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Environmental and Microbial Influences on Corrosion of Selected Types of Petroleum Industry Steel

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ABSTRACT

This study explored the influence of brackish water sediment, mangrove swamp sediment, clayey/lateritic soil, and river water (freshwater) sediment on the corrosion rates of carbon, mild, and stainless steels and the species of sulphate reducing bacteria (SRB) and iron bacteria associated with the process. The material loss following burial of the steel samples for a 9-month period was assessed. Standard and specialised microbiological techniques were employed in the characterisation of the bacterial species. Qualitative assessment for corrosion was done via optical microscopy and macroscopy. Corrosion was highest on steel buried in brackish water sediment and lowest in that from river water sediment. Carbon steel was the most susceptible to corrosion while stainless steel was the most resistant. Sulphite, sulphide, nitrate and phosphate concentrations had a strong impact on corrosion rates. Thiobacillus, Leptothrix and Gallionella dominated amongst the iron bacteria while Desulfobacter and Desulfovibrio dominated amongst the SRB. There were significant differences in corrosion rates and bacterial abundance from one environment to the other. Iron bacteria showed greater abundance than SRB across the different environments and steel types. Iron bacteria counts, however, did not correlate positively with corrosion rates. The findings suggest that oil industry facilities in brackish water environments are more liable to corrosion than those located in fresh water ecosystems.

1. INTRODUCTION

Corrosion is a naturally occurring electrochemical process driven by physical, chemical or biological processes working in synergy. Environmental stimuli around the metal are the most common triggers of physicochemical corrosion. Properties like characteristics of the metal, chloride and SO₂ deposition rates, temperature, humidity, pH, salinity and length of exposure are key initiators of physical and chemical corrosion in steel installations (Yan et al., 2020). Biological corrosion, more commonly tagged microbially influenced corrosion (MIC), is the irreversible deterioration of metal by the activities of microorganisms. It is also termed biocorrosion. MIC results from the combined action of microbial cells, their cellular metabolites, the metal surface and environmental factors (Maluckov, 2012). Groups of microorganisms will often adhere to surfaces via biofilms; MIC then ensues beneath these biofilms via mechanisms like direct electron transfer, cathodic depolarization, build-up of a concentration gradient or galvanic cell formation (Akpan and Iliyasu, 2015; Da Silva et al., 2019). Microbial involvement has been reported to speed up corrosion rates by up to ten times (Liu and Cheng, 2018).

Steel is the material of choice for oil and gas and marine installations. It is used for the construction of platforms and transportation infrastructure for the conveyance of petroleum and water amongst other uses. Most pipelines are constructed with carbon steel. Although highly prone to corrosion and attack by microbes, carbon steel is preferred as it succumbs easily to welding, endures bending well and is less liable to cracking under stress. Furthermore, it is considered durable and of relatively low cost. Mild steel and stainless steel, though not as popular as carbon steel, are also used. Stainless steel is considered expensive and less malleable. The

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susceptibility of steel to corrosion is a chief concern in oil and gas plants as the maintenance of failed pipelines and fittings is often not only expensive but challenging. This is especially true of sub-surface instalments. Mechanical failure with regards to pipelines is usually corrosion-related in form of rupture from loss of wall thickness or fracturing (Hou et al., 2016; Valencia-Cantero and Peña-Cabriales, 2014). Corrosion of carbon steel was reported to be about 6 times greater when SRB are involved with the corrosion pit depth 7.7 times deeper than without SRB (Liu et al., 2019).

Research establishes a 4% and 20% reduction in national Gross Domestic Product (GDP) in developing and developed countries respectively due to corrosion in industry (Kruger, 2011; Hou et al., 2017; Fayomi et al., 2019). Arena-Ortiz et al. (2019) place the global corrosion cost including management measures at \$4 trillion. In 2011, corrosion accounted for \$13.4 billion in annual expenses in the US petroleum industry with biocorrosion consuming \$2 billion of the sum (Bermont-Bouis et al., 2007). Corrosion has been implicated in most cases of pipeline failure in the Gulf of Mexico (Arena-Ortiz et al., 2019). In the global oil and gas sector it is estimated that for 50% of buried installations and about 40% of internal pipelines, MIC accounts for the observed corrosion. For anaerobic environments, the total value for both is lower at about 20% (Bano and Qazi, 2011; Rasheed et al., 2019).

