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Application of mathematical tools and techniques in monitoring and predicting stainless steel corrosion in river water media environment

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ABSTRACT

The application of mathematical tools and techniques were applied in the process of monitoring and predicting the corrosion rate and weight loss of stainless steel in salt and fresh water environment of Niger Delta region in Nigeria. The functional parameters used in the mathematical demonstration to compute the corrosion rate and weight loss were obtained from the experimental data and these functional coefficients were fitted into the power and quadratic model. The experimental corrosion rate and weight loss value was compared with the theoretical computed value for both model of quadratic and power concept approach and the result obtained demonstrate a good match indicating the reliability of the concepts on monitoring and predicting the process. In this case, the corrosion rate and weight loss was experienced to be more rapid in the salt water environment than the fresh water environment; this can be attributed to the characteristics of the salt water concentration of the physicochemical parameters that is a major contributing factor for increase in corrosion rate and weight of metals in aqueous media.

Capsule Summary: The reliability tools and techniques were applied in stainless steel metal corrosion in salt water environment. Increase in corrosion rate was observed with increase in time for both model of power and quadratic concept approach as well as the result obtained demonstrate a good match indicating the reliability of the developed approach on monitoring and predicting metal corrosion in salt water environment.

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INTRODUCTION

The challenge of corrosion impact on the environmental materials has long been identified by engineers as well as its protective mechanism well attributed facility to maintenance. These challenges include the redox reaction that may occur leading to defacing and reduction in weight of stainless steel material subjected into aqueous media of salt and fresh water environment. This process are influential on economic and performance of process equipment as well as the reliability of the process plant (Jelenka, 2010).

Considering the contributed impact of water media on corrosion of metals in the aqueous environment, one may view corrosion definitions with respect the phenomena controlling the process that led to such failure as so many expressions are narrowed to specific form of corrosion, while others broadly covered many forms of corrosion as presented by various research group (Charng and Lansing, 1982; McFarland et al., 2008., Ukpaka, 2005, 2016, 2015a).

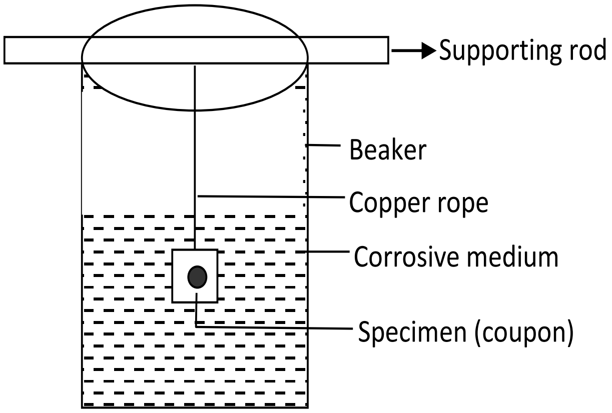

Fig. 1: Specimen arrangement for corrosion test

Corrosion as a natural process that occurs when metals react with oxygen led to the formation of metal oxides as well it necessary to note that word corrosion was derived from the terminology of corrode, indicating that a material has lost its value in terms strength as well as its chemical structure is influenced. Therefore, corrosion can be illustrated as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. Therefore, the corrosion behavior of a material depends on the environment to which it is subjected, and the corrosiveness of an environment depends on the material exposed to it (ASM International, 2000). The environment signifies the physical state (gas, liquid, or solid), chemical composition (constituents and concentrations) and temperature in which the material is expos to. The most commonly noticed corrosion process is the rusting of iron expose to air and moisture and according to Frange (1959), most corrosive reaction occurs between solid-liquid and solid-gas interface. Frange (1959) stated that all metals are unstable when found in aqueous medium and this will tend to react with its environment to produce compounds of metallic oxides. The reaction involves the movement with which electrons are lost varies or corrosive is the metal. Corrosion products formed i.e. oxides are usually insoluble and sometimes, the rate of corrosion may not be rapid as would be expected due to the reactivity characteristics of the metal, for example stainless steel (Frange, 1959).

The aim of this research is to demonstrate the concepts of quadratic and power model approach in monitoring and predicting the corrosion rate and weight loss of stainless steel immersed in aqueous media of salt and fresh water environment, considering the fact that the region of the Niger Delta area of Nigeria heavily polluted with constituent that led to rapid corrosion of metals.

