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Corrosion Inhibition of Mild Steel using Organic Coating in Acidic Medium

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Abstract
The corrosion inhibition of mild steel using Sinclair synthetic car paint, an organic coating in acidic medium (HCl) at four different levels of acidity, pH3, pH4, pH5 and pH6 at room temperature has been investigated. Weight loss method was used, in which test coupons (substrates) with known weights were immersed in the test medium, for a total exposure time of 15 days. The weight losses were measured at interval of three days, and the corrosion rates and inhibition efficiencies were computed. The effects of immersion period and level of acidity pH, of medium on the inhibition efficiency of the paint (inhibitor) were investigated. Three empirical models were also derived, validated and used for the predictive evaluation of the corrosion rate of the mild steel under paint. Deviational analysis indicates tolerable maximum deviations of less than 16% of model predicted corrosion rates from the experimental corrosion rates, with over 84% reliability response coefficient of corrosion rate to the collective operational factors affecting it. It was found that the corrosion rate of mild steel was significantly reduced in the presence of the paint and that it offers good inhibition efficiency at various pH values.

Keywords*: Corrosion, Corrosion Rate, Mild steel, Organic coating, Inhibitor*

1. Introduction

Metals and their alloys are often exposed to the action of acids in industrial processes, which cause severe consequences resulting in great economic loss, loss of material and often times, loss of lives. These effects are of particular consequence in the Chemical and Petrochemical industries, as chemicals (containing acids) are increasingly becoming corrosive, thereby causing significant deterioration of constructional and structural materials (Adebayo, 2014). To this end, much effort have been put forward by many investigators to study the mechanisms of corrosion under coatings in different environments, and consequently predict failure modes of metals due to corrosion damage (Gan and Mark, 2010).But the surface corrosion rate of metals is greatly influenced by operating temperature, pressure, acidity or basicity of medium (ie, pH), period of contact, concentration of medium and many other factors. It is therefore difficult to develop a theoretical model that is capable of describing the relationship between all these factors and the associated corrosion rates (Jayanta et al, 2010).

Many researchers have therefore concentrated on the corrosion inhibition mechanisms, adsorption isotherms, activation parameters, quantum chemistry, better inspection methods, materials redesign, etc (Khadom and Yaro, 2010). Still, because of the high cost and long duration of corrosion experiments, development of improved prediction models is now required.However, a variety of methods can be used to predict future data based on the historical data of the system. These methods include the statistical prediction method, artificial neural networks (ANNs) and fuzzy logic methods (Jia et al, 2011).

Deen et al (2011) investigated the corrosion protection evaluation of mild steel painted surface using electrochemical impedance spectroscopy (EIS). In the study, electrochemical behavior of painted surface was estimated by EIS parameters that contained paint film resistance, paint film capacitance and double layer capacitance. The results show that the deterioration of paint film protectiveness was due to the penetration of the electrolyte through the film which agrees with those of Durowaye et al (2014).

Similarly, the corrosion protection of mild steel by paint containing polyaniline-hydrochloride (PANI-HCl) was investigated by Samuel et al (2012). Humidity cabinet, salt spray and underwater exposure studies were adopted. The results revealed that paint containing lower PANI- HCl, protected mild steel better than that containing higher PANI-HCl. And Kexi, et al (2012), have equally predicted the corrosion rate of wet gas gathering pipelines using Numerical method, in which the Newton – Raphson’s iteration model was used to model the corrosion rate. However, significant errors were recorded in the predicted corrosion rate as only factors with relatively larger weights were selected as the input variables.

Talo et al (2013) investigated Polyaniline epoxy blend coatings on mild steel in neutral, acidic and alkaline solutions using electrochemical methods such and potentiodynamic polarization method. The results confirmed that epoxy blend coatings containing Polyaniline was more effective in acidic solution than in neutral solution.

However, Rosa et al (2013) reported the corrosion behaviour of mild steel reinforced concrete under surface coatings in acid medium in which acrylic and epoxy coatings were applied to concrete cylinders and exposed to an artificial acidic solution for 589 days. The corrosion of the steel reinforcement was evaluated by means of corrosion potential and polarization resistance. The results show that the epoxy coating performed better as barrier in acidic medium.