Sulphate Reducing Bacteria (SRB), Sulphate Oxidising Bacteria (SOB), Iron Oxidising Bacteria (IOB), Iron Reducing Bacteria (IRB), manganeseoxidisers and acid-producing bacteria are the main microbial groups involved in MIC (Beech and Gaylarde, 1999; Bano and Qazi, 2011; Akpan and Iliyasu, 2015). Khouzani et al. (2019) opine that SRB are the main culprits in severe biodeterioration and rupture of buried pipelines. SRB are anaerobic and so where oxygen is present, they tend to occur underneath deposits of soil, sediment or rust on the pipeline or even beneath an already formed biofilm creating the oxygen-deficient microenvironment they require (Liu et al., 2019). Iron bacteria are a group of aerobic bacteria that generate energy by oxidation of ferrous ions as a key part of their metabolism (Bryce et al., 2018). They are the main culprits of rust deposits on metals and are known to cause corrosion by creating an oxygen gradient which splits the metal surface to which the biofilm is attached into small anodic sites surrounded by larger cathodic areas. They are more

commonly associated with the crevice type of corrosion (Beimeng et al., 2015). SRB and iron bacteria often co-exist on buried metal infrastructure and tend to exert a more aggressive corrosive effect as a team than as individual colonisers of the metal surface (Valencia-Cantero and Peña-Cabriales, 2014).

An understanding of the varying influences on the rate of corrosion of steel is essential to predicting its longevity and suitability for purpose. In this study, corrosion of three types of steel used in the petroleum industry was analysed using microscopic assessment and weight loss to establish corrosion rates relative to environmental conditions. Furthermore, the species of autochthonous SRB and iron bacteria associated with the observed corrosion were determined.

2. METHODOLOGY

2.1 Sample sites

The sediment/ soil for this study were mangrove swamp sediment, brackish water sediment, fresh (river) water sediment and clayey/lateritic soil. All the mangrove swamp and brackish water sediment samples were collected from Eagle Island in Nkpolu area of Port Harcourt, Rivers State. The freshwater sediment samples were obtained from the New Calabar River, Choba, Nigeria. The sampling site for the ochre-coloured clayey/lateritic soil was the Postgraduate Hall of Abuja campus, University of Port Harcourt.

2.2 Study design

The study was field based. The steel samples were placed in fabricated wide-mesh plastic baskets before being buried to a depth of 1 m, similar to the minimum depth for pipelines, for a period of 9 months. The baskets were for ease of location and retrieval while allowing the bars to be in complete contact with the environment on all sides. Sediment or soil samples from the area around the metal bars were taken before and during retrieval for physicochemical and microbiological analysis. Sampling was done in triplicates.

2.3 Sample collection

2.3.1 Steel samples

Three types of structural grade customised steel bars were used to monitor the rate of corrosion in the environment-carbon steel ASTM A36, mild steel ASTM A283 and stainless steel ASTM A316L. The samples were supplied by Sirpi AluSteel Construction Ltd., Trans-Amadi Industrial layout, Port Harcourt, Nigeria. The bars measured $80 \text{ mm} \times 25 \text{ mm} \times 6 \text{ mm}$. The minimum recommended pipeline thickness is

6.35 mm (0.25 in). The mechanical properties of the steel bars used are described in Table 1.