MATERIAL AND METHODS

Apparatus and reagents

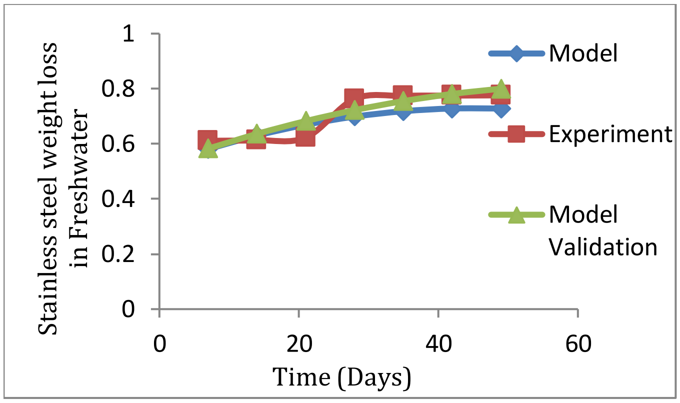

Fig. 2: Stainless steel weight loss comparison of quadratic model and experimental result in freshwater medium

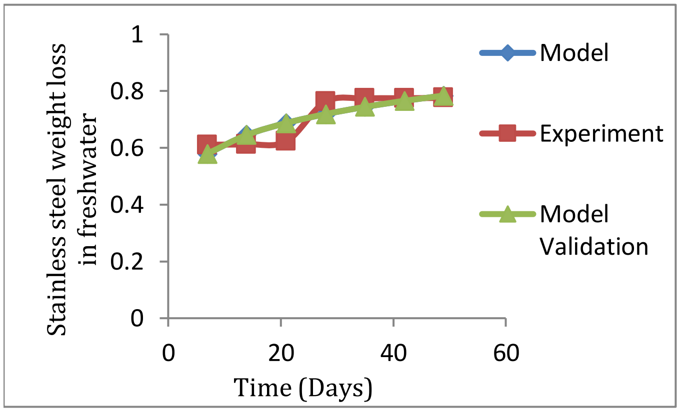

Fig. 3: Stainless steel weight loss comparison of power model and experimental result in freshwater medium

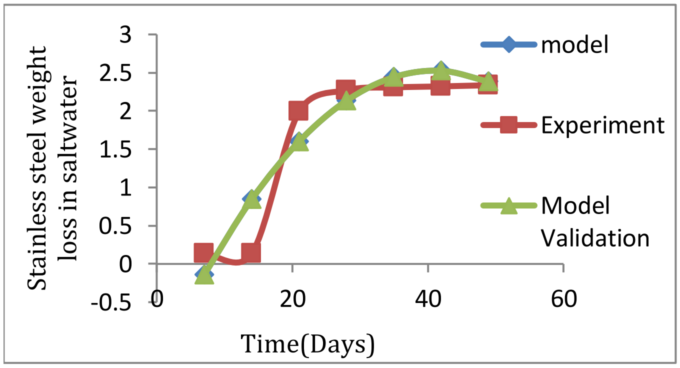

Fig. 4: Stainless steel weight loss comparison of quadratic model and experiment in saltwater medium

The following apparatus will be used for this experiment venier caliper, analytical balance, beaker and conical flask. Also the materials to be used are iron brush file, and paper, distilled water, detergent soap, supporting iron rods and ropes on the stainless steel material used for the investigation on salt and fresh environment.

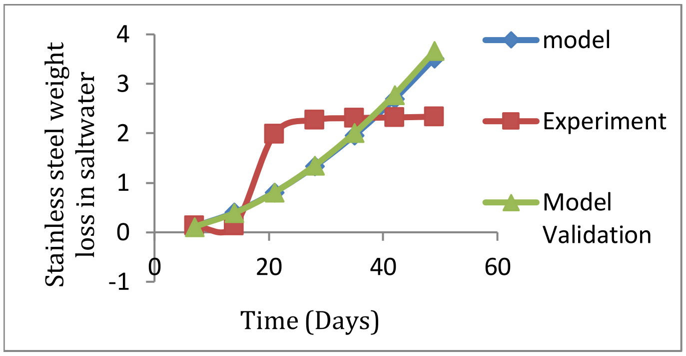

Fig. 5: Stainless steel weight loss comparison of power model and experiment in saltwater medium

