*Research Article*

# Modelling the Kinetics of Microbiologically Influenced Corrosion of Mild Steel in Soil Environments

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## Abstract

The objective of this study was to investigate the microbiologically induced corrosion of mild steel in soil by analyzing the physico-chemical and biological characteristics of the soil environment. Soil from three different locations (Lagos, Port Harcourt and Ogbomoso) was used for the study. Weight loss method, microstructure examination and Fourier transform infrared (FTIR) analysis were used for the investigation. The results of the physicochemical and biological characteristics showed that the levels of measured parameters in soil samples are consistent with the conditions in an environment that promotes and sustain microbiologically influenced corrosion. The weight loss method showed that the mild steel suffered from general corrosion. The microstructure examination showed that the presence of biofilm on the surface of the mild steel coupon (MSC) caused pitting corrosion while FTIR depicted the presence of extracellular polymeric substances in the biofilms capable of inducing corrosion. The corrosion data of MSC in the soil environment were analyzed by first order kinetic model and Monod form of kinetic model (Types A and B), respectively. The kinetic models fitted very well to the corrosion data; however, the Monod form of kinetics (Type B) gave the best correlation ( $R^2$ = 0.9978, 0.9839 and 0.9993) with a maximum specific corrosion rate of 0.893, 0.734 and 0.640 mils per year for MSC buried in Lagos, Port Harcourt and Ogbomoso soil, respectively.

**Keywords**: Bacteria; Biofilms; Corrosion rate; Microbiologically influenced corrosion; Kinetic modelling

## 1. Introduction

Networks of pipeline systems have been employed as the most efficient method to transport many substances such as liquids and gases all around the world [1]. The transportation of petroleum products and natural gas over long distance through buried steel pipelines has been in practice since early 20th century [2]. There are more than 1.28 million miles of buried steel pipelines for natural gas transportation alone [3]. Nevertheless, there is always the chance that pipelines could leak or rupture and this pipeline failure can cause serious human, environmental and financial losses [4]. The failure mechanisms associated with pipelines have been classified into three categories which are third-party damage, material

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defects and corrosion [5 – 7]. However, corrosion has been identified as one of the most dominant or fundamental forms of pipeline deterioration process or structure degradation that reduces both the static and cyclic strength of a pipeline as well as one of the major causes of loss containment for offshore steel pipelines [2, 8]. The influence of corrosion cannot be over emphasized in the world today as many of its contribution to the destruction and impairment of industrial facilities, economic losses, and disruption of aquatic and human life as well as pollution of the environment is well documented [9 - 13]. Pipelines that are buried or located above the ground throughout their service life are susceptible to corrosion [1]. Corrosion may act on the pipelines either internally or externally or both [5]. External corrosion is a major factor that contributes to the deterioration of buried pipelines as it weakens the pipe wall and thus increases the risk of failure [5]. External corrosion is a function of the interaction between the pipelines and the soil that surrounds it [2, 14 – 15]. The common types of corrosion that can occur in a buried pipeline are [2]: (a) pitting corrosion owing to material in-homogeneities, (b) chloride or sulphate induced stress corrosion cracking, (c) corrosion by oxygen concentration cells in soil arising out of differences in oxygen concentration in the soil adjacent to the pipe at different regions, (d) microbiologically induced corrosion under anaerobic conditions by sulphate-reducing bacteria (SRB) and acid-producing bacteria (APB), (e) tuberculation because of the build-up of corrosion products on the internal pipe surfaces and (f) stray current corrosion by earth return direct currents.

Metals are employed in over 90% of pipeline construction in industries [16] and an estimated 40% of the corrosion problems encountered by underground pipelines are caused by microorganisms [17 - 18]. Microbiologically influenced corrosion (MIC) is described as the accelerated deterioration of metals owing to the presence of biofilms on their surfaces [19] or the initiation, facilitation and aggravation of corrosion processes in metals by microbes [20 - 21]. It is the result of the interactions between the metal surface, corrosion products, and bacterial metabolites which include organic and inorganic acids and volatile compounds [22]. Bacteria have been regarded as the primary colonizers of metal surfaces, the common types being sulphate-reducing bacteria (SRB) (*Desulfovibrio* spp.), nitrate-reducing bacteria (NRB) (*Pseudomonas* spp.), iron oxidizing bacteria (IOB) (*Gallionella* spp.), acid-producing bacteria (*Thiobacillus* spp.), and bacteria secreting organic acids and slime [23 – 25]. These bacteria species typically coexist in naturally occurring biofilms, forming complex consortia on metal surfaces, hence propagating corrosion [22].

Microbiologically influenced corrosion has been attributed as rapidly accelerating corrosion in metals by capitalizing on the factors present in the environment such as organic and inorganic compounds, dissolved oxygen, and pH [12]. Due to its economic, human and environmental importance, MIC has been the widespread subject of investigation in order to develop and explain the mechanisms for its operation [19]. In the construction of industrial pipelines, mild steel is a more readily preferable material due to its low cost and numerous favourable characteristics. It contains about 0.05–0.15% carbon, accounting for its brittleness and ductility [26]. Owing to the necessity of underground steel pipelines to have longer working lives, mild steel is usually employed to minimize the susceptibility of such pipelines to corrosion. The corrosion problems encountered by pipelines buried in the soil could be traced to the unfavourable interactions between soil and water which can cause swelling, shrinkage and cohesion decline resulting in deterioration of pipelines [27].

Soil is a porous heterogeneous and discontinuous environment made up of complex mass of fine-grained rock with mineral or organic solid phase, water liquid phase and air or other gas phase [10, 28]. It possesses several properties such as hydrological parameters (water flow through ground layers), geological parameters (pH, electrical conductivity, electrical resistivity and soil type), soil chemical composition and microbial activity which contribute immensely to the process of corrosion in metals [27, 29]. Ferreira et al. [28] defined soil as an electrolyte and this can be understood by means of electrochemical theory. The study of the soil as a corrosive environment is necessary due to the large number of buried pipelines, tank and other structures, as their deterioration can represent a real economic and environmental problem throughout the years. It has been stated by Mughabghab and Sullivan [30] that there are four major areas that contribute to underground corrosion: soil texture and aeration (control of the amount of oxygen and moisture), electrolyte factors (e.g., dissolved salts, pH and resistivity), electrical factors (e.g., pipe-to-soil potential) and miscellaneous factors (e.g., microbial corrosion and non-uniform backfilling). Each of these factors can contribute to the formation of anodic and cathodic areas on a metal surface in a soil environment.