Table 1. Mechanical Properties	of the	Metal	Samples
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Sample	CS ASTM A36	MS ASTM A283	SS ASTM A316L
Туре	Structural quality carbon	Structural quality carbon	Austenite
Condition of steel	AS Rolled	AS Rolled	Annealed
Tensile strength (KSI)	58-80	55-60	75 minimum
Yield strength (KSI)	36 minimum	30 minimum	30
% Elongation in "2"	23	25	60 minimum
% Elongation in "8"	20	22	65
Approx. Brinell hardness	137	133	180
Carbon content (%)	0.26-0.29	0.24	0.03

CS=Carbon steel; MS=Mild steel; SS=Stainless steel

The steel bars of known weight were first degreased using analytical grade acetone and then rinsed with distilled water. This was followed by sterilisation by immersion in ethanol for 30 sec. They were then dried and kept desiccated (Rasheed et al., 2019). The final weights of the steel bars in the desiccator were determined prior to burial.

2.3.2 Soil/sediment sample collection

Samples of soil and sediment were collected for analyses prior to burial of the steel bars and after their retrieval. The soil samples were collected for analyses using a hand trowel and put in heat resistant plastic bottles. Sediment samples were obtained using a sediment grab. Water samples were collected using a 1 L clean plastic container. All the samples were appropriately labelled with date, time and place of collection.

2.4 Determination of physicochemical parameters

physicochemical parameters The were measured in the environments before burial and at retrieval. Salinity was determined using a digital salinometer (Hanna Instruments), while for pH, a pH meter (Wintab digital pH meter, Germany) was used. The sulphate (SO_4^{2-}) , sulphite (SO_3^{2-}) and sulphide (S^{2-}) concentrations were determined using the method of Fogg and Wilkinson (1952). The ferric ion (Fe^{3+}) concentration was measured using the ferrozine assay. Electrical conductivity was determined using a benchtop combination meter. The nitrite (NO2-) and nitrate ion (NO3-) content was measured using the spectrophotometric method described by Narayana and Sunil (2009). The combined modified methods of spectroscopy and molybdenum blue phosphorus

method of Kharat and Pagar (2019) was used for analysis of phosphate ion (PO_4^{3-}) content.

2.5 Determination of loss in material and corrosion analysis

The outer debris on the steel bars was carefully rinsed off with distilled water. Following removal of any attached biological material via probe sonication and drying in an oven (ThermoFisher Scientific PR305225M, USA) at 70°C for 15 min, the dimensions of the bars were determined using calipers and a ruler. The weights of the steel bars were measured as well using an analytical balance (Mettler Toledo New Classic ML204T, Switzerland). The Area was calculated. The volume of the bars was determined using the modified water displacement technique of Hargens et al. (2014).

Corrosion analysis was via the weight loss technique. Assuming uniform corrosion over the entire surface of the bars, the corrosion rate in millimetre per year was determined using the formula from Daille et al. (2020):

$$CR = \frac{KW}{ATD}$$

Where; CR=corrosion Rate, K is a constant (8.76×10^4) , W=weight loss in grams, A=area in cm², T=time of exposure in hours, and D=density in g/cm³.

2.6 Qualitative analysis of steel bars

The cleaned corroded surfaces of the retrieved bars were observed under the x400 magnification of the optical microscope. Visible (non-microscopic) changes were also recorded.

2.7 Enumeration and characterisation of microorganisms from biofilms

The biofilms formed on the retrieved metal samples were scrapped off using sterile surgical blade. Any possible remaining biological material was extracted by sonification. The scrapings were collected in sterile bottles containing about 5 mL phosphate buffered saline at pH 7. Following fourfold serial dilution, 1 mL aliquots were plated out on specialised media in triplicates using the pour plate technique. Discrete colonies were purified by streaking unto fresh media. Pure cultures were preserved on relevant media slants for further investigation.

The iron bacteria medium described by APHA (2012) at pH 5.0 was used for the isolation of iron bacteria. Incubation was at room temperature for 7-14 days. Postgate B medium was used for the isolation of the sulphate reducing bacteria, SRB. Inoculation was done via the tube method. After inoculation, the tubes were rapidly cooled with screw caps to seal the tubes to prevent aeration and dehydration of the medium. The cultures were incubated at room temperature in an anaerobic jar containing Gas Pak for about 4 weeks with regular observation for the black colonies representative of sulphate reducing bacteria (SRB).