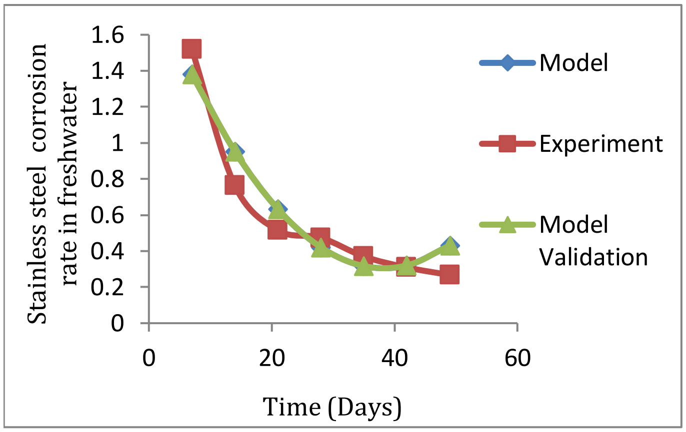

Fig. 6: Stainless steel corrosion rate comparison of quadratic model and experiment in freshwater medium

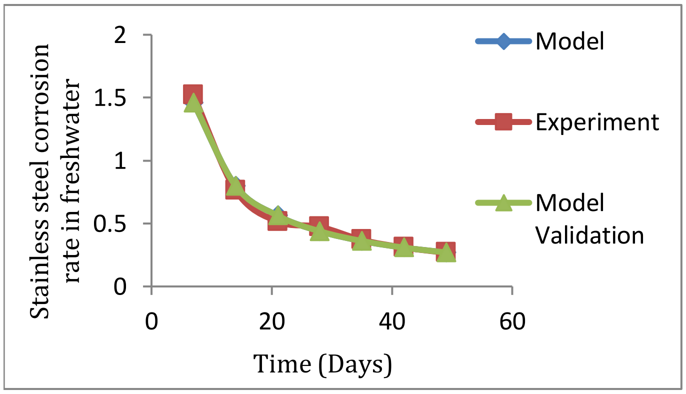

Fig. 7: Stainless steel corrosion rate comparison of power model and experiment in freshwater medium

Preparation techniques

The metals were cut into shapes length of 6cm and width 5 cm. The metals are not of the same thickness the thickness varied from 0.80 mm to 0.86 mm. A smoothing file and sand paper will be used to dress the edges of the medium to remove rough filling to avoid accelerated corrosion at the edges. A hole was made at the edges of each metals medium for insertion of the ropes. Each medium washed thoroughly in distilled water using a clean brush and afterward dried and store in a plastic bags.

Initial weighting of specimen

The metals were taken and each weighted carefully using an analytical balance. Reading was taken to two decimal places. The weight of each specimen was recorded and the specimen will be marked and rest separately to avoid mix up.

Specimen arrangement for corrosion test

Six Pyrex beakers was used for the corrosive media. Each metal was suspended in the corrosive medium through a supporting rod and a rope. This is to ensure uniform contact of the specimen as shown in the Figure 1.

Experimental procedure

The four beakers were divided into three sets. Each of the set s contain saltwater and freshwater respectively. Labels were used to distinguish the beakers.

This will followed by the introduction of the metal specimens (coupons) into the medium by suspending the metal from a supporting rod as shown above for easy immersion and removal. For every seven days (168 hours) after setting the experiment, the new weight readings of metals were taken, these routine checks were carried out for a period of forty-nine (49) days.

Table 1: Presents the initial mass, volume and densities of stainless steel and determined before the start of the experiment while table 2 is the chemical analyses of freshwater and saltwater determined using approved standard methods.

Data treatment techniques

Data tabulation, mathematical formulas and graphical methods were used for the computation and analysis of data collected during the experiment survey.

