better $R_{corr.}$ than P1 with $E_{corr.}$ of -133 mV_{SCE} and $I_{corr.}$ of 2,498 $\mu A/cm^2$. $I_{corr.}$ and $E_{corr.}$ of P1 indicates a higher tendency for corrosion than C1. The dynamic variations between E_{corr} and I_{corr} show the steady deposition of corrosion products on the samples.

Fig. 3c shows positive shift in $E_{corr.}$ and decrease in I_{corr} showing better $R^1_{corr.}$ of the samples. Corrosion parameters of C2 ($I_{corr.}$ as 7,076 $\mu A/cm^2$, $E_{corr.}$ as 1.0 mV) and P2 ($I_{corr.}$ as 6,110 $\mu A/cm^2$, $E_{corr.}$ as 20mV) showing apparent $R^1_{corr.}$ improvement compare with C1 and P1. The improvement of $R^1_{corr.}$ on samples is believed to be gradual build-up of oxide layers which inhibited further corrosive activity.

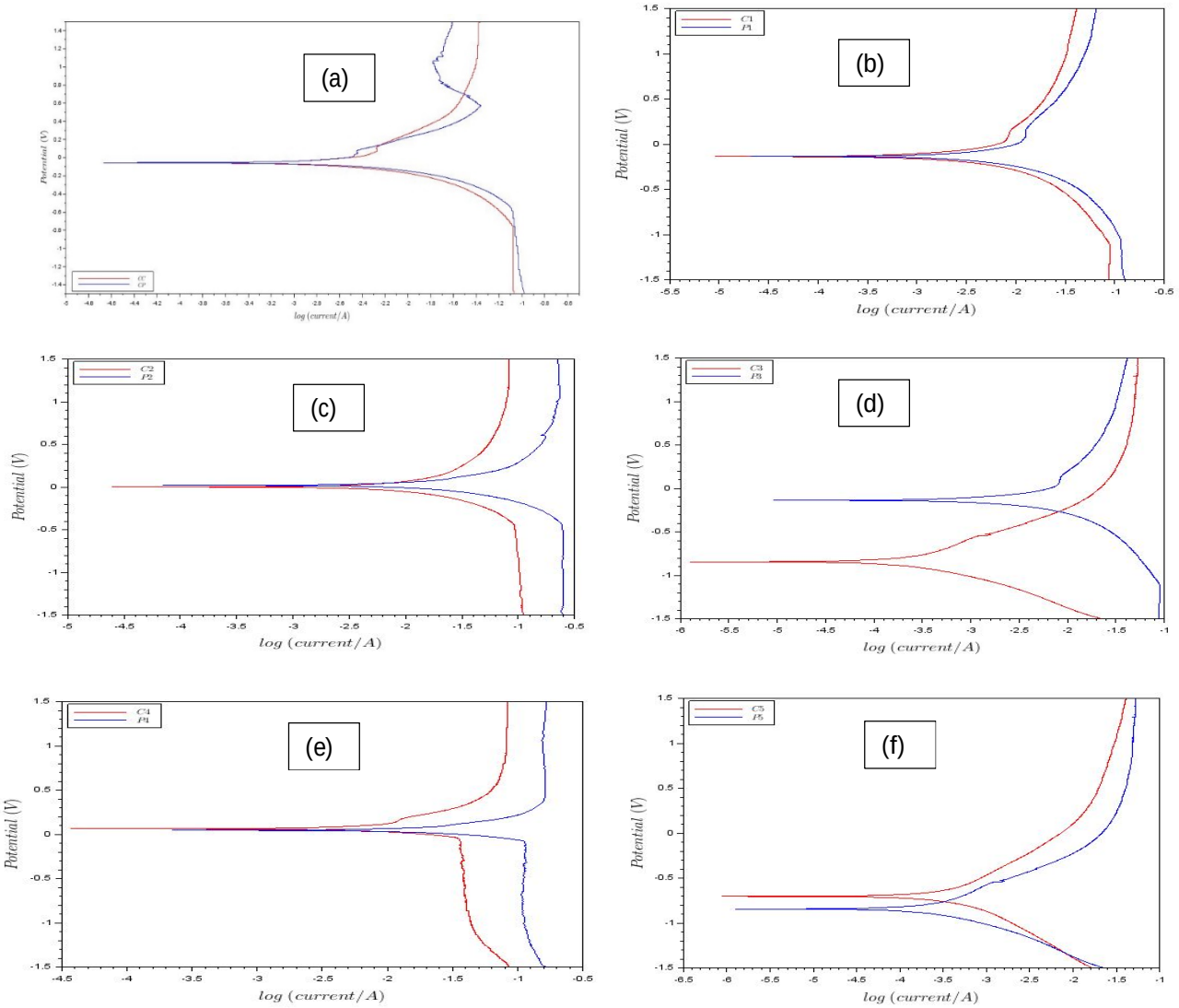
In Fig. 3d, $I_{corr.}$ of P3 decreases to 109.54 $\mu A/cm^2$ with -8 mV_{SCE} increase in $E_{corr.}$ postulating that passive corrosion products resides on the surface and slow down its $R_{corr.}$ (26.98 mils/yr.). The anodic partial curve of sample P3, which has a comparatively low passive I_{corr}, suggests high corrosion resistance under pig slurry conditions. Sample C3 exhibits a lower $E_{corr.}$ (-16 mV_{SCE}) and higher $I_{corr.}$ (6,189.7 $\mu A/cm^2$) indicating a higher tendency for corrosion. However, both C3 and P3 samples have wide difference in $E_{corr.}$ and $I_{corr.}$ with P3 possessing a better $R^1_{corr.}$ than C3, which could be ascribed to corrosive constituents of the cattle slurry.