The abundance of the SRB and iron bacteria isolates was determined in colony forming units per

gram (CFU/g) using an automated colony counter. Identification of the isolates was on the basis of cell morphology and cultural and biochemical characteristics. Apart from the microscopic observation of the cells and observation of colony characteristics, several standard biochemical tests were employed in the characterisation of the isolates; some of the tests include Gram's staining, urease production, lysine utilisation, nitrate reduction, hydrogen sulphide production, citrate utilisation, motility, methyl red, Voges Proskauer reaction, ornithine utilisation, gelatine liquefaction, triple sugar iron test, phenylamine deamination, indole production, starch utilisation, catalase reaction, oxidase production, ONPG and utilisation of 10 simple and complex sugars.

2.8 Statistical analysis

The relationship between corrosion rates and SRB and iron bacteria counts and physicochemical parameters from one environment to the other was assessed using Microsoft Excel 2016.

3. RESULTS AND DISCUSSION

3.1 Physicochemical influences

The changes in the physicochemical properties of the different environments studied before burial of the bars and at retrieval are shown in Table 2.

Parameters	Brackish water sediment		Mangrove swamp		Clayey/lateritic soil		River water sediment	
	At burial	At retrieval ^a	At burial	At retrieval ^a	At burial	At retrieval ^a	At burial	At retrieval ^a
pH	7.65	7.10	3.72	6.88	6.27	6.84	6.14	6.05
Salinity (ppt)	15.303	13.000	13.100	10.327	0.011	0.010	0.002	0.001
Conductivity (µS/m)	738	1011	1724	814	212	484	388	548
PO4 ³⁻ (mg/kg)	0.149	1.40	0.0002	0.05	0.0121	0.50	0.0086	0.70
NO ₃ ⁻ (mg/kg)	1.00	93.60	1.10	112.20	1.20	835.70	1.40	54.90
S ²⁻ (mg/kg)	30.40	41.20	29.30	53.60	17.00	32.28	13.30	5.59
SO4 ²⁻ (mg/kg)	0.10	8.29	0.25	3.39	0.25	0.077	0.15	0.219
SO3 ²⁻ (mg/kg)	0.10	7.50	0.25	12.50	0.25	11.00	0.15	11.00
Fe^{3+} (mg/kg)	0.07	7.97	0.02	5.37	0.03	5.54	0.06	34.94
NO2 ⁻ (mg/kg)	0.00	2.20	0.20	0.16	0.20	0.70	0.30	0.59

 Table 2. Observed variation physicochemical characteristics during the study

a=month 9-peak of wet season

A study on biocorrosion by SRB in the Yucatan Peninsula concluded that physicochemical properties have a strong influence on corrosion rates (Arena-Ortiz et al., 2019). In the same vein, Obuekwe et al. (1987) demonstrated extensive pitting of mild steel when ferrous and sulphide ions were being formed concurrently. When only sulphide was produced, corrosion rates first increased and then declined due to the formation of a protective iron sulphide (FeS) film. Gubner and Andersson (2007) and Agarry et al. (2015) both linked corrosion rates to pH levels. It has been found that pH exerts a stronger impact on corrosion

rates than salinity or nitrate concentration with the more acidic pH levels encouraging faster corrosion rates. The observed pH in this current study generally revolved around neutral except in the mangrove swamp sediment where more acidic values were originally observed.

3.2 Observed corrosion, corrosion rates, and environmental influences

The steel samples from brackish water sediment and Mangrove swamp sediment demonstrated the greatest loss in material and the highest corrosion rates. Stainless steel samples fared best having the lowest material loss while carbon steel showed relatively high material loss. Table 3 outlines the mean

Table 3. Mean percentage material loss in the steel samples

percentage material loss in thickness, area, volume and weight observed.