The development of a mathematical model for the prediction of corrosion rate behaviour for mild steel in 0.5M sulphuric acid was reported by Suleiman et al (2013), in which grewiavenusta (wild jute tree) plant extract was used as inhibitor to model the corrosion rate of mild steel. Linear regression equation and analysis of variance (ANOVA) were employed to investigate the influence of process parameters on the corrosion rate of the samples. It was concluded that the predicted corrosion rate of the sample was found to be very close to those experimentally observed.

Anees (2013) reported the modelling of corrosion reaction data in inhibited acid environment using neural networks, while Anees and Ali (2014) modelled the corrosion rate of mild steel in nitric using kinetic and mathematical approaches, wherein the combined effect of temperature and acid concentration was modelled using a non-linear regression method. Both results show that the polynomial equations are able to accurately predict the measured data, with high correlation coefficients and that the corrosion reaction was approximately first order, and further buttress the findings by Srdjan et al (2010).

Abida and Harikrishna (2014) developed a polynomial equation to relate the concentration of hydrochloric acid as corrosive medium for mild steel, to the variables like inhibitor concentration, temperature and time. The inhibitor used was Castor seed oil. The model allows the prediction of the extent of corrosion inhibition at different concentrations. ANOVA was used to validate the model. A maximum of 84.1% inhibitor efficiency was achieved under optimum conditions of 50% v/v inhibitors concentration, 48 hours time and 303K temperature.

In this study however, Sinclair synthetic car paint, has been applied to mild steel and the corrosion rate based on the steel's structural weight loss, immersion-point pH and time while serving in HCl acid was evaluated. Empirical models are derived, validated and used to correlate the corrosion rate data and the factors affecting corrosion rate of mild steel.

2. Materials and Methods

Mild steel specimens, 0.5M HCl acid, distilled water, beakers, digital weighing balance, polymeric threads, acetone, Sinclair synthetic car paint (an organic coating), water, pH meter, emeryl cloth.

2.1 Specimen Preparation and Experimentation

A 0.5M of hydrochloric acid was prepared and diluted with distilled water to obtain HCl acid solution of pH values of 3, 4, 5 and 6. The beakers used were thoroughly washed and rinsed. Each beaker contained 500ml of 0.5M hydrochloric acid with pH values 3, 4, 5 and 6 respectively. Sheets of mild steel (composition given in Table 1), 1mm thick, were cut into coupons of size 32mm by 30mm. A 5mm diameter hole was drilled in each coupon to facilitate ease of suspension and immersion in the environment by polymeric thread. The coupons were then washed with acetone and dried to remove all traces of corrosion products that may serve as corrosion initiation sites. A total of twenty pieces of the washed coupons were painted with Sinclair synthetic car paint while another twenty coupons were left uncoated. All painted coupons were allowed to dry and set for two days. The method adopted in this investigation is the gravimetric or weight loss technique. The weight loss of the test pieces due to corrosion were measured by exposing the metal specimens of known area and weight to the corrosive environment for a period of time and the difference in weight before and after exposure is calculated. All coupons (coated and uncoated) were weighed using the digital weighing balance, before immersion in the corrosive media. The solutions were taken in a 500 ml beaker. The weighed coupons were then wholly immersed in the corrosive medium by means of polymeric threads. Five uncoated coupons were suspended in each of four beakers containing HCl acid of pH3, pH4, pH5 and pH6 respectively as control. Another five coupons painted with Sinclair synthetic car paint were suspended in each of another four beakers containing the same corrosive medium. All test coupons were weighed before and after immersion in the corrosive medium. The coupons' exposure period was a total of 15 days with five measurements taken at an interval of 3 days. Figure 1, shows the snap shot of the experimental set up.