In Fig. 3e, C4 (with $E_{corr.}$ as 74 mV_{SCE} and $I_{corr.}$ as 41.61 $\mu A/cm^2$) and P4 (with $E_{corr.}$ as 63 mV_{SCE} and $I_{corr.}$ as 10,720 $\mu A/cm^2$) exhibit higher $E_{corr.}$ and $I_{corr.}$ with time. Comparatively, C4 after 56 days in cattle slurry possessed a lower $I_{corr.}$ (41.61 $\mu A/cm^2$) indicating better $R^1_{corr.}$ than P4 sample with higher $I_{corr.}$

In Fig. 3f, P5 curve shifted upward leading to an increase of $E_{corr.}$ to -645 mV_{SCE} and decrease in $I_{corr.}$ to 213.73 $\mu A/cm^2$ compared with sample C5 with a low $E_{corr.}$ of -704 mV_{SCE} and high $I_{corr.}$ of 233.7 $\mu A/cm^2$ due to corrosion effects of slurry. The changes in corrosion parameters indicate that P5 possesses better and high $R^1_{corr.}$ than C5 after 70 days in pig slurry.

Sample P6 in Fig. 8g possess better $R^1_{corr.}$ (high $E_{corr.}$ of -810 mV_{SCE} and low $I_{corr.}$ of 161.421 $\mu A/cm^2$) than C6 (low $E_{corr.}$ of -874 mV_{SCE} and high $I_{corr.}$ of 267.41 $\mu A/cm^2$) indicating higher corrosion susceptibility. Both samples (C6 and P6) show that polarization occurs at the cathode branch and hence, $R_{corr.}$ are cathodically controlled. The anodic and cathodic reactions were significantly accelerated by AD slurry. Thus, the plots' ability to repassivate is diminished with time, resulting in increased corrosion.

In Fig. 3h, $E_{corr.}$ and $I_{corr.}$ for C7 and P7 gave negative values showing that polarization occurred at cathode region. Comparing corrosion parameters of C7 ($I_{corr.}$ of 148.023 µA/cm^2 and $E_{corr.}$ of -628 mV_{SCE}) and P7 ($I_{corr.}$ as 194.52 µA/cm^2 and $E_{corr.}$ of -734 mV_{SCE}), C7 possess a better $R^1_{corr.}$ in cattle slurry than P7.
In Fig. 3j, it was noted that increase in time generated significant changes in corrosion parameters ($E_{corr.}$, $I_{corr.}$, β_a, β_c and $R_{corr.}$) of samples in pig slurry compared with samples in cattle slurry. The modifications could be attributable to the biogas produced after 84 days, which accelerated R_{corr}. Samples in pig slurry had lower passive I_{corr}. than samples in cow slurry.