Generally, conceptual, deterministic and probabilistic models of varying degrees of accuracy have been reported for various stages of the corrosion process [31 – 34]. Shi and Mahadevan [34] proposed a comprehensive probabilistic corrosion model that incorporates all the seven stages of corrosion life which consists of pit nucleation, pit growth, transition from pitting to fatigue crack nucleation, short crack growth, and transition from short crack to long crack, long crack growth and fracture. Moreover, the intricacy of physical corrosion models may prevent pipeline operators from using them in their maintenance program. Thus, there is an immense need for new empirical model capable of estimating the rate of external corrosion under the influence of soil microorganisms or soil properties. For buried gas or petroleum products pipelines, the external corrosion is of great concern than the internal corrosion due to severe exposure to various condition of soil. The internal corrosion for buried gas or petroleum products pipelines is less critical because the pipelines are used to transport processed gas or cleaned gas and petroleum products with less impurity. However, understanding the physicochemical composition of soil is a key to unravelling how a soil can influence corrosion reaction. There are several parameters that can affect the corrosivity of a soil such as resistivity, pH, redox potential, and moisture content, type of soil, chloride and sulphide. Few workers have carried out experiments regarding the corrosion rate of steel and its interactions with soil properties as well as established regression correlation between corrosion rate and soil properties such as soil resistivity, moisture content, clay content and pH [1, 35 – 39]. To date, empirical model for predicting the rate of external corrosion defects on buried pipelines is limited and more importantly corrosion influenced by microorganisms. Most of the established models are meant for internal corrosion growth rate which are governed by the flown product properties and operational condition.

The objective of this study is to determine the physico-chemical and biological analysis of soil obtained from three different locations (Lagos, Port Harcourt and Ogbomoso) with preference to oil producing area, a commercial centre and a non-commercial area as to whether it has diagnostic and predictive values to implicate soil corrosion and to investigate the MIC of mild steel buried in the different soil environments. The metal loss information will also be utilised to model the external corrosion rate as experienced by buried pipelines exposed to various soil conditions. It is of importance to identify the relationship between soil microorganisms and the severity of corrosion rate so that the modelling of corrosion dynamic can simulate the actual mechanism as accurate as possible. This would help to reduce the uncertainties in the estimation of corrosion growth, in the predictions of future corrosion severity for each and every corrosion defect since corrosion does not grow at the same rate throughout a pipeline, when to conduct future repairs and when to re-inspect the pipeline and to greatly assist pipeline operators or engineers in making decisions related to design, operations and control.

## 2. Materials and Methods

### 2.1 Collection of soil samples

The Lagos, Port-Harcourt and Ogbomoso soil samples used were collected at pipeline area Alagbole-Akute, Ojodu-Berger Local Government Area, Lagos state; Shell pipeline, White-house pipeline area of Obio Akpor Local Government Area, Rivers State and Ajanwa, Ogbomoso-North Local Government Area, Oyo State respectively within the months of September to November, 2014. At each of the selected locations, four samples were collected at a depth of about 1 m in consistency with the specifications of Rim-Rukeh and Puyate [40]. The distance between two samples taken was about 200 to 500 meters. The samples were stored in polyethylene bags before their transfer to the laboratory for analysis.

### 2.2 Preparation of mild steel coupons

The chemical composition of the mild steel used is consistent with that of the oil pipelines and is given in Table 1.

Source [41]

Sheets of mild steel of density 7.85 gcm$^{-2}$ were obtained from the Mechanical Engineering Workshop of Ladoke Akintola University of Technology, Ogbomoso, Nigeria, and cut into coupons of dimensions (4 cm × 2 cm × 0.1 cm) by cold-cut technique (saw cutting of the metal). This method of cutting was considered because of the assurance it renders in retaining the properties of the mild steel coupons as opposed to hot-cut technique where the use of heat is involved which might lead to the formation of heat affected zone (HAZ) that can affect corrosion rate [25]. Sand paper was used for surface finishing of the coupons to get rid of superficial rust. Thereafter, the coupons were rinsed by immersion in pure ethanol, cleansed with cotton wool and then dried in a desiccator. The exposed surface area of each coupon is 17.2 cm$^2$ and is calculated as:

$$A = 2(LB + LH + BH) \tag{1}$$

Where $L$ = 4 cm (length of each mild steel coupon), $B$ = 2 cm (width of each mild steel coupon) $H$ = 0.1 cm (thickness of mild steel coupon).

The prepared coupons were weighed before each test using a weighing balance (Setra BL-410S) with the mass of each coupon determined to the nearest 0.001g.

**Table 1.** Elemental composition of mild steel used.

| C (%) | Mn (%) | Si (%) | P (%) | S (%) | Cr (%) | Ni (%) | Mo (%) | V (%) | Ti (%) | Al (%) | Fe (%) | Cu (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.06 | 1.05 | 0.27 | 0.006 | 0.002 | 0.02 | 0.02 | 0.008 | 0.05 | 0.02 | 0.05 | 9.424 | 0.02 |

### 2.3 Analysis of soil samples

The soil samples were characterized by the following physicochemical parameters: soil type, pH, temperature, electrical conductivity, resistivity, redox potential, moisture content, chloride content and for the biological parameter - total microbial count (TMC). Ten gram of each soil sample was weighed using digital weighing balance (Setra BL-410S) and then transferred into separate beakers. Ten millilitre of de-ionised water was added and the mixture was shaken vigorously for 30 min. The probe of Sension MM-150 Multi-meter was inserted into the mixture to determine the pH, temperature, electrical conductivity and redox potential. Argentometric titration was used to determine the amount of chloride content in soil. Chloride content in the 1:2 soil-water suspensions was determined by the titration of the soil suspension against standard silver nitrate solution using potassium chromate as an indicator [36, 41]. The TMC was determined using pour plate method [42]. To 95 ml of 0.1% (w/v) solution of sodium pyrophosphate was added 10 g of each soil sample. It was thereafter homogenized for 30 min and the solution was decimally diluted ($10^{-1}$ to $10^{-7}$). Aliquots of the resulting solutions were plated on appropriate culture media made up of nutrient agar and sabouraud dextrose agar, swirled to allow for mixing and then incubated at 30 °C for 48 to 96 h after which the colony forming units (CFU) were counted. The soil resistivity was obtained as a reciprocal of electrical conductivity. Soil type was evaluated by making use of the following characteristics: ability of water to penetrate soil, the ease with which soil was washed off the equipment and the consistency of the soil when manipulated in the hand [10].

The moisture content was determined using the weight loss technique. The soil samples were dried in an oven at $105^{\circ}$C for 24 h. The weight difference of the samples before and after drying was obtained and recorded as the moisture content. All the experiments or analyses were done in triplicate.

### 2.4 Corrosion studies

Four earthen pots were filled with 70 g of dried Lagos soil sample. The same was done for Port Harcourt and Ogbomoso soil samples. The soil samples were moistened with 10 ml of water and then pre-weighed mild steel coupons were buried into each of them (one in each case). One setup for each soil sample was allowed to stand for 10 days after which the buried coupons were removed while the remaining 3 sets for each soil sample were allowed to stand for 20, 30 and 40 days, respectively. The biomass formed on the corroded coupons retrieved after the exposure periods were scrapped into pre-weighed filter papers after which the total weight of both was determined in each case. The surface characteristics of both the control mild steel coupon and the corroded ones retrieved after the 40 day exposure period were viewed under inverted metallurgical microscope (XJL-17) with fitted digital camera at a magnification of ($x10$) to observe the degree of corrosion. The final weights of the corroded mild steel coupons which have been washed in distilled water, cleaned with ethanol and dried with the aid of a desiccator, were determined and their corrosion rates were calculated in mils per year (mpy) as specified by Bradford [43] in Eq. 2.

$$C = \frac{k\Delta M}{A\rho t} \qquad (2)$$

Where $C$ = corrosion rate of rectangular coupon (mpy), $k$ = corrosion rate constant (3.45 × $10^6$ mpy), $\Delta M$ = weight loss of coupon (g), $A$ = total exposed surface area of coupon ($cm^2$), $\rho$ = density of coupon ($g/cm^3$) and $t$ = time of immersion (h)

It is important to note that the corrosion rates were calculated assuming uniform corrosion over the entire surface area of the mild steel coupons [12].