Table 1: Chemical Composition (%) of Mild Steel(C-35)

Cr	Ni	Mo	Cu	Mn	C	S	Si	Zn	Fe
1.01	0.25	0.047	0.82	1.17	0.350	0.011	0.280	1.55	94.50

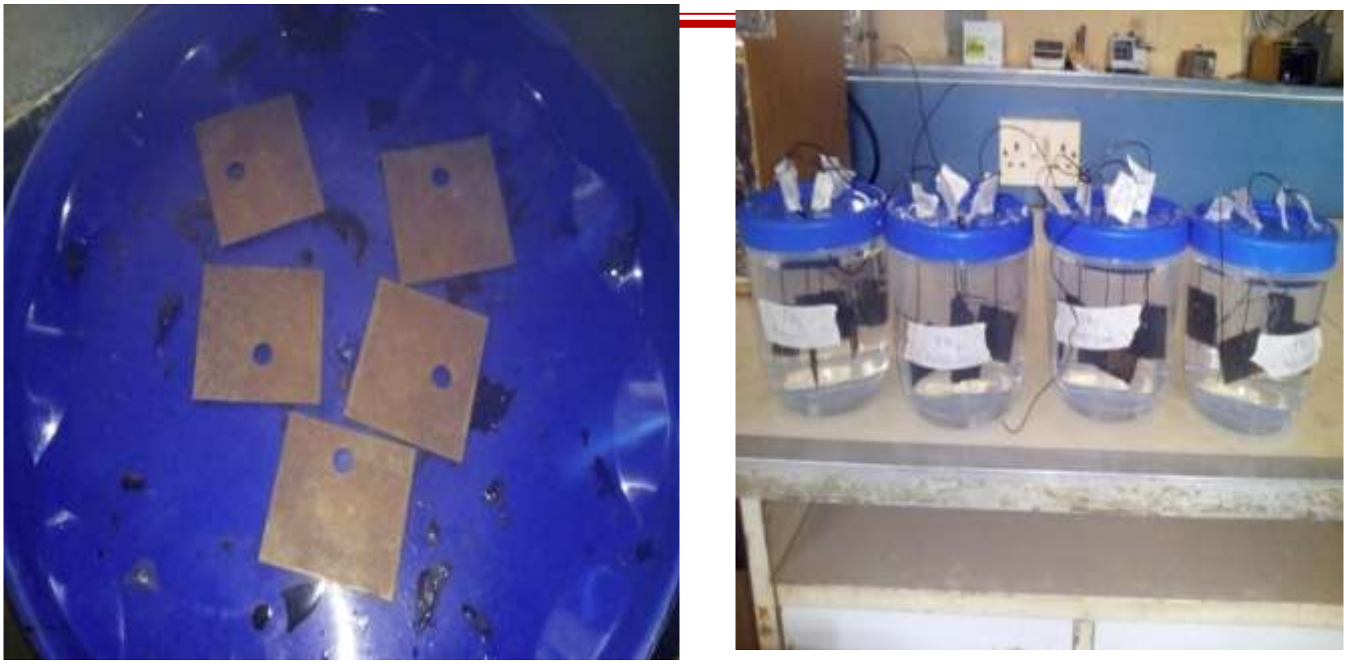

Figure 1: (a) Uncoated Mild Steel Substrates (b) Substrates immersed in corrosive medium

2.2.2 Models formulation

The experimental corrosion rate results of substrates (coated and uncoated) in HCl acid as a function of acidity level, pH and immersion period are correlated using three empirical models of first degree presented as follows.

Model 1: $\boldsymbol{\zeta = f(\vartheta, \varepsilon)}$

where, ζ = Corrosion rate of mild steel (mm/yr), ϑ = Exposure time (yr) and ε= Initial weight (Kg). Table 2 gives the data for Model 1.

Table 2: **Variation of corrosion rate ζ of mild steel with its exposure time ϑ and initial weight, ε**

(ζ) (mm/yr)	(ϑ) (days)	(ϑ) (yrs)	(ε) (g)	(ε) (kg)
0.00000085	3	0.0082	5.4425	0.00544
0.00000078	6	0.0164	5.3794	0.00538
0.00000069	12	0.0329	5.7077	0.00578
0.00000072	15	0.0411	5.4035	0.00540

Computational analysis of generated experimental data shown in Table 2, (for Model 1) indicates that;

$$\boldsymbol{\zeta = -K\vartheta + N\varepsilon + \text{ƅ}} \quad (1)$$

Introducing the values of K, N and ƅ yields

$$\boldsymbol{\zeta = -4 \times 10^{-6}\,\vartheta + 0.000012\,\varepsilon + 8.6 \times 10^{-7}} \quad (2)$$

Where, $K = 4 \times 10^{-6}$, $N = 0.000012$ and $\text{ƅ} = 8.6 \times 10^{-7}$ are empirical constants (determined using C-NIKBRAN [Nwoye, 2008]).