Table 4 highlights the physical changes observed in the different steel samples following retrieval while Figure 1 provides a comparison of corrosion rates across the four environments studied. Carbon steel showed the greatest corrosion rates across the board followed by mild steel. Corrosion rates ranged from 0.07214-0.76505 mm/year, 0.0668-0.55143 mm/year, 0.00991-0.23851 mm/year and 0.00762-0.23038 mm/year for brackish water sediment, mangrove swamp sediment, lateritic soil, and river water sediment, respectively, from stainless steel (lowest observed values) to carbon steel (highest values).

Sample	% Loss in area	% Loss in thickness	% Loss in volume	% Loss in weight	
CS E ₁	5.63	6.86	12.10	2.66	
CS E ₂	5.60	20.59	25.04	2.35	
CS E ₃	1.15	6.13	7.20	1.32	
CS E ₄	0.72	4.68	5.37	0.82	
MS E ₁	1.71	1.12	2.81	1.41	
MS E ₂	2.53	3.66	6.10	0.86	
MS E ₃	0.58	2.84	3.40	0.48	
MS E ₄	0.69	2.22	4.57	0.27	
SS E ₁	0.39	0.004	0.78	0.41	
SS E ₂	0.69	1.69	2.38	0.34	
SS E ₃	1.80	0.00	0.00	0.05	
SS E ₄	0.002	0.20	0.20	0.005	

CS=Carbon steel; MS= Mild steel SS=Stainless steel

E1= Brackish water sediment E2=Mangrove swamp bottom sediment; E3=Clayey/lateritic soil; E4=River Water sediment

Table 4. Qualitative assessment of the retrieved steel bars

Sample	Corrosion-related observations after retrieval						
Carbon Steel A	Carbon Steel ASTM A36						
CS E ₁	Generalised corrosion (iron oxide). Very heavy pitting on most of the surfaces. Presence of crevices. Severe edge corrosion. Presence of sulphide coatings						
CS E ₂	Extensive corrosion. Crevice corrosion and surface corrosion. Deposition of iron oxide as well as sulphide coatings. Pitting significantly present.						
CS E ₃	Generalised surface corrosion. Sulphide coating on one side of the slab surface. Scanty blister formations. Localised deep pitting on one side of the slab surface. Scaling effect along the edges.						
CS E ₄	Generalised surface corrosion with deposition of iron oxide. No pitting or sulphide coating seen. Scaling effect not too severe.						
Mild Steel AS	TM A283						
MS E ₁	Generalised corrosion (iron oxide). Deep pitting, sulphide coating, scaling along the edges.						
MS E ₂	Extensive corrosion. Heavy pitting and skinning effects concentrated around the edges. Presence of sulphide cover.						
MS E ₃	Generalised corrosion. Less pitting and skinning effect. Sulphide cover on one side of the slab. No crevices observed						
MS E ₄	Generalised corrosion, no pitting or skinning						

CS=Carbon steel; MS= Mild steel SS=Stainless steel

E1= Brackish water sediment E2=Mangrove swamp bottom sediment; E3=Clayey/lateritic soil; E4=River Water sediment

Tab	le 4.	Qu	alitative	assessment	of th	ne retri	eved	steel	bars
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Sample	Corrosion-related observations after retrieval				
Stainless Steel ASTM A316L					
SS E ₁	Only slight corrosion observed on both surfaces of the slab, localised pitting observed.				
SS E ₂	Localised pitting and blackening on both surfaces of the slab and along edges. Concentrated deposition of iron oxide				
	along the edges where blackening was observed.				
SS E ₃	Localised fine pitting on a small area of only one surface				
SS E ₄	Two separate pitting portions with formation of iron oxide on only one surface. Fine localised pitting observed.				