### 2.5 Fourier transform infrared spectroscopy analysis

Fourier transform infrared spectroscopy was conducted on the biomass for their biochemical characteristics with the aid of Buck M-530 infrared spectrophotometer. The spectrum was taken in the mid IR region of 400 – 4000 cm$^{-1}$. The spectrum was recorded using attenuated total reflectance (ATR) technique. A portion of the sample was directly placed in the zinc selenide crystal and the spectrum was recorded in the transmittance mode.

## 3. Results and Discussion

Several scoring scales to rate the corrosivity (i.e. corrosivity index) of soil towards buried metallic pipes have been developed by different researchers [44 - 45]. The most widely known of these approaches is the 10-point scoring method proposed by the American Water Works Association (AWWA) and the American National Standards Institute (ANSI) [46]. The 10-point system was proposed to identify the aggressiveness or corrosivity of soil to metallic pipes [47]. The summary of the point system is presented in Table 2.

### 3.1 Soil corrosivity characterization

**Table 2.** AWWA C105 soil-test evaluation.

| Soil Characteristics | Values | Points |
|---|---|---|
| Resistivity ($\Omega\cdot$cm) | <1,500 | 10 |
| | ≥ 1500 – 1800 | 8 |
| | >1800 – 2100 | 5 |
| | >2100 – 2500 | 2 |
| | >2500 – 3000 | 1 |
| | >3000 | 0 |
| pH | 0 - 2 | 5 |
| | 2 – 4 | 3 |
| | 4 – 6.5 | 0 |
| | 6.5 – 7.5 | $0^*$ |
| | 7.5 – 8.5 | 0 |
| | >8.5 | 3 |
| Redox Potential (mV) | >+100 | 0 |
| | +50 - +100 | 3.5 |
| | 0 - +50 | 4 |
| | <0 | 5 |
| Sulfides | Positive | 3.5 |
| | Trace | 2 |
| | Negative | 0 |
| Moisture | Poor drainage (continuous wet) | 2 |
| | Fair drainage (generally moist) | 1 |
| | Good drainage (generally dry) | 0 |

* If Sulfides are present and low or negative redox-potential results are obtained, give 3 points for this range

Considering the weighted aggregation of five soil properties (i.e. soil pH, soil electrical resistivity, soil redox potential, soil chlorides content and soil moisture content), soil of less than 10-point corrosivity index (score) was considered as non-corrosive or non-aggressive to metallic pipes whereas the soil greater or equal to 10-points corrosivity index is categorized as corrosive or aggressive to metallic pipes. However, the 10-point method does not provide information on the intensity of corrosivity [44], thus the intensity of soil corrosivity based on some soil characteristics has been provided according to Bhattarai, [36] as presented in Table 3.

**Table 3**. Rating of soil corrosivity intensity based on the soil characteristics [36].

| Soil Characteristics | Values | Soil Corrosivity Rate |
|---|---|---|
| Resistivity (Ω·cm) | >20,000 | Essentially non-corrosive |
| | 10,000 – 20,000 | Mildly corrosive |
| | 5,000 – 10,000 | Moderately corrosive |
| | 3,000 – 5,000 | Corrosive |
| | 1,000 – 3,000 | Highly corrosive |
| | >1,000 | Extremely corrosive |
| Redox Potential (mV) | >400 | Non-corrosive |
| | 201 - 400 | Mildly corrosive |
| | 100 - 200 | Moderately corrosive |
| | <100 | Severe corrosive |
| Sulfides (ppm) | <200 | Mildly corrosive |
| Chloride (ppm) | <100 | Mildly corrosive |

The results of the soil analyses in terms of pH, temperature, electrical conductivity, redox potential, resistivity, total viable count, and moisture content carried out on soil samples obtained from Lagos, Ogbomoso and Port Harcourt are presented in Table 4.

**Table 4.** Physico-chemical and biological characterization of experimental soil samples and their corrosivity index.

| Soil Parameters | Soil Samples from Lagos Location | | | | |
|---|---|---|---|---|---|
| | Site 1 | Site 2 | Site 3 | Site 4 | AWWA Points[*] |
| Soil Type | Clay | Clay | Clay | Clay | 2,2,2,2 |
| pH | 5.9 ± 0.1 | 6.2± 0.1 | 5.4± 0.1 | 5.6± 0.1 | 0,0,0,0 |
| Temperature (ºC) | 29.3± 0.1 | 29.7± 0.2 | 28.2± 0.2 | 28.7± 0.1 | N/A[**] |
| Electrical Conductivity (µs/cm) | 568.5± 0.3 | 570.8± 0.4 | 562.4± 0.1 | 567.5± 0.1 | N/A |
| Resistivity (Ω·cm ) | 1759± 2.0 | 1751± 1.0 | 1778± 2.0 | 1762± 3.0 | 8,8,8,8 |
| Redox Potential (mV) | -173± 0.3 | -185± 0.3 | -161± 0.4 | -173± 0.1 | 5,5,5,5 |
| Moisture Content (%) | 40± 0.1 | 45± 0.2 | 38± 0.3 | 35± 0.2 | 2,2,2,2 |
| Chloride (µg/g) | 200± 4.0 | 212± 1.5 | 188± 2.0 | 185± 1.0 | N/A |
| Total Microbial Count (cfu/g) | $0.1\pm3.8\times10^{8}$ | $0.1\pm4.5\times10^{8}$ | $0.3\pm3.1\times10^{8}$ | $0.2\pm2.8\times10^{8}$ | N/A |
| Soil Parameters | Soil Samples from Port Harcourt Location | | | | |
| | Site 1 | Site 2 | Site 3 | Site 4 | AWWA Points[*] |
| Soil Type | Sandy clay | Sandy clay | Sandy clay | Sandy clay | 1,1,1,1 |
| pH | 6.2± 0.1 | 5.8± 0.1 | 6.6± 0.2 | 6.4± 0.1 | 0,0,3,0 |
| Temperature (ºC) | 28.2± 0.2 | 27.0± 0.2 | 28.4± 0.1 | 28.0± 0.1 | N/A |
| Electrical Conductivity (µs/cm) | 526.95± 0.1 | 516.80± 0.2 | 537.10± 0.3 | 529.0± 0.3 | N/A |
| Resistivity (Ω·cm ) | 1898± 1.0 | 1935± 3.0 | 1862± 2.0 | 1890± 3.0 | 5,5,5,5 |
| Redox Potential (mV) | -153.4± 0.1 | -150.2± 0.1 | -156.6± 0.1 | -155.4± 0.1 | 5,5,5,5 |
| Moisture Content (%) | 38± 0.4 | 35± 0.2 | 40± 0.2 | 37± 0.3 | 2,2,2,2 |
| Chloride (µg/g) | 192± 1.0 | 188± 0.4 | 196± 1.1 | 194± 0.6 | N/A |
| Total Microbial Count (cfu/g) | $0.3\pm3.8\times10^{7}$ | $0.1\pm3.4\times10^{7}$ | $0.4\pm4.2\times10^{7}$ | $0.3\pm4.0\times10^{7}$ | N/A |
| Soil Parameters | Soil Samples from Ogbomoso Location | | | | |
| | Site 1 | Site 2 | Site 3 | Site 4 | AWWA Points[*] |
| Soil Type | Sandy clay | Sandy clay | Sandy clay | Sandy clay | 1,1,1,1 |
| pH | 7.5± 0.2 | 7.3± 0.1 | 7.9± 0.2 | 7.7± 0.2 | 3,3,0,0 |
| Temperature (ºC) | 31.4± 0.3 | 31.0± 0.1 | 32.2± 0.3 | 31.8± 0.2 | N/A |
| Electrical Conductivity (µs/cm) | 419.78± 0.2 | 417.66± 0.2 | 429.90± 0.3 | 424.84± 0.1 | N/A |
| Resistivity (Ω·cm ) | 2382± 1.0 | 2394± 1.6 | 2326± 2.0 | 2354± 1.4 | 2,2,2,2 |
| Redox Potential (mV) | -156± 0.1 | -152.6± 0.2 | -159.4± 0.2 | -157.7± 0.1 | 5,5,5,5 |
| Moisture Content (%) | 32± 0.2 | 29± 0.1 | 37± 0.3 | 34± 0.2 | 2,2,2,2 |
| Chloride (µg/g) | 168± 1.0 | 164± 1.5 | 177± 2.0 | 174± 1.3 | N/A |
| Total Microbial Count (cfu/g) | $0.2\pm2.2\times10^{7}$ | $0.1\pm1.8\times10^{7}$ | $0.1\pm2.9\times10^{7}$ | $0.2\pm2.5\times10^{7}$ | N/A |