Model 2: $\boldsymbol{\zeta = f(\vartheta, ɤ)}$
where, ζ = Corrosion rate of mild steel (mm/yr), ϑ = Exposure time (yrs) and $ɤ$ = Weight loss (Kg). Table 3 gives the data for Model 2.

Table 3: Variation of corrosion rate ζ of mild steel with its exposure time ϑ and weight loss $ɤ$

(ζ) (mm/yr)	(ϑ) (days)	(ϑ) (yrs)	($ɤ$) (g)
0.00000085	3	0.0082	0.0103
0.00000078	6	0.0164	0.0189
0.00000069	12	0.0329	0.0336
0.00000072	15	0.0411	0.0436

Computational analysis of generated experimental data shown in Table 3, (for Model 2) indicates that;

$$\boldsymbol{\zeta = -K\ln(ɤ) + N\vartheta + S} \tag{3}$$

Introducing the values of K, N and

$$\boldsymbol{\zeta = -10^{-7}\ln(ɤ) + 0.000001\vartheta + 4 \text{ x } 10^{-7}} \tag{4}$$

Wher, $K = 10^{-7}$, $N = 0.000001$ and $S = 4 \text{ x } 10^{-7}$ are empirical constants (determined using C-NIKBRAN [Nwoye, 2008]).

Model 3: $\boldsymbol{E = f(ȿ, \vartheta)}$
where, E= Inhibition efficiency of paint (%), $ȿ$ = Corrosive medium pH[-] and ϑ = Exposure time (days). Table 4 gives the data for model 3.

Table 4: Variation of inhibition efficiency with corrosive media pH, $ȿ$ at constant exposure time ϑ

(E) (%)	($ȿ$)[-]	(ϑ) days	(ϑ) (yrs)
65.78	3	6	0.0164
63.16	4	6	0.0164
54.63	5	6	0.0164
11.11	6	6	0.0164

Computational analysis of generated experimental data shown in Table 4, (for Model 3) indicates that;

$$\boldsymbol{\zeta = -(Kȿ^2 + S\vartheta + S_e) + Nȿ} \tag{5}$$

Introducing the values of K, N and S

$$\boldsymbol{\zeta = -(10.225ȿ^2 + 0.002\,\vartheta + 68.01) + 74.77ȿ} \tag{6}$$

where,K = 10.225, N = 74.77, S= 0.002 and S_e = 68.01 are empirical constants (determined using C-NIKBRAN [Nwoye, 2008]).

The derived models are equations (2), (4) and (6).These empirical models are two-factorial in nature since each is composed of two input process factors. This implies that the predicted corrosion rate of mild steel is dependent on these factors.

2.2 Boundary and Initial Conditions

Consider a piece of mild steel, interacting with some corrosion-induced agents. The corrosive medium is assumed to be affected by unwanted dissolved gases. For Model 1, the range of exposure time considered: 3 – 15 days (0.0082 - 0.0411yrs), range of mild steel initial weight and corrosion rate are: 0.00538 – 0.00578 kg and 0.00000069 – 0.00000085 mm/yr respectively. The pH of corrosive media was 6.0. For Model 2, the range of exposure time, mild steel weight loss and corrosion rate are: 3 – 15 days (0.0082 - 0.0411 yrs), 0.0103 – 0.0436 g and 0.00000069 – 0.00000085 mm/yr respectively. The pH of corrosive media was 6.0. For Model 3, the range of pH of corrosive media and inhibition efficiency of car paint are: 3-6.0 and 11.11 – 65.78 % respectively. The exposure time for the process was 6 days (0.0164 yrs). The boundary conditions are: aerobic environment for the corrosive medium since the atmosphere contains oxygen. At the bottom of the exposed steel, a zero gradient for the gas scalar are assumed. The exposed mild steel is stationary. The sides of the solid are taken to be symmetries.