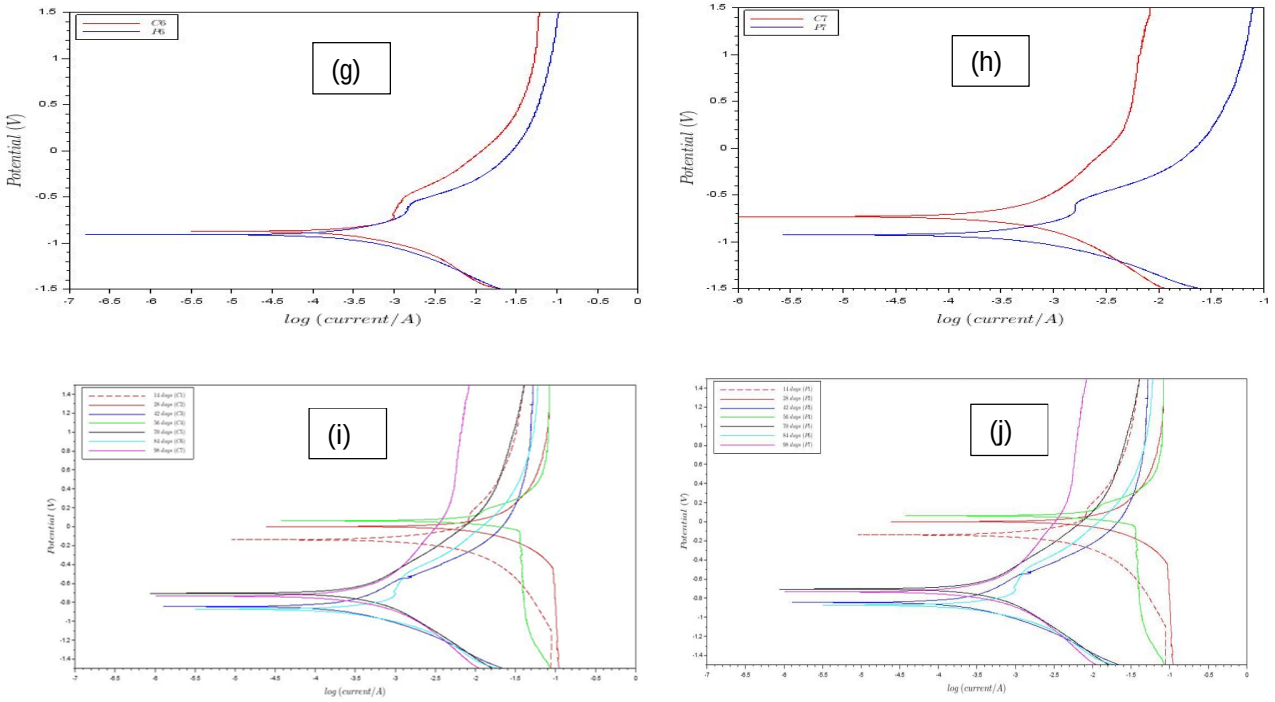


Fig. 3: Tafel of samples in cattle and pig slurries. (a) Control samples, (b) C1 and P1 in 14 days, (c) C2 and P2 after 28 days, (d) C3 and P3 after 42 days, (e) C4 and P4 after 56 days, (f) C5 and P5 after 70 days, (g) C6 and P6 after 84 days, (h) C7 and P8 after 98 days, (i) plots of all samples in cattle slurry, (j) All samples in pig slurry

b. OCP-T Polarization Measurements

Fig. 4a to j exhibit the OCP-T of all samples at different time intervals. In Fig. 4a, $E_{corr.}$ of CC (-79.7 mV_{SCE}) and CP (-78.1 mV_{SCE}) show negative shift, which reveals that most and significant variation in corrosion parameters occur at the initial time. The samples show low tendency for corrosion after 14 days in slurry. $E_{corr.}$ for CC and CP increased during the initial immersion time, then became relatively stable with time. Figure 4b has a negative E_{corr}, indicating a lesser potential for corrosion. As a result, causes for delayed corrosion might be attributed to the production of passive iron oxides, which increased with immersion time.

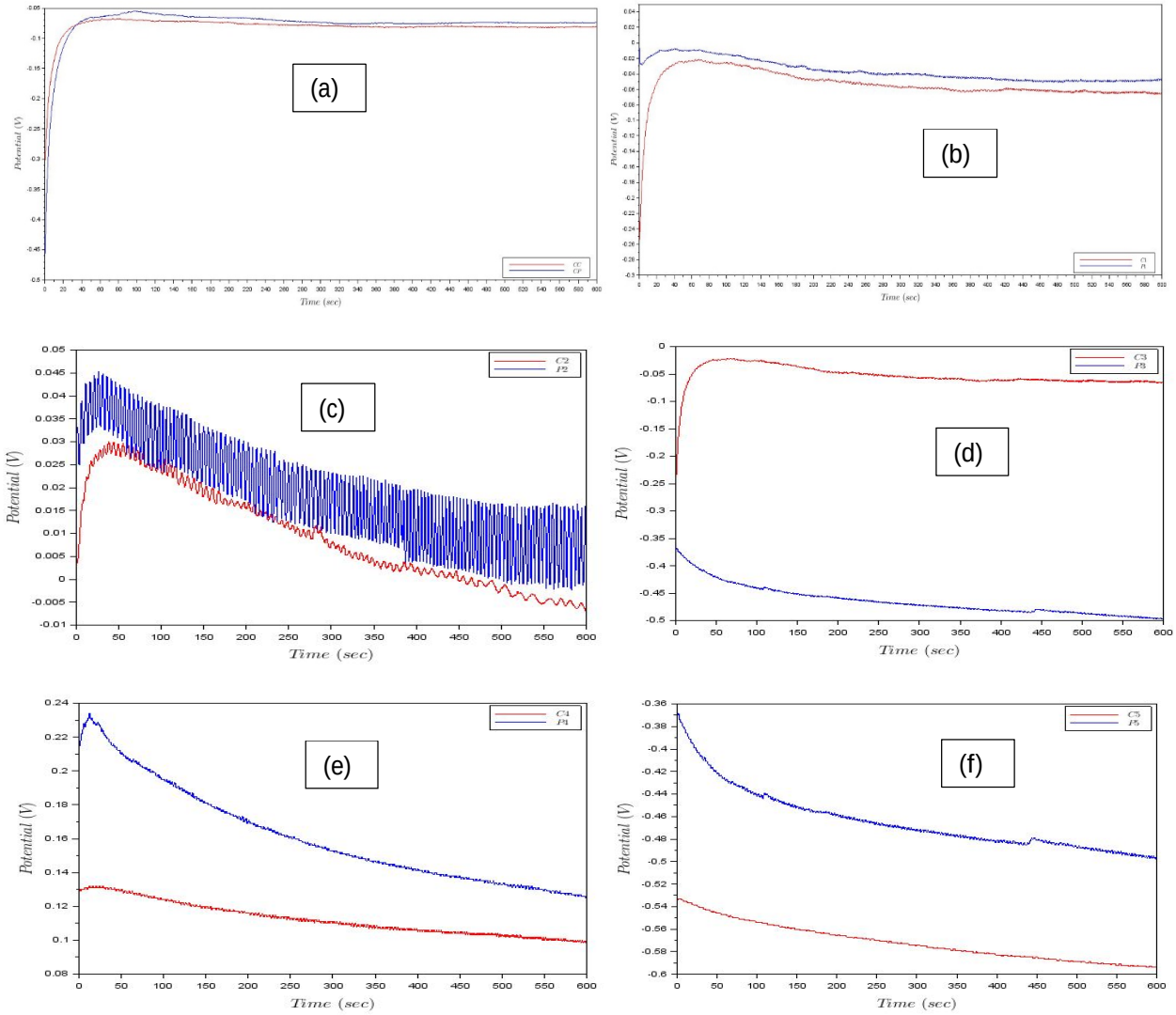
Figure 4c of C2 and P2 depict pitting corrosion features at positive $E_{corr.}$ before passivating. Sample P2 peaked at $E_{corr.}$ of 44.5 mV_{SCE} before passivation and dropped at 7.1 mV_{SCE} indicating pitting corrosion whereas C2 peaked at $E_{corr.}$ of 29.6 mV_{SCE} and dropped at $E_{corr.}$ of 6.3 mV_{SCE} showing high corrosion tendency. Pitting corrosion was detected on P2 rather than C2, which could be related to slurry effects on mild steel material. The $E_{corr.}$ of the samples in Figure 4d gave negative values at cathodic branch showing lower tendency for corrosion. $E_{corr.}$ of P3 peaked at -375 mV_{SCE} before passivating showing better $R^1_{corr.}$ than C3.