The following parameters were estimated:

(i) Metal weight loss

This is the change in weight of metal at any point in time and it is obtained by the equations:

Weight loss = Initial weight – final weight of metal at time, t.

$$\Delta w = w_o - w_t \tag{1}$$

(ii) Corrosion rate

This is the change in weight of metal per surface area exposed per unit time and is obtained by the equation below

$$C_R = \frac{534\,\Delta w}{\rho A t} \tag{2}$$

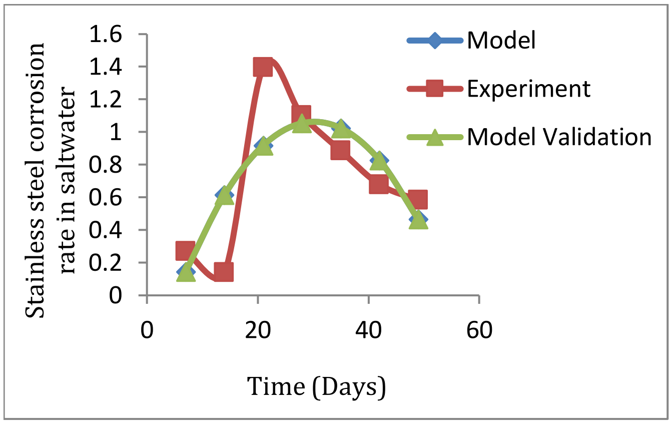

Fig. 8: Stainless steel corrosion rate comparison of quadratic model and experiment in saltwater medium

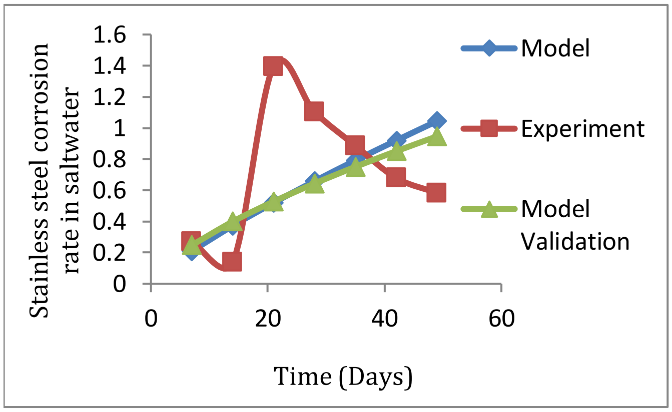

Fig. 9: Stainless steel corrosion rate comparison of power model and experiment in saltwater medium

Where, $w_o =$ Initial weight of material (gm), $w_t =$ Instantaneous weight of material (gm) $\rho =$ Density of material (gm/mm^3), $A =$ Cross- sectional area of material (mm^2), $t =$ Time (Day)

Models for experimental data analysis

(i) Quadratic Model

The quadratic model was determined using regression analysis and it is represented by the equation (3).

$$y = at^2 + bt + c \tag{3}$$

$$e = y - at^2 - bt - c \tag{4}$$

$$S_r = \sum e^2 = \sum \left(y - at^2 - bt - c\right)^2 \tag{5}$$

Differentiating equation (5) with respect to a, b and c, gives:

$$\frac{\partial Sr}{\partial a} = -2\sum \left(y - at^2 - bt - c\right)t^2 \tag{6}$$

$$\frac{\partial Sr}{\partial b} = -2\sum \left(y - at^2 - bt - c\right)t \tag{7}$$

$$\frac{\partial Sr}{\partial c} = -2\sum \left(y - at^2 - bt - c\right) \tag{8}$$

For minimum error, equation (6) through (8) reduces to zero that is

$\frac{\partial S_r}{\partial a} = 0$, $\frac{\partial S_r}{\partial b} = 0$ and $\frac{\partial S_r}{\partial c} = 0$.