2.3 Model Validity

The validity of the models is strongly rooted on equations (2), (4) and (6) which are the core equations. Tables 2.2(a-c) also agree with equations (2), (4) and (6) respectively following the constants in the equations evaluated from the experimental results. Furthermore, the derived models were validated by comparing the corrosion rates predicted by the respective models and that obtained from the experiment. This was done using various analytical techniques.

3. Results and Discussions

The experimental corrosion rate results of substrates (coated and uncoated) in HCl acid as a function of acidity level, pH and immersion period, are correlated using three empirical models of first degree as given by equations (2), (4), and (6).These empirical models are two-factorial in nature since each is composed of two input process factors and agrees with the work of Nwigbo et al, (2017). This implies that the predicted corrosion rate of mild steel is dependent on these factors.

3.1 Graphical analysis

Graphical analysis of Figures 2 & 3 (for Model 1 results), Figures 4 & 5 (for Model 2 results), as well as Figure 3.1(e) (for Model 3 results), shows very close alignment of the curves from derived model and experiment. It is strongly believed that the degree of alignment of these curves is indicative of the proximate agreement between Experimental and Model predicted results.

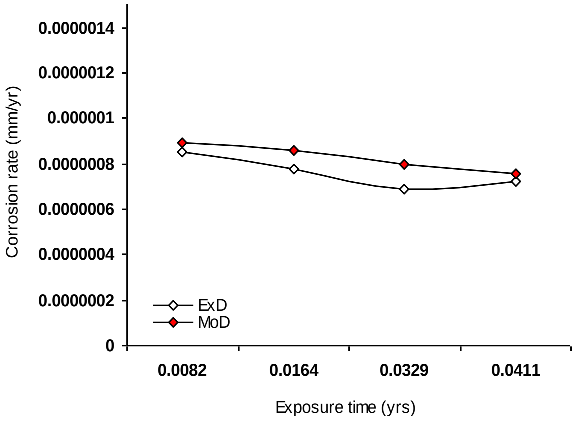

Figure 2 Comparison of the mild steel corrosion rates (relative to exposure time) as obtained from experiment and derived model.

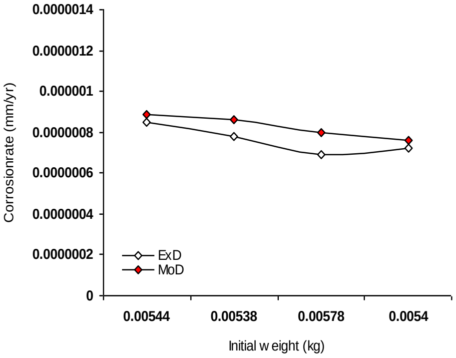

Figure 3 Comparison of the mild steel corrosion rates (relative to initial weight) as obtained from experiment and derived model.

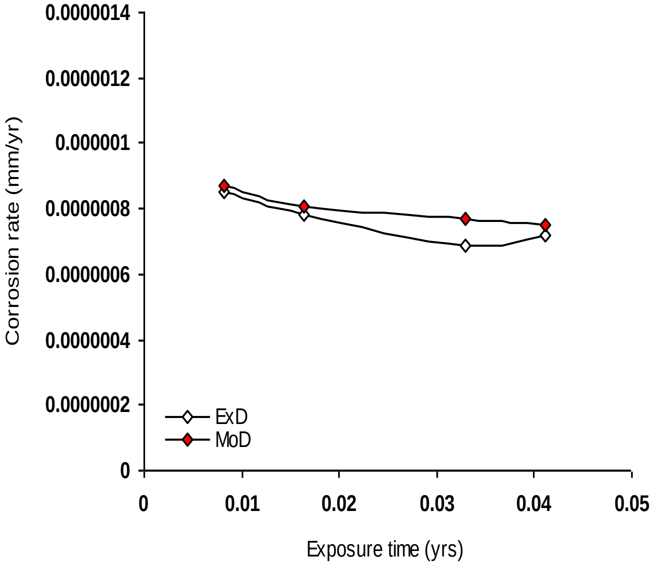

Figure 4 Comparison of the mild steel corrosion rates (relative to exposure time) as obtained from experiment and derived model.