The P3 curve climbed swiftly at first and then fell sharply, meanwhile, $E_{corr.}$ for C3 increased from -227.6 to 71.1 mV_{SCE} with time. Fig. 4e shows that increase in time generates a significant change in $E_{corr.}$ of C4 and P4. P4 shows a high $E_{corr.}$ at 234.5 mV_{SCE} and distinct drop at 126 mV_{SCE} indicating passivation. Meanwhile, E_{corr} (131.8 mV_{SCE}) of C4 shows minor changes and eventually settles at E_{corr} of 99mV_{SCE}.

Fig. 4f demonstrates better anti-corrosion performance of both samples with negative E_{corr}. The passivation of both samples could be connected to corrosion products caused by action of slurry constituents. P5 showed a negative shift in E_{corr} with pitting corrosion indications compared to C5. In Fig. 4g, linear plot was observed at C6 with initial $E_{corr.}$ of 364.1 mV_{SCE} with increase at 367.3 mV_{SCE} and a final declined at 374.7 mV_{SCE}. It may be attributable to corrosion from cow slurry, which made

its $E_{corr.}$ consistently greater than P6. The $E_{corr.}$ of P6 decreases at 359.7 mV_{SCE} before passivating at -447.1 mV_{SCE} demonstrating a higher $R^1_{corr.}$ than C7.

In Fig. 4h, $E_{corr.}$ value for C7 peaked at 475.5 mV_{SCE} and dropped at -0.5047 mV_{SCE} before passivation showing better $R^1_{corr.}$ compared to P7. Sample P7 exhibits linear curve at $E_{corr.}$ of 396.8 mV_{SCE} with drop at 410.3 mV_{SCE} indicating general corrosion with pitting. Fig. 4i and j depict OCP-T of all samples in cattle and pig slurries after 98 days respectively. Some samples exhibited general corrosion features due to slurry effects whereas some exhibited passivation due to corrosion products. Figure 9j shows that samples in slurries on the 14th, 42nd, 70th, 84th, and 98th days had negative E_{corr}, indicating general corrosion, whereas samples on the 28th and 56th days had positive E_{corr}, indicating passivation.