Hence rewriting equation (6) to (8) we have as follows:

From equation (6), we have

$$\sum \left(y - at^2 - bt - c\right)t^2 = 0$$

$$\sum t^2 y - a\sum t^4 - b\sum t^3 - c\sum t^2 = 0$$

$$c\sum t^2 + b\sum t^3 + a\sum t^4 = \sum t^2 y \tag{9}$$

From equation (7)

$$\sum\left(y - at^2 - bt - c\right)t = 0$$

$$\sum ty - a\sum t^3 - b\sum t^2 - c\sum t = 0$$

$$c\sum t + b\sum t^2 + a\sum t^3 = \sum ty \tag{10}$$

From equation (8)

$$\sum\left(y - at^2 - bt - c\right) = 0$$

$$\sum y - a\sum t^2 - b\sum t - \sum c = 0$$

But $\sum c = nc$

$$nc + b\sum t + at^2 = \sum y \tag{11}$$

Arrange the above equation (9) to (11) in matrix form gives:

$$\begin{bmatrix} n & \sum t & \sum t^2 \\ \sum t & \sum^2 & \sum t^3 \\ \sum t^2 & \sum t^3 & \sum t^4 \end{bmatrix} \begin{Bmatrix} c \\ b \\ a \end{Bmatrix} = \begin{Bmatrix} \sum y \\ \sum ty \\ \sum t^2 y \end{Bmatrix} \tag{12}$$

Equation (12) is used for the determination of the quadratic model for each of the materials studied in this research. The data for calculation of the constants as well as the calculations are presented in the appendix.

(ii) Power model

The power model is represented by the equation (13), we have

$$y = kt^{\alpha} \tag{13}$$

Equation (13) is a non-linear expression thus, upon linearization, gives

$$\log y = \log k + \alpha \log t \tag{14}$$

Equation (14) is a linear expression thus,

$$\log y = Y$$

$$\log k = C$$

$$\log t = X$$

$$\alpha = M$$

Hence, the linear equation is expressed thus

$$Y = MX + C \tag{15}$$

The error, $e = Y - MX - C$ (16)

To obtain the best fit of data in equation (16), the sum of the residual errors for all the available data would be minimized as follow:

$$\sum_{i=1}^{n} e^2 = \sum_{1=1}^{n} \left(Y_{measured} - Y_{\text{model}}\right) \tag{17}$$

$$S_r = \sum_{i=1}^{n} e^2 = \sum_{i=1}^{n} \left(Y - MX - C\right)^2 \tag{18}$$

To determine the values of M and C, equation (18) is differentiated with respect to M and C as follows:

$$\frac{\partial S_r}{\partial c} = -2\sum\left(Y - MX - C\right) \tag{19}$$

$$\frac{\partial Sr}{\partial M} = -2\sum\left(Y - MX - C\right)X \tag{20}$$

To minimize S_r, equation (19) and (20) is set to zero i.e

$$0 = \sum Y - M\sum X - \sum C \tag{21}$$

$$0 = \sum XY - M\sum X^2 - C\sum X \tag{22}$$

But $\sum C = nC$ (23)

Solving equation (21) and (22) simultaneously gives

$$M = \frac{n\sum XY - \sum X \sum Y}{n\sum X^2 - \left(\sum X\right)^2} \tag{24}$$

C in equation (15) is given as

$$C = \overline{Y} - M\overline{X} \tag{25}$$

Where, $\overline{X}$ = Mean of X data, $\overline{Y}$ = Mean of Y data

Correlation coefficient (R)

The correlation Coefficient, R is determined by the formula

$$R = \frac{n\sum XY - \left(\sum X\right)\left(\sum Y\right)}{\sqrt{n\sum X^2 - \left(\sum X\right)^2} \times \sqrt{n\sum Y^2 - \left(\sum Y\right)^2}} \tag{26}$$

Hence, the coefficient of determination, R^2 is determined by taking the square of equation (26). The implication of R^2 tells how the model explains the original model.

Determination of error

The error between the experimental results and the models are determined using the expression stated below.

$$err = \sqrt{\frac{\left(y_e - y_m\right)^2}{n}} \tag{27}$$

Where: y_e = Experimental Result for both weight loss and corrosion rate, y_m = Model result for both weight loss and corrosion rate. The data for calculation of the above parameters as well as the calculations are presented in the appendix.