[*] AWWA Points = each point or score stand for each site (site 1 to site 4); [**] N/A = Not Applicable

From Table 4, it could be seen that the pH of the soil samples in site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations are within the range of 5.4 – 6.2; 5.8 – 6.6; and 7.3 – 7.9, respectively. This indicates that the Lagos and Port Harcourt soil samples are relatively acidic while the Ogbomoso soil sample is slightly alkaline. A pH value within the range of 4 - 9 has been identified by Costerton et al. [48] to be suitable for bacteria growth. Bradford [43] suggested that acidic environments with pH < 6 as well as alkaline environment with pH > 8 are more corrosive than pH 6-8. The result shows that Ogbomoso soil sample has the highest pH range of 7.3 – 7.9 thus making it slightly alkaline and least acidic followed by that of Port Harcourt soil sample with pH range of 5.8 - 6.6 and Lagos soil sample which relatively has the lowest pH range of 5.4 – 6.2 thus making it more acidic. Using AWWA C105 numerical scale in Table 2 for soil corrosivity, the pH was each assigned 0 point for soil samples of site 1 to site 4 from Lagos locations. The pH of soil samples of site 1, site 2 and site 4 from Port Harcourt location was each assigned 0 point and site 3 assigned 3 points (since the pH of the soil is within the range of 6.5 – 7.5 and the soil having a negative redox potential). The soil sample pH of site 1and site 2 from Ogbomoso location was each assigned 3 points (since the pH of the soil is within the range of 6.5 – 7.5 and the soil having a negative redox potential) while the soil sample pH of site 3 and site 4 was each assigned 0 point as presented in Table 4.

Temperature is an important parameter in the investigation of biocorrosion of mild steel in soil environment, because it can modify the interaction between the metal and soil conditions. Temperature of the soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations are within the range of 28.2 – 29.7°C; 27 – 28.4°C; and 31 – 32.2°C, respectively. This temperature is suitable for bacteria growth of which the optimal growth temperature for bacteria lies between $25^0$C and $35^0$C [49].

Moisture content of the soil samples in site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations ranged between 35 - 45%; 35 - 40%; and 29 - 37%, respectively. The high moisture content of the samples could be attributed to the rainy season period of the year when the samples were obtained. Generally corrosion rate increases with increasing moisture content [1]. Thus, the sample with the highest moisture content will corrode faster as it promotes the growth of micro-organism. Using AWWA C105 numerical scale in Table 2 for soil corrosivity, the moisture content was respectively assigned 2 points for soil samples in site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations as presented in Table 4. This is in agreement with the report of Rim-Rukeh and Awatefe [10].

Chloride by nature is conductive and so its contribution to soil corrosivity is very significant as its existence in soil help to promote corrosion by increasing the ability of electrolytes to conduct current [39] and can also inhibit passivity of the metal (i.e. inhibit oxide layer formation on the metal surface which protects the metal from corrosion) [10]. In addition, its presence in soil tends to decrease soil resistivity [10]. Result showed that the chloride levels present in soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations are within the range of 185 – 212 μg/g; 192 – 196 μg/g; and 164 - 177 μg/g, respectively. Thus, using the AWWA C105 point system for soil corrosivity rating, the chloride level for soil samples in site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations was assigned no point, respectively (Table 4). However, with the use of the corrosivity rating in Table 3, the soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations can respectively be classified as highly corrosive. Reduction-oxidation (Redox) potential refers to the relative potential of an electrochemical reaction under equilibrium condition. It is the affinity of a medium for electrons and its electronegativity compared with hydrogen. The Redox potential of a soil indicates whether or not a soil is capable of sustaining SRB, which contribute greatly to the bio corrosion problem [10, 49]. A low potential indicates that the oxygen content of the soil is low and consequently, the conditions are ideal for the proliferation of SRB. The results showed that the soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations have very high negative redox potential values that ranged from -161 to -185; -150.2 to 156.6; and -152.6 to -159.4 mV, respectively. The soil samples correspond to an environment that is highly susceptible for corrosion problem. Using AWWA C105 numerical scale in Table 2 for soil corrosivity, the redox potential was assigned 5 points to each of the soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations, respectively (Table 4). In addition, with the use of corrosivity rating in Table 3, the soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations can respectively be classified as severe corrosive. This indicates a high degree of corrosiveness of the environment. Spectrum of redox potential under which microbial life can be found ranges from -450 mV to +850 mV, where the negative side of the spectrum favours methanogenic bacteria, and the positive side corresponds to iron bacteria [50].

Soil resistivity is a measure of the ability of a soil to resist the conduct of current. The lower is the resistivity of the soil, the better the soil electrolytic properties and the higher at which the rate of corrosion can proceed. The soil resistivity value ranges from 1751 - 1778; 1862 – 1935; and 2326 - 2394 Ω·cm for soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations, respectively. It has been reported that soil resistivity values decreases according to the increase in moisture and temperature to support ionic exchange between buried pipe surface and corrosive soil environment [10]. Generally, as soil resistivity decreases so also corrosivity increases [1, 10]. Using the AWWA C105 numerical scale for soil corrosivity (Table 2), the soil resistivity was assigned 8 points for each soil samples of site 1 to site 4 from Lagos location; 5 points for each soil samples of site 1 to site 4 from Port Harcourt location; and 2 points for each soil sample of site 1 to site 4 from Ogbomoso location, respectively (Table 4). Using the corrosivity rating in Table 3, the soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations can respectively be classified as highly corrosive.