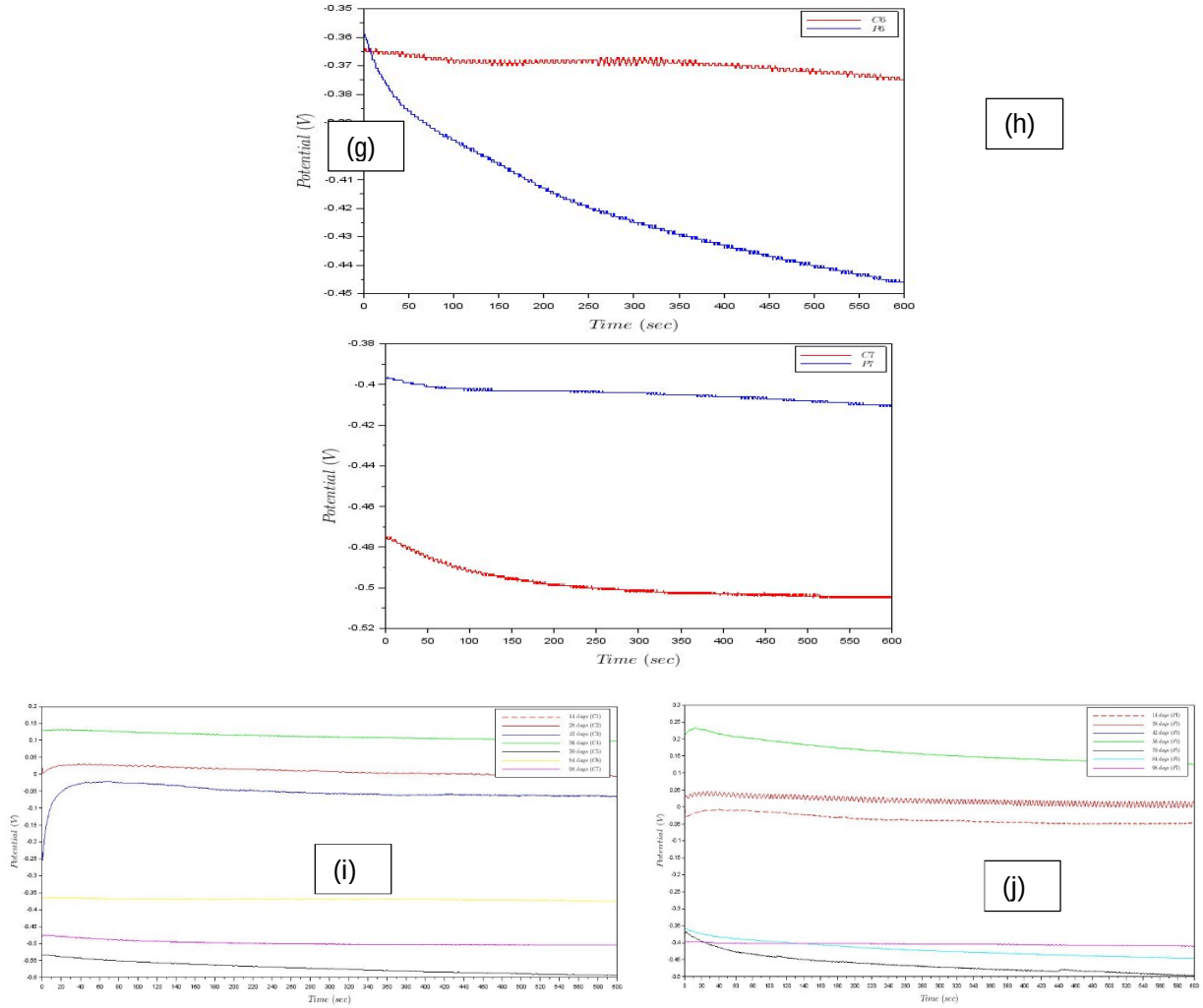


Fig.4: OCP-T of samples (a) Control sample, (b) C1 and P1 after 14 days, (c) C2 and P2 after 28 days (d) C3 and P3 after 42 days, (e) C4 and P4 after 56 days, (f) C5 and P5 after 70 days, (g) C6 and P6 after 84 days (h) C7 and P8 after 98 days immersion (i) plots of all samples in cattle slurry (j) plots of all samples in pig slurry

c. Comparison of Corrosion Rate of the Samples

Corrosion of mild steel is primarily determined by two factors: $R_{corr.}$ that is related to $I_{corr.}$ and corrosion tendency that is represented by E_{corr} (Roberge, 2008) (Kelly, Scully, Shoesmith, & Buchheit, 2003). In Table 5, $R_{corr.}$ for C1 (240.9 mils/yr. at pH of 5.61) declined in 14 days and further increased from 28th day (1,619 mils/yr. at pH of 4.32), 42th day (1,380 mils/yr. at pH of 4.17) to 56th day (1,529 mils/yr. at pH of 3.75). The $R_{corr.}$ declined to the 70th day (53.49 mils/yr. at pH of 3.45), 84th day (61.20 mils/yr. at pH of 3.25) to 98th day (30.79 mils/yr. at pH of 3.14). It has been revealed that high temperature (low pH) increases chemical passivity of a solution and $R_{corr.}$ of the material (Pourbaix, Aguiar, & Clarinval, 1993). The high $R_{corr.}$ of C2, C3 and C4 could be linked to the high temperature of the slurry, while low $R_{corr.}$ of sample C1, C5, C6 and C7 could be connected to corrosion products formed during the immersion.