CS=Carbon steel; MS= Mild steel SS=Stainless steel

E1= Brackish water sediment E2=Mangrove swamp bottom sediment; E3=Clayey/lateritic soil; E4=River Water sediment



Figure 1. Mean corrosion rates of the different steel types

Pure iron is innately reactive and so naturally corrodes quite rapidly. The addition of carbon makes iron more stable; this stability is informed by both the concentrations of incorporated carbon and the presence of other alloying elements. The greatest mean material loss and highest corrosion rate was seen with the carbon steel bars most likely because it is the steel with the highest percentage of incorporated carbon (0.26-0.29%) in the absence of other alloying metals. The mild steel bars (0.24% carbon) from the results come next in mean material loss and corrosion rates. Stainless steel (0.03% carbon) demonstrated a stronger resistance to MIC than the other steel types having the lowest mean material loss and corrosion rate. Apart from its low carbon content, this resistance could be further attributed to the presence of certain alloving elements like chromium and nickel. Its chromium content (10.5-11.0%) particularly, results in the formation of an oxidation-inhibiting chromium oxide layer in oxygenated systems.

Average percentage weight loss (APWL) values under microbial influence, in one study, were found to be 2.8% and 5.4% for MS in sandy soil and waterlogged soil, respectively, and 3.6% and 4.5% for CS in sandy soil and water- logged soil, respectively. For the SS, APWL was 0.12% and 0.08% for the water-logged soil and the sandy soil, respectively (Oparaodu and Okpokwasili, 2014). While this corroborates the finding in this study that MIC proceeds at faster rates in anaerobic or low oxygen environments, the APWL values in the present study are lower than those recorded.

The higher corrosion rates observed in the mangrove swamp and brackish water sediment corresponds with conclusions from a study on the biocorrosion of stainless steel in varying tidal cycles in a coastal region that high salinity tends to be associated with increased corrosion rates (Daille et al., 2020). Several studies report similar microorganism-induced corrosion rates as recorded in the current study. An assessment of microbial biofilms on carbon steel found comparable corrosion rates of 0.45 ± 0.01 - 0.12 ± 0.01 mm/year dependent on environmental conditions (De Melo et al., 2011). Pratikno and Titah (2016) observed corrosion rates of 0.5797-0.6173 mm/year in steel during a ten-day study in saline and

seawater environments. With the introduction of microorganisms, these rates reached levels 2-3 times greater. In the presence of *Thiobacillus ferroxidans*, this value increased to 1.253-1.3212 mm/year. Other studies, however, recorded corrosion rates much greater than this study. Corrosion rates in a study in Nigeria were 3.51 mm/year, 5.58 mm/year, and 0.32 mm/year for CS, MS and SS, respectively, in water-logged soil and 3.67 mm/year, 3.18 mm/year, and 0.19 mm/year, respectively, in sandy soil (Oparaodu and Okpokwasili, 2014). Maximum biocorrosion rates of



3.3 Microbial influences

The isolates obtained from the biofilms and their occurrence are illustrated in Figure 2. For iron bacteria, 5 genera from 17 isolates were observed, while SRB had 7 genera from 48 isolates.



Figure 2. Distribution of Iron Bacteria (A) and SRB (B) Genera Isolated

The mean counts observed for iron bacteria and SRB across the different environments before and after retrieval of the steel bars is summarised in Table 5. SRB generally showed lower counts than iron bacteria but had the higher mean percentage increase in counts compared to the control; 82.14-1081.48% increase in SRB abundance compared to the 79.88-147.94% increase seen in iron bacteria counts. The greatest SRB counts were seen in brackish water sediment for CS and MS and mangrove swamp sediment for CS. Iron bacteria showed the highest abundance in clayey/lateritic soil and river water sediment. The highest abundance of iron bacteria counts was seen with carbon steel in clayey/lateritic soil.