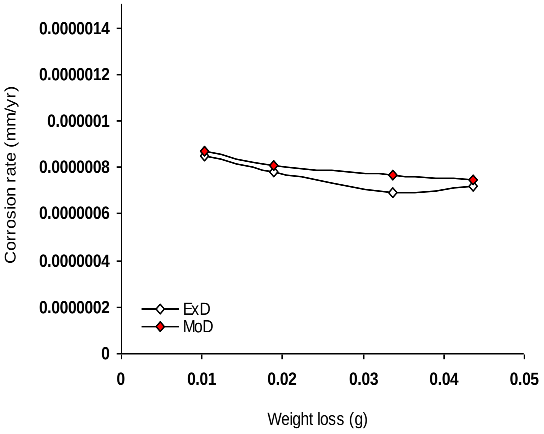

Fig.ure5 Comparison of the mild steel corrosion rates (relative to weight loss) as obtained from experiment and derived model.

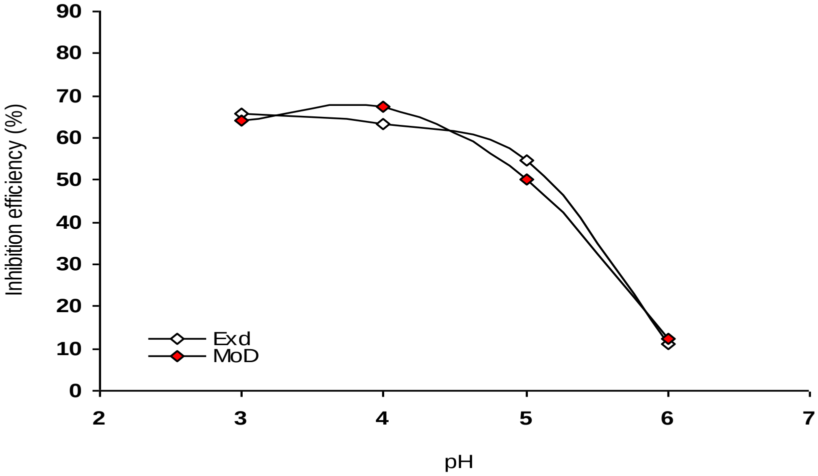

Figure 6 Comparison of the car paint inhibition efficiencies (relative to pH) as obtained from experiment and derived model.

3.2 Statistical analysis

3.2.1 Standard error

The standard errors incurred in predicting the mild steel (uncoated) corrosion rate for each value of exposure time and initial weight considered as obtained from experiment and derived models were 3.71 x 10^{-8} and 4.23 x 10^{-9} & 7.02 x 10^{-8} and 6.92 x 10^{-8} % respectively *(for MODEL 1)*, for each value of exposure time & weight loss considered: 1.68 x 10^{-8} and 3.71 x 10^{-8} ; 4.03 x 10^{-8} and 1.69 x 10^{-8} % respectively *(for MODEL 2)*. Also the standard errors incurred in predicting the inhibition efficiency of car paint for each value of corrosive medium pH considered (at constant exposure time) as obtained from experiment and derived model were 15.17and 14.46 % respectively *(for MODEL 3)*. These results deviate slightly from those predicted by David et al, (2013).The standard error was evaluated using Microsoft Excel version 2003.

3.2.2 Deviational analysis

Comparative analysis of the corrosion rates/inhibition efficiencies/weight losses precisely obtained from experiment and derived model shows that the model-predicted values deviated from experimental results. This was attributed to the fact that the effects of the surface properties of the mild steel which played vital roles during the corrosion process were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted corrosion rate to those of the corresponding experimental values. The deviation Dv, of model-predicted corrosion rate from the corresponding experimental result was given by

$$D_v = \frac{(\zeta_{mod} - \zeta_{exp})}{\zeta_{exp}} \text{ x } 100 \qquad (7)$$

where, ζ_{exp} and ζ_{mod} are corrosion rate values evaluated from experiment and derived model respectively.