Table 5: Corrosion rate of samples in cattle slurry after 98 days

Sample	CC	C1	C2	C3	C4	C5	C6	C7
Time (day)	0	14	28	42	56	70	84	98
Temperature (°C)	25.0	24.2	24.4	24.7	24.0	23.8	23.5	24.5
pH value	6.35	5.61	4.32	4.17	3.75	3.45	3.25	3.14
$R_{corr.}$ (mils/yr.)	692.2	240.9	1,619	1,380	1,529	53.49	61.20	30.79

The $R_{corr.}$ of samples in pig slurry (as shown previously) decreased drastically at14th (571.6 mils/yr. at pH of 6.05) and 42th day (26.98 mils/yr. at pH of 5.15), and further increased at 28th day (2,542 mils/yr. at pH of 5.67). Also, there was a decrease of $R_{corr.}$ at 70th (48.9 mils/yr.) and 84th day (36.93 mils/yr.) to 98th day.

Table 6: Corrosion rate of samples in pig slurry after 98 days

Sample	CP	P1	P2	P3	P4	P5	P6	P7
Time (day)	0	14	28	42	56	70	84	98
Temperature (°C)	25.3	23.7	24.2	24.5	24.4	23.5	3.92	3.70
pH value	6.46	6.05	5.67	5.15	4.81	4.46	3.92	3.70
$R_{corr.}$ (mils/yr.)	1,223	571.6	2,542	26.98	3,741	48.9	36.93	56.76

H. Comparison of Corrosion Resistance of the Samples

Table 7 and 8 show the corrosion parameters ($E_{corr.}$, $I_{corr.}$, $R_{corr.}$, β_a and β_c) of all samples in cattle and pig slurries after 98 days. The tangential lines of anodic and cathodic curves were extrapolated to reach an intersection point to yield $E_{corr.}$, $I_{corr.}$ and Tafel slopes (β_a and β_c) following the standard approach. In Table 7, the average value of $E_{corr.}$ for cattle slurry is -344.29 mV_{SCE}, whereas maximum and minimum values are 54 mV_{SCE} and -874 mV_{SCE}, respectively. The average $I_{corr.}$ in cattle slurry is 3,052.42 $\mu A/cm^2$ with maximum value of 7,076 $\mu A/cm^2$ and minimum of 194.52 $\mu A/cm^2$. The average value of $E_{corr.}$ for pig slurry is -305.86 mV_{SCE}, while maximum and minimum values are 63 mV_{SCE} and -810 mV_{SCE}, respectively.

Table 7: Comparison of corrosion resistance of samples in cattle slurry

Sample Number	Time (day)	$I_{corro.}$ ($\mu A/cm^2$)	$E_{corr.}$ (mV_{SCE})	β_a (mV/dec.)	β_a Range	β_c (mV/dec.)	β_c Range	$R_{corr.}$ (mil/yr)
CC	0	3,024.0	-57	89.198	0.003 to 0.063	306.843	-0.177 to -0.117	692.20
C1	14	1,052.0	-137	153.753	-0.077 to -0.017	155.521	-0.257 to -0.197	240.90
C2	28	7,076.0	1	210.305	0.061 to 0.121	187.864	-0.119 to -0.059	1,619.0
C3	42	6,189.7	-16	189.863	0.044 to 0.104	10,967.21	-0.136 to -0.076	1,380.0
C4	56	6,681.0	74	41.610	0.123 to 0.183	12,987.03	-0.057 to 0.003	1,529.0
C5	70	233.70	-804	226.347	-0.644 to -0.584	187.582	-0.824 to -0.764	53.49
C6	84	267.41	-874	217.155	-0.814 to -0.754	157.307	-0.994 to -0.934	61.20
C7	98	194.52	-734	260.824	-0.674 to -0.614	112.032	-0.854 to -0.794	30.79
Average	-	3,052.42	-344.29	-	-	-	-	-
Maximum	-	7,076.0	54	-	-	-	-	-
Minimum	-	194.52	-874	-	-	-	-	-

Table 8: Comparison of corrosion resistance of samples in pig slurry

Sample Number	Time (day)	$I_{corro.}$ ($\mu A/cm^2$)	$E_{corr.}$ (mV_{SCE})	β_a (mV/dec)	β_a Range	β_c (mV/dec)	β_c Range	$R_{corr.}$ (mil/yr)
CP	0	5,353.0	-56	122.160	0.004 to 0.064	302.939	-0.176 to -0.116	1,223.0
P1	14	2,498.0	-133	183.959	-0.076 to -0.016	162.443	0.256 to -0.196	571.60
P2	28	6,110.0	20	211.730	0.080 to 0.140	171.999	-0.100 to -0.040	2,542.0
P3	42	109.540	-8	297.875	0.052 to 0.112	170.873	-0.128 to -0.068	26.98
P4	56	10,720.0	63	174.490	0.105 to 0.165	172.414	-0.075 to -0.015	3,741.0
P5	70	213.730	-645	130.429	-0.785 to -0.725	248.139	-0.965 to -0.905	48.90
P6	84	161.421	-810	164.940	-0.850 to -0.790	148.302	-1.030 to 0.970	36.93