Soil electrical conductivity is the ability of a soil to conduct current. The soil samples electrical conductivity ranges from 562.4 – 570.8; 516.8 – 537.10; and 417.66 – 429.90 µs/cm for soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations, respectively. The higher is the electrical conductivity of a soil, the highly susceptible it is for biocorrosion. The higher electrical conductivity of Lagos soil sample will favour the rapid corrosion rates of the steel samples buried in it.

Soil is normally classified and named according to their particle size range or grain diameter. For example, cobble (> 60mm), gravel (2mm- 60mm), sand (2mm-0.063mm), silt (0.063m-0.002mm) and clay (<0.002m). Soil texture is one of the first factors to be considered during corrosion surveys because it determines the degree of aeration and the permeability of the soil [51]. Soil with poor drainage due to its fine grain size, like clay and silt are more corrosive as compared to sand and gravel (good drainage) [1]. As seen from Table 4, the soil type from each of the different location obtained at the depth of about 1m was clayey in nature for Lagos sample while it is sandy-clay in nature for both Port Harcourt and Ogbomoso samples. Applying the AWWA C105 standard for soil corrosivity rating (Table 2), the studied soil samples of site 1 to site 4 obtained from Lagos has a rating of 2 points each while those of site 1 to site 4 from Port Harcourt and Ogbomoso locations has a rating of 1 point each, respectively against the factor of soil type (based on the drainage characteristics under moisture) (Table 4). Based on the appropriate point allocated to each parameter depending on the extent to which the factor contributed to soil corrosivity, the final corrosivity index was summed up to be 17 each for soil samples of site 1 to site 4 from Lagos location, 13 each for soil samples of site 1, site 2 and site 4 and 16 of site 3 from Port Harcourt location as well as 13 each for soil samples of site 1 and site 2 and 10 each for site 3 and site 4 from Ogbomoso location, as shown in Figure 1. Thus, the soil obtained from Lagos, Port Harcourt and Ogbomoso locations are respectively corrosive.

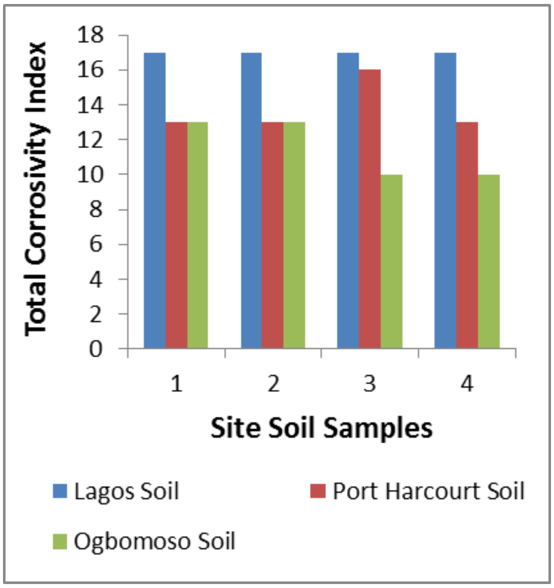


**Figure 1.** Corrosivity evaluation of soil from different location.

### 3.2 Corrosion studies

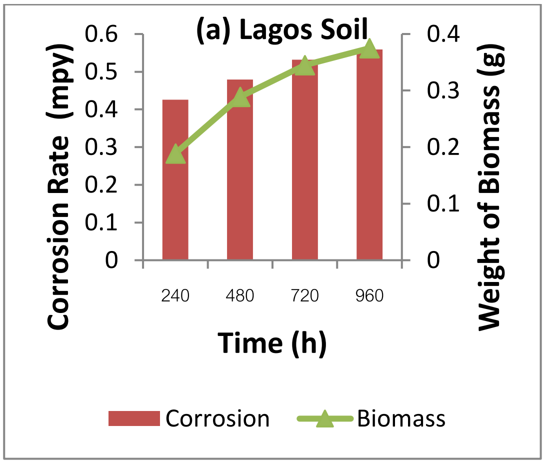
Corrosion rates of mild steel influenced by biofilms formation on the surface of metal in the natural soil environment are presented in Table 5.

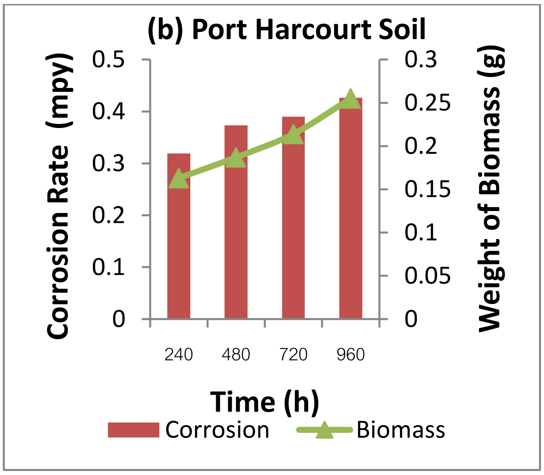
**Table 5.** Weight loss, weight of superficial biomass and corrosion rates of mild steel in soil environment.

| Soil samples | Time (h) | $M_i$ (g) | $M_b$ (g) | $M_f$ (g) | X (g) | $\Delta M$ (g) | C (mpy) |
|---|---|---|---|---|---|---|---|
| Lagos | 240 | 6.824 | 7.042 | 6.820 | 0.218 | 0.004 | 0.426 |
| | 480 | 6.860 | 7.139 | 6.851 | 0.279 | 0.009 | 0.479 |
| | 720 | 6.870 | 7.215 | 6.855 | 0.345 | 0.015 | 0.532 |
| | 960 | 5.273 | 5.648 | 5.252 | 0.375 | 0.021 | 0.559 |
| Port Harcourt | 240 | 6.837 | 7.003 | 6.834 | 0.166 | 0.003 | 0.319 |
| | 480 | 6.237 | 6.440 | 6.230 | 0.203 | 0.007 | 0.373 |
| | 720 | 5.426 | 5.674 | 5.415 | 0.248 | 0.011 | 0.390 |
| | 960 | 6.954 | 7.249 | 6.938 | 0.295 | 0.016 | 0.426 |
| Ogbomoso | 240 | 6.952 | 7.072 | 6.950 | 0.120 | 0.002 | 0.213 |
| | 480 | 5.438 | 5.605 | 5.433 | 0.167 | 0.005 | 0.266 |
| | 720 | 6.792 | 7.121 | 6.783 | 0.229 | 0.009 | 0.319 |
| | 960 | 5.309 | 5.579 | 5.286 | 0.270 | 0.013 | 0.346 |

$M_i$ =initial weight of MSC; $M_b$ = weight of biocorroded MSC; $M_f$ = final weight of MSC; X = weight of biomass; $\Delta M$ = weight loss; C = corrosion rate

Figures 2(a), 2(b), and 2(c) show the variation of corrosion rate and mass of biomass formed with time of mild steel buried in soil obtained from Lagos, Port Harcourt and Ogbomoso, respectively.