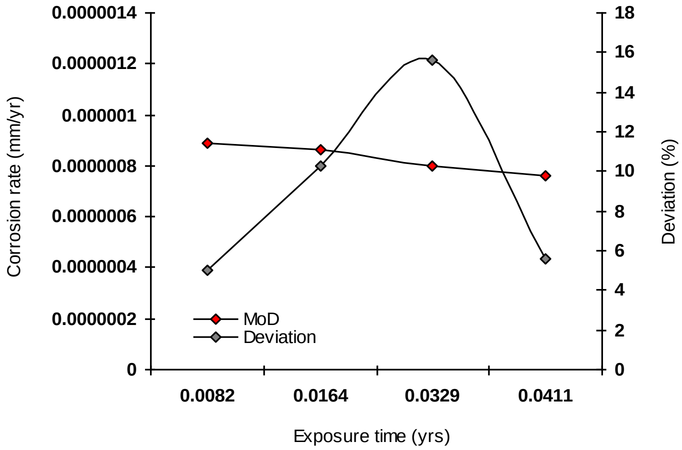

Figure 7 Variation of model-predicted corrosion rate with associated deviation from experimental results (relative to exposure time)

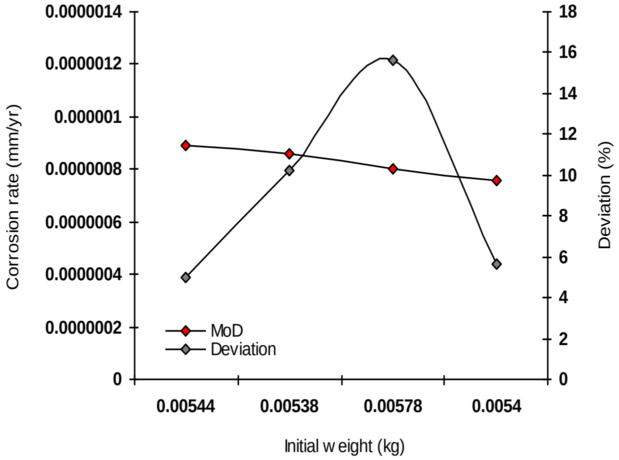

Figure 8 Variation of model-predicted corrosion rate with associated deviation from experimental results (relative to initial weight)

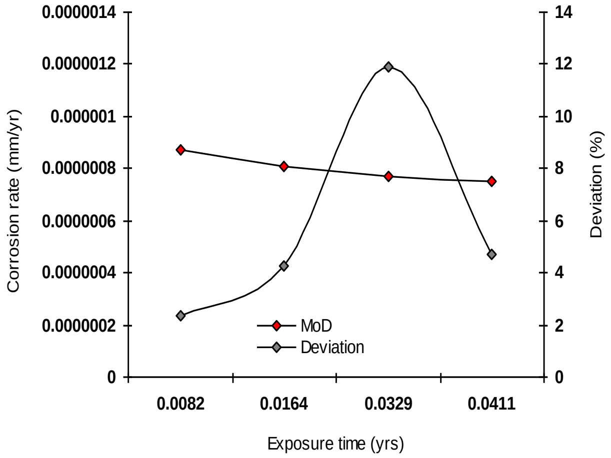

Figure 9 Variation of model-predicted corrosion rate with associated deviation from experimental results (relative to exposure time)

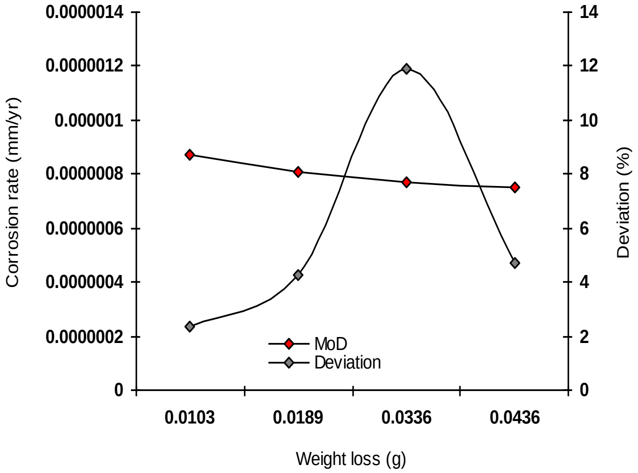

Figure 10 Variation of model-predicted corrosion rate with associated deviation from experimental results (relative to weight loss)

Comparative analysis of Figures 7 and 8 (for MODEL 1 results) and Figures 9 & 10 (for MODEL 2 results), show tolerable maximum deviations which are less than 16 %, translating to over 84% operational confidence level for the derived models as well as over 0.84 reliability response coefficient of corrosion rate to the collective operational factors affecting it.