P7	98	148.023	-628	181.851	-0.868 to -0.808	156.152	-1.048 to -0.988	56.76
Average	-	2,851.53	-305.86	-	-	-	-	-
Maximum	-	10,720.0	63	-		-	-	-
Minimum	-	148.023	-810	-	-	-	-	-

In Table 8, the average $I_{corr.}$ of samples in pig slurry is 2,851.53 µA/cm^2 whereas maximum and minimum values gave 10,720 µA/cm^2 and 148.023 µA/cm^2 respectively. After 98 days, $E_{corr.}$ at -734 mV_{SCE} for cattle gave $I_{corr.}$ of 194.52 µA/cm^2 and for pig, at -628 mV_{SCE} with $I_{corr.}$ of 148.023 µA/cm^2. There is corrosion effects which for pig slurry is very high at average of -305.86 mV_{SCE} compared to cattle at -344.29 mV_{SCE}. In contrast, $E_{corr.}$ and $I_{corr.}$ of C1 (-137 mV_{SCE}; 1,052 µA/cm^2), C2 (1 mV_{SCE}; 7,076 µA/cm^2), C3 (-16 mV_{SCE}; 6,189.7 µA/cm^2), C4 (74 mV_{SCE}; 6,681µA/cm^2) after 14, 28, 42 and 56 days in cattle slurry respectively and P1 (-133 mV_{SCE}; 2,498 µA/cm^2), P2 (20 mV_{SCE}; 6,110 µA/cm^2) and P4 (63 mV_{SCE}; 10,720 µA/cm^2) respectively after 14, 28, 56 days in pig slurry respectively, show higher $I_{corr.}$.

Anodic partial curves of sample C5, C6, C7, P5, P6 and P7 have relatively passive $I_{corr.}$ 233.70 µA/cm^2, 267.41 µA/cm^2, 194.52 µA/cm^2, 213.730 µA/cm^2, 161.421 µA/cm^2 and 148.023 µA/cm^2 respectively. The least impact of $R_{corr.}$ (26.98 mils/year) was observed on P3 followed by C7 (30.79 mils/year). This could be attributed to low corrosive matters in pig waste with 6.13% protein than cattle with 5.70% protein. In Table 7 and 8, $I_{corr.}$ of samples in cattle slurry increases from C7, C5, C6, C1, C3, C4 to C2 while $E_{corr.}$ increases from C6, C7, C5, C1, C3, C2 to C4. C7 (194.52 µA/cm^2) possesses the highest $R^1_{corr.}$ followed by C5, C6 and C1 while $E_{corr.}$ of C6 and C7 are the lowest showing higher corrosion susceptibility in cattle slurry.

$E_{corr.}$ of samples in pig slurry increases from P6, P5, P7, P1, P3, P2 to P4 while $I_{corr.}$ increases from P3, P7, P6, P5, P1, P2 to P4. P3 (109.540 µA/cm^2) possesses highest $R^1_{corr.}$ followed by P7, P6 and P5 compared to P1, P2 and P4 while $E_{corr.}$ of P6 and P5 are the lowest indicating higher tendency for corrosion. $E_{corr.}$ of sample in cattle slurry after 98 days was -734 mV_{SCE} with $I_{corr.}$ of 194.52 µA/cm^2. This clearly demonstrates a higher tendency to corrosion compared to pig slurry (-628 mV_{SCE} with $I_{corr.}$ of 148.023 µA/cm^2). Hence, passive $I_{corr.}$ ratio measured in cattle to pig slurry after 98 days is 1.134 (194.52 µA/cm^2/148.023 µA/cm^2).

IV CONCLUSION

Mild steel (MS) was chosen for the investigation because of its availability, low cost, and satisfactory mechanical qualities (weldability, fabricability and formability). Meanwhile, cattle and pig waste are being considered for the experiment because they are commonly used in the production of biogas energy. The reacting compositions of the waste were determined to be moisture, protein, NH_3, CO_2, K, $(NH_4)_2SO_4$, Mg, N, Na and Ca. Compositions of moisture (62.20%), $(NH_4)_2SO_4$ (6.63%), CO_2 (24.04 mg/kg) and NH_3 (2.25%) in cattle waste were higher than pig with 39.75% moisture, 4.34% $(NH_4)_2SO_4$, 18.03 mg/kg CO_2 and 1.12% NH_3. The cattle waste with 5.70% protein was found to be more aggressive of the media whereas pig with 6.13% protein, was less corrosive medium. Various corrosion tests carried out (chemical compositions, SEM, EDS, Tafel and OCP-T) showed that samples in pig slurry possessed better $R^1_{corr.}$ than samples in cattle slurry. The SEM micrograph of the samples in the waste for different retention periods showed evidence of different degrees of corrosive effects of cattle and pig slurries on MS which progresses with time. There were both general and localized corrosion on the samples. It was also discovered that an increase in time caused considerable changes in corrosion parameters ($E_{corr.}$, $I_{corr.}$, β_a, β_c and $R_{corr.}$) samples in pig slurry compared to samples in cattle slurry, which might be attributable to biogas produced after 84 days. As a result, the mild steel AISI 1020 material was found to be unsuitable for animal waste digestion in the absence of some inhibitors.