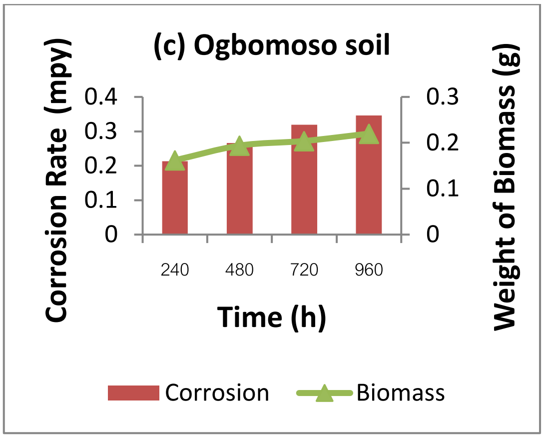


**Figure 2.** Biocorrosion rate profile of mild steel coupon buried in (a) Lagos (b) Port Harcourt and (c) Ogbomoso soil.

It could be seen that the corrosion rate increased with increase in time for mild steel buried in Lagos soil, Port Harcourt soil and Ogbomoso soil, respectively. This increase in corrosion rates with time was very pronounced in the first 240 h (10 days) of the immersion period and then minimally increased for the rest part of the immersion period. This observation indicates the typical behaviour of a metal that demonstrates passivity effects. Similar observations have been reported [38, 52-53]. Nevertheless, the behaviour of the mild steel can be divided into two regions: active and passive. The minimal increase in corrosion rates could be attributed to the presence of biofilm (biomass) formed on the surface of the metal [25, 54 - 55]. Picioreanu et al. [56] had observed that biofilm have the potential of protecting a metal from corrosion. The relationship between the superficial biomass formed on the mild steel surfaces with time during the experimental period is also shown in Figure 2. It is seen that biomass accumulation on the surface of the mild steel buried in Lagos soil, Port Harcourt soil and Ogbomoso soil respectively increased with time. This is because biomass accumulation is the net result of growth and detachment [57]. This suggests that biofilm growth rate is faster than the biofilm detachment rate. This is in agreement with the observation of Loosdrecht et al. [58] and Rim-Rukeh and Irerhievwie [57], respectively. The rate of biofilm detachment must be slower for biofilm structure formation because it is the primary process that balances growth. The process of detachment results to increase in the availability of substrate for the remaining and hence subsequent biofilm increase. Furthermore, the corrosion rates of mild steel coupon buried in Lagos soil at the end of day 40 (960 h) was observed to be higher and relatively followed by that buried in Port Harcourt soil and Ogbomoso soil, respectively (Figure 3). The reasons for this observation may be due to lower pH and soil resistivity as well as higher redox potential, electrical conductivity, moisture content and total bacterial count which promotes higher soil corrosivity.

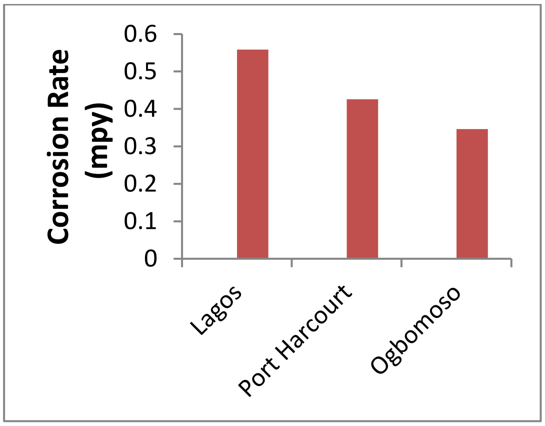


**Figure 3.** The corrosion rate of mild steel coupon buried in Lagos, Port Harcourt and Ogbomoso soil.

### 3.2.1 Microstructure examination

Figures 4(a), 4(b), 4(c), and 4(d) show the metallurgical inverted microscope image of both the un-corroded and corroded mild steel coupons that were buried in the various soil samples.

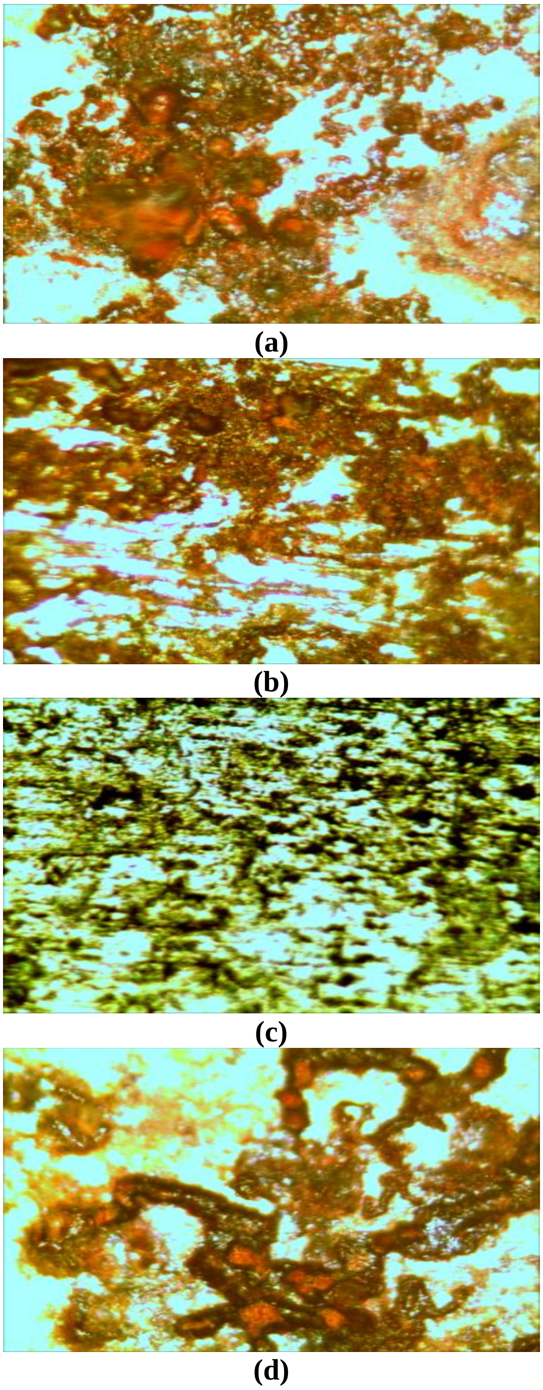


**Figure 4.** (a) Micrograph of uncorroded mild steel coupon not buried in any soil (control sample) (b) Micrograph of biocorroded mild steel coupon buried in Port Harcourt soil (c) Micrograph of biocorroded mild steel coupon buried in Lagos soil (d) Micrograph of biocorroded mild steel coupon buried in Ogbomoso soil.