RESULTS AND DISCUSSION

Effect of fresh water medium on weight of materials

The effect of freshwater on stainless steel material was investigated using experimental approach. Figure 2 and 3 shows the effect of freshwater on stainless steel material over a period of 49 days. The experimental result for stainless steel shows that the weight reduced by 0.776 gm over the sampling period (from 122.900 to 122.124 gm), representing 0.631% weight loss. It was shown from the result of the experimental that the weight loss of stainless in freshwater medium was relatively unaffected until nearly the 21st day when increase in weight loss was observed. However, the quadratic model shows that the weight loss of stainless steel in freshwater media increases gradually with time and the error between the experiment and the model given as $err_q = 0.0471$. The quadratic model expression for stainless steel weight loss is given as $y = -0.0001t^2 + 0.0091t + 0.5224$ while the validating model is expressed as $y = -0.00007t^2 + 0.091t + 0.5224$ with coefficient of determination, $R^2 = 0.8052$. The power model shown in Figure 3 shows that weight loss of stainless steel in freshwater medium increases with time and has same expression as the model validation represented by the equation $y = 0.4298t^{.01551}$ with coefficient of determination,

Table 1: Initial mass, volume and density of water

S/No	Samples	Mass (g)	Volume	Density g/ml
1.	Stainless steel (saltwater)	122.30	35 ml	3.494 g/ml
2.	Stainless steel (freshwater)	113.07	50 ml	2.261 g/ml

Table 2: Chemical analysis of water

S/No	Parameter	Test Method	Salt	Fresh	Standard
1.	pH	ASTMD1293	580	6.80	65-8.5
2.	Chloride (mg/l)	APHA4500Cl^{-B}	1783.51	36.19	250
3.	Sulphate (mg/l)	ASTMD516	188.27	45.10	400
4.	Salinity (mg/l)	ASTMD4880	2939.24	41.02	400
5.	Acidity (mg/l)	APHA46	0.16	0.11	0.3
6.	Alkalinity (mg/l)	ASTMD1067b	1256.20	40.90	400
7.	Iron (mg/l)	APHA311b	0.27	0.18	0-0.30
8.	Total Hardness (mg/l)	APHA2340C	74.06	53.70	500

$R^2 = 0.7677$. The error between experimental and model results is given as $err_p = 0.0362$.

Effect of saltwater medium on weight of materials

Like in the freshwater media, the weight of stainless steel shows remarkable reduction over the period of the experiment. Hence, the weight loss increases with time under the influence of saltwater. The weight loss in saltwater media of the three materials for the experimental results, the model and model validation for the quadratic and power model are shown in Figure 4 and 5.

The effect of saltwater on stainless steel over the period of the experiment is shown in Figure 4 and 5. The experimental result shows that the weight loss of stainless in saltwater medium decreases within the first fourteen days and then increases at a very high rate between the 14th and 21st. After the third week, weight loss became relatively constant. Generally, the weight of stainless steel which was initially 115.00 gm reduced to 112.164 gm at the end of the experiment with a weight loss of 2.336gm representing 2.031% material loss of stainless steel in saltwater. However, the weight loss of stainless steel in saltwater compared with both the quadratic and power models show that there was no lag or period of relative constant weight loss. Again, the quadratic model and the model validation are the same by expression for stainless steel weight loss in saltwater medium and it is given as $y = -0.0023t^2 + 0.1889t - 1.3521$ with coefficient of determination, $R^2 = 0.8781$ and the error between experimental and model results is given as $err_q = 0.3438$. The expression for the power model is given as $y = 0.0041t^{1.7345}$ while the model validation is given as $y = 0.0035t^{1.7867}$ with coefficient of determination, $R^2 = 0.7807$ and the error between the experimental results is $err_p = 0.7560$.

Effect of corrosion rate on materials in freshwater media

The rate of corrosion of the three materials as a function of weight loss was observed to be affected by freshwater, but the effects differ according to material type. The experimental values of the corrosion rate of the materials studied were compared with quadratic and power models as illustrated in Figure 6 and 7.