The enhanced abundance of SRB and iron bacteria after retrieval of the steel bars is considered confirmation that the observed corrosion is microbially influenced (Beech et al., 2000). The number of SRBs decreased as one moved from E1-E4 possibly because of the change in environment from anaerobic to fairly aerobic. Aerobic because soil and river water samples are not water-logged and where inundated still allow the diffusion of oxygen as the inhibiting salt molecules found in anaerobic environments are absent. The mostly anaerobic and halophytic nature of the mangrove swamp aids in the expulsion of oxygen (Knight et al., 2013). Iron bacteria counts, in contrast, increased as one moved from E_1 - E_4 . Iron bacteria show a proclivity for more acidic environments so the observed counts tended to increase as their iron precipitating activity makes the environment more acidic further encouraging their growth. This corresponds with the findings of Agarry et al. (2015) that pitting corrosion (commonly associated with the iron bacteria) of mild steel in an acidic environment was more severe. The lack of a sulphide coating on the steel samples from the river water sediment found in the current study, tallies with the low SRB counts observed in the river water sediment (Table 4). It would mean that MIC in the more aerated systems is dominated by iron bacteria over the SRB.

Sample	Sulphate reducing bacteria $\times 10^2$ (CFU/g)		Iron bacteria $\times 10^2$ (CFU/g)		
	Before burial	At retrieval	Before burial	At retrieval	
Brackish water sediment	4.65	8.50	6.80	9.11	
$CS E_1$	-	12.05	-	14.10	
MS E ₁	-	11.50	-	14.01	
SS E ₁	-	8.53	-	13.65	
Control	4.65	4.03	6.80	7.23	
Mangrove swamp sediment	1.75	6.30	8.30	8.56	
CS E ₂	-	11.35	-	15.49	
MS E ₂	-	9.40	-	15.22	
SS E ₂	-	5.10	-	14.93	
Control	1.75	2.89	8.30	8.52	
Clayey/lateritic soil	0.40	2.90	13.04	18.80	
CS E ₃	-	4.20	-	24.99	
MS E ₃	-	3.19	-	24.46	
SS E ₃	-	1.02	-	23.71	
Control	0.40	0.33	13.04	12.99	
River water sediment	0.49	1.20	8.97	17.41	
CS E ₄	-	1.70	-	22.24	
MS E ₄	-	1.15	-	22.05	
SS E4	-	0.75	-	21.10	
Control	0.49	0.40	8.97	9.04	

Table 5. Mean abundance of SRB and iron bacteria

E1=Brackish Water Sediment; E2=Mangrove Swamp Bottom Sediment; E3=Clayey/Lateritic Soil; E4=River Water Sediment

The presence of substantial numbers of iron oxidising bacteria, iron reducing bacteria and sulphate reducing bacteria has been recorded in biofilms from carbon steel associated with diesel and biodiesel mixtures (De Melo et al., 2011). SRB counts in soils around corroded pipelines ranged from 2.5×10^3 CFU/g - 6.50×10^4 CFU/g. The microbial community analysis in an offshore oil production facility indicated that, like in the current study, Desulfovibrio species, dominated in the biofilms (Vigneron et al., 2016). The species of SRB identified in biofilms of corroded oil pipelines in Rivers state, Nigeria were **Desulfuromonas** acetoxidans, Desulfobulbus propionicus, and Desulfosarcina variabilis, while *Desulfobulbus* sp. and *Desulfobacterium* sp. dominated in a study on a drinking water reservoir in Eastern China (Akpan and Iliyasu, 2015; Yang et al., 2015). Akin to the current study where abundance varied but diversity was relatively the same from one environment to the other, a study on four different environments in Mexico concluded that the distribution of SRB genera was relatively consistent across the different environment but the abundance differed. The SRB group implicated in corrosion of steel out of 37 isolates were Desulfatibacillum, Desulfatitalea, Desulfobacula, Desulfobulbus,

Desulfotignum, Desulfotomaculum, Desulfovibrio, and Sulfurospirillum. Desulfatibacillum was more abundant in the lagoon and the sea while Desulfovibrio were more abundant in the freshwater environment. In the wetlands, Desulfotignum, Desulfovibrio, and Desulfatibacillum had the highest counts. Desulfotomaculum was spread across the sampling sites (Arena-Ortiz et al., 2019).