As shown in Figure 4, it is obvious that there is pitting corrosion as depicted in Figures 4(b), 4(c), and 4(d) in mild steel buried in Lagos soil, Port Harcourt soil and Ogbomoso soil, respectively, in comparison with the uncorroded mild steel (Figure 4(a)). The observed pitting corrosion (which is a localized accelerated dissolution of the metal as a result of the breakdown of the passive protective film on the metal surface) in the mild steel revealed that the soil samples were corrosive to the mild steel which is in agreement with the soil corrosivity rating or index obtained for each of the soil samples. The pitting corrosion occurred due to the presence of anionic species such as chloride ion in the soil [59] and enhanced with the presence of moisture, air and microorganisms that forms biofilm on the metal surface. The severity of this corrosion varied with the logarithm of the bulk chloride concentration in each of the soil sample. Thus, the extent of this corrosion is more severe in mild steel coupon buried in Lagos soil and relatively followed by that buried in Port Harcourt and Ogbomoso soil, respectively. Thus mild steel coupon buried in Ogbomoso soil is the least corroded.

### 3.2.2 FTIR analysis of the biofilm formed on mild steel coupon surfaces

Tables 6 to 8 show the FTIR spectrum of the biofilm (biomass) formed on the surface of mild steel coupons that were buried in Lagos, Ogbomoso and Port Harcourt soil, respectively.

**Table 6.** FTIR spectrum elucidation of microbial biomass on mild steel coupon surface buried in Lagos soil.

| Absorption Peak Number ($cm^{-1}$) | Suspected Functional Groups |
|---|---|
| 3970 - 3893 | OH (alcohol/carboxylic), C-H (stretch), OH (non-bonding), N-H stretching |

**Table 7.** FTIR spectrum elucidation of microbial biomass on mild steel coupon surface buried in Port Harcourt soil.

| Absorption Peak Number ($cm^{-1}$) | Suspected Functional Groups |
|---|---|
| 3334-3167 | OH (alcohol/phenol), N-H |

**Table 8.** FTIR spectrum elucidation of microbial biomass on mild steel coupon surface buried in Ogbomoso soil.

| Absorption Peak Number ($cm^{-1}$) | Suspected Functional Groups |
|---|---|
| 2690-2263 | C-H (stretch), COOH, C≡N |

The FTIR spectrum analysis of the mild steel coupon buried in Lagos soil (Table 6) showed a peak between 3893 and 3970 $cm^{-1}$, which indicates the presence of OH stretching (alcohol and carboxylic acid), OH non-bonding, N-H stretching (amines), and C-H stretching (alkanes). The FTIR spectrum of the biofilm on the surface of the mild steel coupon buried in Port Harcourt soil (Table 7) showed a broad peak between 3167 and 3334 $cm^{-1}$, which indicates the presence of adsorbed water molecule and OH/NH groups [60]. While the FTIR spectrum of the biofilm on the surface of the mild steel coupon buried in Ogbomoso soil (Table 8) revealed a broad peak between 2263 and 2690 $cm^{-1}$ indicating the presence of C-H, COOH (carboxylic acid) and nitriles. As investigated by Lin and Ballim [61], extracellular polymeric substances (EPS) which are the major building blocks of biofilms are composed of polysaccharides, lipids, and proteins containing functional groups including carboxylic acid (COOH) and amino acid groups ($NH_2$). Kumar et al. [62] also established that the presence of hydroxyl group (OH) and COOH in biofilms indicate the presence of EPS which are able to bind metallic ions. Therefore, the OH, COOH and $NH_2$ functional groups identified in the biofilms formed on the mild steel coupon surfaces depict the presence of EPS which are capable of inducing the corrosion observed on the mild steel coupons buried in the soil obtained from Lagos, Port Harcourt and Ogbomoso, respectively.

### 3.2.3 Kinetic modelling of biocorrosion

Since corrosion is regarded as a degradation or deterioration of a metal or material brought about by chemical, mechanical and biological reaction with the environment [1, ], thus, there is a definite need for robust kinetic models which can contribute to explain the factors influencing corrosion rates of steels and metals in the environment and may ultimately be used to characterize the mass-loss of the metal at any time as well as predict timescales and the level likely to be present at some future time. The model would therefore serve as an aid towards taking appropriate action as to avoid pipe failures and save significant future repair and replacement costs. Corrosion rate of steel and metals can be described in terms of mass-loss of metal as given in Eq. (3) as well as in terms of mass of superficial microbial biomass on the metal surface (Eq. (4)) for corrosion influenced by microorganisms.

$$C = \frac{C_m \Delta M}{k + \Delta M} \tag{3}$$

$$C = \frac{C_m X}{k + X} \tag{4}$$

Eq. (3) and Eq. (4) are typical form of Monod kinetic model which can be referred to as Monod form of kinetics (Type A) and Monod form of kinetics (Type B), respectively. Where $C$ is corrosion rate, $C_m$ is maximum specific corrosion rate, $\Delta M$ is the mass loss (g) (i.e. change in mass of metal/steel), $X$ is mass of microbial biomass (g) and $k$ is half-saturation constant (g). $C_m$ and $k$ can respectively be obtained from the slope and intercept of the plot of $(1/C)$ versus $(1/\Delta M)$ or the plot of $(1/C)$ versus $(1/X)$ as shown in Figure 5.

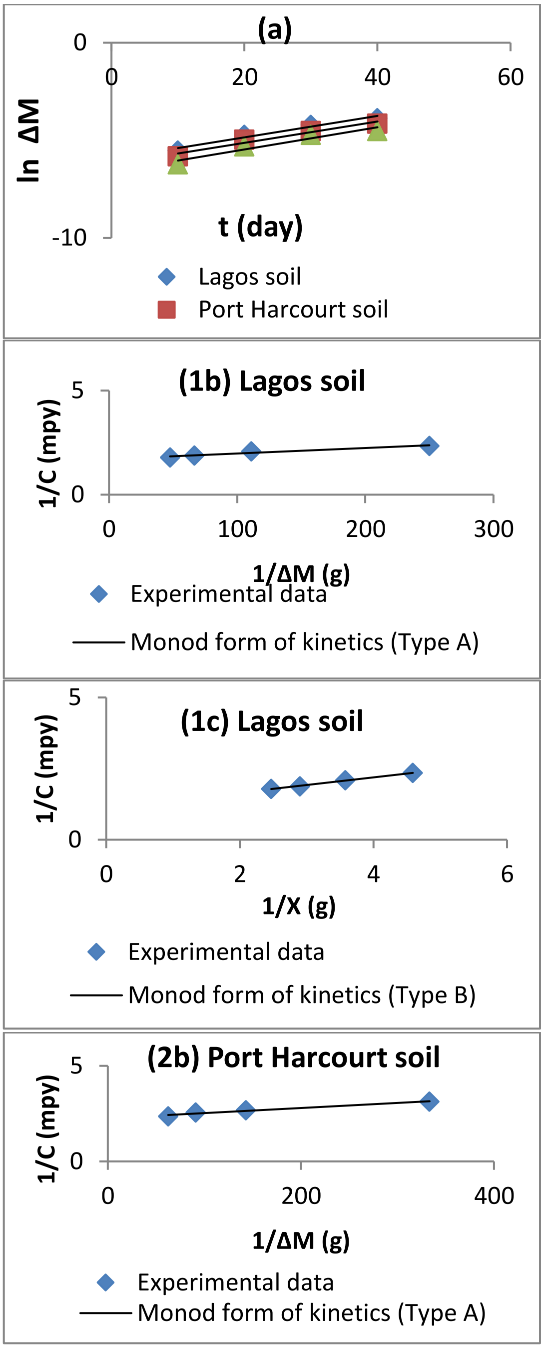
If $\Delta M \ll k$; Eq. (3) can be reduced to