REFERENCES

Akdogan, A., & Eker, B. (2000). The Effects of Corrosion on Agricultural Machinery and Prevention Methods. *Denizli Material Congress.* Turkey.

Elliot, P., Foister, C. M., Johnson, J. B., & Wood, G. C. (1983). Corrosion and materials degradation in the agricultural industry. *The Agricultural Engineers, 38*, 13-20.

Englert, G. E., & Muller, I. L. (1996). The Corrosion Behavior of Mild Steel and Stainless Steel in an Anaerobic Biodigester. *International Biodeterioration and Biodegradation, 37(3-4)*, 173-180.

Furhman, R. E. (1949). Digester Corrosion Problems. *Sewage Work Journal, 21, No. 4*, 725-728.

Hassler, J. W. (1995). A Laboratory Approach to the Study of Digester Corrosion. *TAPPI JOURNAL, 38 (5),* 265-274.

Hopper, E. (1953). Some Observations on the Causes and Prevention of Digester Corrosion. *TAPPI Journal, 36, No. 8,* 345-352.

Kelly, G. R., Scully, R. J., Shoesmith, W. D., & Buchheit, R. G. (2003). *Electrochemical Techniques in Corrosion Science and Engineering*. New York: Marcel Dekker, Inc.

Okeke, C. E. (2001). Renewable Energy Technology Development in Nigeria. *Paper presented at a National Workshop on Creating Demand and Removing Barriers to Renewable Energy Marked Development in Nigeria,* (pp. 13-14). Sheraton Hotels and Towers Abuja.

Okoroigwe, E. C., Ibe, C. N., & Ezema, C. G. (2014). Experimental Study of Anaerobic Digestion of Dog Waste. *Scientific Research and Essays, 9(6),* 121-127.

Okoroigwe, E. C., Ibeto, C. N., & Okpara, C. G. (2010). Comparative Study of Potential of Dog Waste for Biogas Production. *Trends in Applied Sciences Research , 5(1),* 71-99.

Okoroigwe, E. C., Iloeje, O. C., Enibe, S. O., & Eze, J. I. (2006). Design, Construction and Performance Evaluation of a 1200 liter Plastic Biodigester. *Nigeria Journal of Solar Energy, 16,* 170-186.

Oparaku, N. F., Ofomatah, A. C., & Okoroigwe, E. C. (2013). Biodigestion of Cassava Peels Blended with Pig Dung for Methane Generation. *African Journal of Biotechnology, 12 (40),* 5956-5961.

Ostlund, O., Emerfeldt, B. S., & Linder, M. (1989). Investigations Regarding Corrosion in Batch Digesters . *Proceedings Sixth International Symposium on Corrosion in the Pulp and Paper Industry* . Helsinki, Pp. 48-59 .

Parker, W. B. (1955). A Review of Digester Corrosion Causes. *TAPPI Journal, 38, No. 5,* 261-264.

Pfeiffer, L. G., Scheil, M. A., & Schmidt, E. H. (1955). Design Features Affecting Digester Corrosion . *TAPPI Journal, 38, No. 11,* 652-659.

Pourbaix, A., Aguiar, L. E., & Clarinval, M. C. (1993). Advances in Corrosion and Protection. Manchester, United Kingdom: Corrosion Science.

Roberge, P. R. (2008). *Corrosion Engineering: Principles and Practice.* New York: McGraw-Hill Companies Inc.

Robert, C., & Anders, H. (2017). Corrosion in Digesters. *Water Environment and Technology, 32,* 1-20.

Troselius, L. (1995). Field Exposure of Carbon Steel and Stainless Steel in Digesters. *Procedure Eighth International Symposium on Corrosion in the Pulp and Paper Industry.* Stockholm, Pp. 46-57.

Ungar, A., & Caywood, T. E. (1954). Comparative Analysis of Digester Corrosion Measurements. *TAPPI Journal, 37, No. 3* , 177-190.

Wensley, A. (1997). Materials for Fabrication and Repair of Batch Digesters. *NACE Corrosion 98 Conference.*

Wensley, A. (1998). Corrosion of Batch and Continuous Digesters. *Paper Presented at the Ninth International Symposium on Corrosion in the Pulp and Paper Industry.* Ottawa, Canada.

Wensley, A. (2000). Corrosion of Carbon Steel and Stainless Steel in Digesters. *Presented at the NACE Corrosion 2000 Conference in Orlando, Florida, Paper No. (589), Pp. 1-14.*

Wensley, A., & Dykstra, H. (1997). Corrosion of Batch Digesters. *Procedure TAPPI Engineering and Papermakers Conference,* 1527-1536.

Wensley, A., Moskal, M., & Wilton, W. (1997). “Materials Selection for Batch Digesters,” . *NACE Corrosion 97 Conference; Paper No. (378).*