It has been noted that SRB and IR work in tandem, the product of one being the antecedent for the other's growth. SRB oxidise sulphides back to sulphates in oxygenated soils producing gypsum if calcium is present in the soil or sulphuric acid in the absence of calcium with a resultant reduction in pH to around 2-3. This drop in pH restricts the growth of SRB but supports the proliferation of iron bacteria. A lack of correlation between the degree of corrosion and the counts of attached microbial cells in a biofilm layer was reported by Beech et al. (2000). This observation is corroborated by a number of researchers who state that the metabolic by-products of microorganisms have a stronger influence on MIC rates than abundance. Certain researchers maintain that mean corrosion rates generally correlate with soil moisture content (Wan et al., 2013; Oparaodu and Okpokwasili, 2014). This seems to contradict certain findings in the current study

as corrosion rates in clayey/lateritic soil were greater than in river water sediment.

3.4 Statistical analyses

There were statistically significant differences in corrosion rates of MS, CS, and SS from one environment to the other and within each different environment. While iron bacteria counts differed from one environment to the other, SRB counts did not. SRB counts differed significantly from iron bacteria counts across board. A strong positive correlation was observed between corrosion rates for the three types of steel and SO_3^{2-} (r=0.850, mean value) and S^{2-} (r=0.876, mean value) concentrations, but a weak positive correlation between corrosion rates and SO₄²⁻ concentration (r=0.266, mean value) and SRB counts (r=0.147, mean value) was seen for CS and SS. For MS, a strong positive correlation (r=0.710) was recorded with regards to SO₄²⁻ concentration. This relationship is confirmed by Carbini et al. (2018) who confirmed that sulphite ions increase the corrosion rate of steel. Generally, sulphide formation drives corrosion rates by promoting the establishment of pits in the metal. These pits provide microenvironments for SRB where their activities eventually lead to stress corrosion cracking or hydrogen blistering. Iron bacteria counts, however, did not correlate positively with corrosion rates. A weak negative correlation (r=-0.181, mean value) was observed.

The increase in ferric ion (Fe^{3+}) concentration is indicative of the oxidation of iron, an occurrence fundamental to the corrosion process. Some researchers also maintain that it points to the activities of iron bacteria. Iron bacteria are known to precipitate Fe³⁺ which impedes corrosion unlike Fe²⁺ or Fe(SO₄)₃ that fuels the corrosion process. Iron bacteria hardly instigate corrosion but often facilitate the process using the by-products formed. An alternative influence of Fe²⁺ ions on corrosion rates lies in their proven capacity for enzyme regulation. Cheung and Beech (1996) established the regulatory action of ferrous ion (Fe²⁺) on hydrogenase enzyme activity in Desulfovibrio vulgaris. The presence of Fe³⁺ ion did not have the same effect. A strong negative correlation (r=-0.598, mean value) was observed between NO₃⁻ concentrations and corrosion rates. This could be due to the ability of some SRB species to metabolise NO3⁻ under low SO₄²⁻ concentrations. There was a greater build-up of nitrate ions (NO_3^-) than nitrites (NO_2^-) as corrosion proceeded. No relationship was observed between nitrite (NO2⁻) concentrations and corrosion

rate. The results for phosphate (PO_4^{3-}) indicated that an increase in phosphate concentration would precipitate a resultant increase in corrosion rates as a strong positive correlation was found between phosphate concentration and corrosion rates.

4. CONCLUSION

The study suggests that environmental conditions and the presence of SRB and iron bacteria play a significant role in the corrosion rate of steel. The findings showed that the more saline environments of the mangrove swamp and brackish water sediment had a stronger influence on corrosion rates. Sulphite, sulphide, nitrate and phosphate concentrations had a strong impact on observed corrosion rates. SRB showed greater influence in the more anaerobic mangrove swamp sediment and brackish water sediment, while iron bacteria had greater impact in the relatively aerobic lateritic soil and river water sediment. The different metals in order of resistance to corrosion and microbial attack were Stainless steel>Mild steel>Carbon steel. Stainless steel is, therefore, recommended for oil and gas installations where feasible.

CONFLICT OF INTEREST STATEMENT

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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