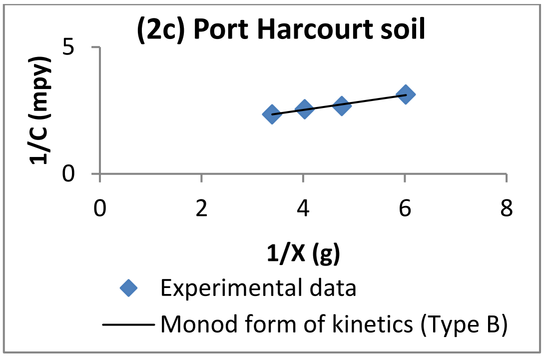
$$C = \frac{C_m \Delta M}{k} \tag{5}$$

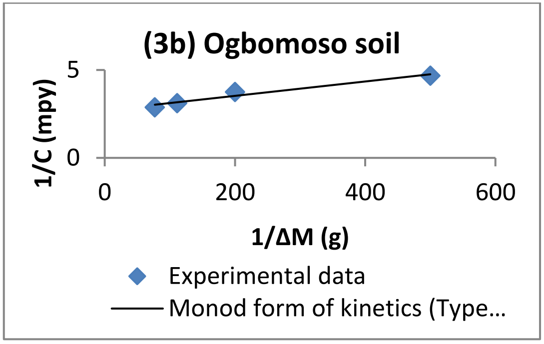
Eq. (5) is a typical first-order model. Assuming $k_1 = (C_m/k)$ and integrating Eq. (5), the following relation of mass-loss to time can be obtained as given in Eq. (6):

$$\ln \Delta M = a + k_1 t \tag{6}$$

Where $t$ is time (day) and $k_1$, corrosion rate constant. Based on the corrosion data acquired in the present study, Eq. (3), Eq. (4) and Eq. (6) were applied using mass-loss and microbial biomass abundances as dependent variables. When the natural logarithm of mass-loss is plotted against time, an approximate linear relationship is obtained (Figure 5), confirming a first-order chemical reaction between the microorganism and the metal. Similar observations have been reported for the biocorrosion of metal surfaces [53, 63 - 64].







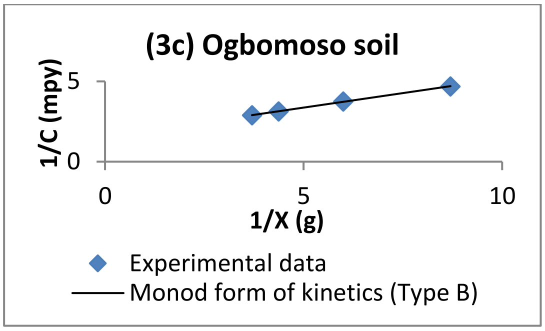


**Figure 5.** (1a) First order kinetic model, (1b,2b,3b) Monod form of kinetic model (Type A), (1c,2c,3c) Monod form of kinetic model (Type B) fitted to the corrosion data of mild steel coupon buried in Lagos soil, Port Harcourt soil and Ogbomoso soil.

The kinetic results of mild steel coupon corrosion in Lagos soil, Port Harcourt soil and Ogbomoso soil, respectively, are presented in Table 9.

**Table 9.** Values of kinetic models parameters (constants) with correlation coefficient ( $R^2$ ) of kinetic models fitted to the corrosion data of mild steel coupon in soil environment.

| Soil Sample | First-Order Kinetics | | Monod form of Kinetics (Type A) | | | Monod form of Kinetics (Type B) | | |
|---|---|---|---|---|---|---|---|---|
| | $k_1$ (day$^{-1}$) | $R^2$ | $C_m$ (mpy) | $k$ (g) | $R^2$ | $C_m$ (mpy) | $k$ (g) | $R^2$ |
| Lagos | 0.0549 | 0.9641 | 0.584 | 0.00152 | 0.9469 | 0.893 | 0.239 | 0.9978 |
| Port Harcourt | 0.0546 | 0.9596 | 0.442 | 0.00119 | 0.9662 | 0.734 | 0.213 | 0.9839 |
| Ogbomoso | 0.0569 | 0.9276 | 0.369 | 0.00151 | 0.9600 | 0.640 | 0.231 | 0.9993 |

Generally, the results in Table 9 as indicated by the high correlation coefficients ( $R^2$ ) showed that the corrosion of mild steel coupon in soil samples collected from three different locations (Lagos, Port Harcourt and Ogbomoso) fitted very well to both the first-order kinetics and Monod form of kinetics (Types A and B), respectively. However, in comparison of the models, the Monod form of kinetics (Type B) provided the best fit to the corrosion data of mild steel coupon buried in Lagos soil, Port Harcourt soil and Ogbomoso soil, respectively, having the highest $R^2$ that ranges between 0.9839 and 0.9993. Therefore, using the Monod form of kinetics (Type B), the maximum specific corrosion rates of mild steel coupon buried in Lagos soil, Port Harcourt soil and Ogbomoso are 0.893, 0.734 and 0.640 mpy, respectively.

## 4. Conclusions

Physicochemical and biological characteristics of soil samples collected from three different locations, Lagos, Port Harcourt and Ogbomoso cities in Nigeria have been presented. It is shown that the levels of measured parameters in soil samples are consistent with the conditions in an environment that favours corrosion activity. The soil samples of site 1 to site 4 from Lagos, Port Harcourt and Ogbomoso locations exhibits the necessary qualities for promotion and sustenance of microbiologically influenced corrosion based on the soil corrosivity rating or index of 17:17:17:17, 13:13:16:13 and 13:13:10:10, respectively. It is shown that corrosion coupons made of mild steel immersed in the natural soil collected from Lagos, Port Harcourt corroded microbiologically at the rate of 0.559, 0.426 and 0.346 mpy respectively after 40 days (960 h) of test period. The microstructure examination showed that the presence of biofilm on the surface of the mild steel caused pitting corrosion while the identification of hydroxyl, carboxylic and amino functional groups from FTIR analysis of the isolated biofilms indicated the presence of extracellular polymeric substances which are the major building blocks of biofilm; thus validating the role of microbial biofilms in the corrosion processes of metals. The superficial biomass formed on the mild steel surfaces during biocorrosion increased with time during the test period. The corrosion data of mild steel in the soil environment were analyzed by first order kinetic model and Monod form of kinetic model (Types A and B), respectively. The kinetic models fitted very well to the corrosion data; however, the Monod form of kinetics (Type B) gave the best correlation ( = 0.9978, 0.9839 and 0.9993) with a maximum specific corrosion rate of 0.893, 0.734 and 0.640 mpy for mild steel coupon buried in Lagos, Port Harcourt and Ogbomoso soil, respectively. Buried steel structures in the areas where the soil were collected must therefore be protected by a full protective system defined by an active cathodic protection to maintain steel in its potentials protection in addition to passive coatings protector aimed to avoid any corrosion interaction between steel surface and soil environment.

## 5. Acknowledgement

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