In Figure 6 and 7, the rate of corrosion for stainless steel in freshwater was observed to sharply increase from zero to 1.520mm/day for the first 7 days, which also was the peak value, but there was a steady decline from the 7th day to the 49th day. The comparison of experimental values with the quadratic model for rate of corrosion of stainless steel material as presented in figure 6 showed a similar decline in corrosion rate with an equation represented by $y = 0.0011t^2 - 0.0842t + 1.9163$ and coefficient of determination, $R^2 = 0.9225$. In figure 4.16, the comparison of experimental values with the power models for rate of corrosion shows that stainless steel decrease with increase in time in similar

Table 3: Experimental results of investigated materials

Time	Parameter	STL1	STL2
0 day	Length (mm)	139	11
	Thickness (mm)	62	53
	Breadth (mm)	3.2	3.3
	Weight (gm)	122	115
7 days	Length (mm)	138.97	112.9
	Thickness (mm)	61.984	52.84
	Breadth (mm)	3.984	3.14
	Weight (gm)	122.289	114.87
14 days	Length (mm)	138.99	112.898
	Thickness (mm)	61.981	52.838
	Breadth (mm)	3.974	3.138
	Weight (gm)	122.287	114.867
21 days	Length (mm)	138.968	112.758
	Thickness (mm)	61.971	52.628
	Breadth (mm)	3.964	3.112
	Weight (gm)	122.277	113.01
28 days	Length (mm)	138.828	112.498
	Thickness (mm)	61.831	52.378
	Breadth (mm)	3.828	2.872
	Weight (gm)	61.831	112.73
35 days	Length (mm)	138.817	112.461
	Thickness (mm)	51.864	52.341
	Breadth (mm)	3.823	2.835
	Weight (gm)	122.126	112.693
42 days	Length (mm)	138.8158	122.447
	Thickness (mm)	61.8188	52.327
	Breadth (mm)	3.8308	2.821
	Weight (gm)	122.1248	112.679
49 days	Length (mm)	138.8145	122.432
	Thickness (mm)	61.8175	52.312
	Breadth (mm)	3.8295	2.806
	Weight (gm)	122.1235	112.664

STL1= stainless steel in freshwater, STL2= stainless steel in saltwater

manner as that obtained from the experiment and it is expressed as $y = 7.8759t^{-0.867}$ while the model validation equation is expressed as $y = 7.8763t^{-0.867}$ with coefficient of determination, $R^2 = 0.9913$. These results show that both the quadratic and power model fit very well into the experimental data used in obtaining the rate of corrosion for stainless steel in freshwater media with error between experimental and model results for the quadratic and power model given as $err_q = 0.1209$ and $err_p = 0.0354$ respectively.

Effect of corrosion on materials in saltwater media

The effect of saltwater on the rate of corrosion of mild steel, stainless steel and aluminum was investigated as illustrated in Figure 8 and 9. The experimental result shows that corrosion rate initially decreases within the first seven days (0.271 to 0.139 mm/day) and increased to its maximum value at the 21st day. From this maximum value, a steady decrease was observed throughout the rest of experiment (1.396 to 0.583 mm/day). The comparison of experimental values with the quadratic model for rate of corrosion of stainless steel as presented in Figure 8 shows that corrosion rate increases steadily to a maximum value of 1.0546 mm/day at the 28th day and then decreases to 0.4645 mm/day at the 49th day with an equation represented by $y = 0.0017t^2 + 0.1028t - 0.4910$ and coefficient of determination, $R^2 = 0.5562$. In figure 9, the comparison of experimental values with the power models for rate of corrosion shows that stainless steel in saltwater increases almost linearly with time from 0.2102 to 1.0445mm/day with equation expressed as $y = 0.0423t^{0.8239}$ while the model validation equation is expressed as $y = 0.0647t^{0.6894}$ with coefficient of determination, $R^2 = 0.3337$. These results show that the quadratic model only explained 55.62% of the experimental results while the power model did not fit into the experimental data used in obtaining the rate of corrosion for stainless steel in saltwater media. The error between experimental and model results for the quadratic and power model for stainless steel corrosion rate in saltwater media are given as $err_q = 0.2748$ and $err_p = 0.4315$, respectively.

CONCLUSIONS

The corrosion rate and weight was rapid in the salt water environment than the fresh water medium. The application of the quadratic and power model is a good tools and concept for the monitoring and predicting the rate of corrosion and weight loss of stainless steel as well as other metal materials subjected into such environment. The characteristics of water medium influence the rapid rate of stainless steel corrosion. Other contributing factors are environmental pollution leading to high deposited of impurities that are contributing agent to initiate corrosion. It is also observed that increase in crude oil component discharged into the water body, will lead increase in microbial activity, which with time will multiply to induce the metal concentration as well as result to rapid degradation of the environment including metals.

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