4. Conclusion

The corrosion inhibition of mild steel (C-35), in 0.5M HCl acid using Sinclair synthetic car paint (an organic coating), at four different levels of acidity (pH3, pH4, pH5, and pH6), using gravimetric method has been studied. It was concluded that, corrosion of mild steel in acidic media can prove detrimental in a short period of time if not inhibited and that the rate of corrosion is proportional to the time of exposure and the corrosive medium immersion point, pH. This may be caused by desorption of substrate ions by the paint caused by the level of acidity of the medium. Furthermore, the three models suggested to represent the corrosion rate data of mild steel in HCl acid in the presence of Sinclair synthetic car paint, as a corrosion inhibitor were very suitable at different levels of acidity at constant temperature. The validity of the models was ascertained using some graphical tools, statistical tools and computational tools. Deviational analysis indicates tolerable maximum deviations of less than 16% of model predicted corrosion rates from the experimental corrosion rates, with over 84% reliability response coefficient of corrosion rate to the collective operational factors affecting it.

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References

Abida, B. and Harikrishna, S. (2014), Factorial Design Application for the Protection of Mild Steel From Corrosive Medium Using Castor Seed Oil As Inhibitor, Int. J. Chem. Tech. Research, 6(4), 2385 – 2390.

Anees, A. K. and Ali, A. A. (2014) Kinetic and Mathematical Approaches to the Corrosion of Mild steel in Nitric Acid, www.researchgate.net/publication/262572239, (Retrieved, 16/ 10/2016).

Anees, A. K. (2013) Modeling of corrosion reaction data in inhibited acid environment using regression and artificial neural networks, Korean J. Chem. Eng., 30(12), 2197-2204

Adebayo, E.O, (2014), Corrosion Control of Petroleum Pipelines, B. Eng. Project, Department of Mechanical Engineering, University of Illorin, Illorin.

David, E.A., Achika, J., Paul, O.A. and Crystal, A. (2013), A Review on the Assessment of Polymeric Materials Used as Corrosion Inhibitor of Metals and AlloysInt. J. Industrial chemistry 4:2

Deen, k. M., Ahmad, R. and Khan, H. I. (2011), Corrosion Protection Evaluation of Mild Steel Painted Surface by Electrochemical Impedance Spectroscopy, Journal of Quality and Technology Management, www.scirp.org/journal/jqtm, (Retrieved from, 17/11/2016).

Durowaye, S.I.,Durowaye, V.O., and Begusa, B.M. (2014), Corrosion Inhibition of Mild Steel inAcidic Medium by Methyl Red, Int. J. Eng. and Tech., 4(8), 469-475.

Gan, E. C. and Mark, E. O. (2010), A Mathematical Model of the Corrosion of Iron in Sulphuric Acid, J. Eelectrochem. Tech., 134(6), 1357-1365

Israel, O., Onyinyechi, C.N.,Ijeoma, I.D., John, O. I. and Lebe, A. N. (2014), Inhibition of Mild Steel Corrosion by Aspilia Africana in Acidic Solution, American J. Materials Science, 4(3), 144-149.

Jayanta, K.S., Mitra, P.K., Paul, S. and Singh, S.N. (2010), Performance of Different Organic Coatings on Steel Substrate By Accelerated and in Atmospheric Exposure Tests, Indian J. Chem. Tech., 17,102-110.

Jia, A. N., Peter, N. U., Terry, K. and Amstrong, P. (2011), Operational Evaluation of Organic Coatings in Acid medium, American J. Materials Science, 2(3), 141-149.

Kexi, L., Quanke, Y., Xia, W. and Wenlong, J. (2012), A Numerical Corrosion Rate Prediction Method for Direct Assessment of Wet Gas Gathering Pipelines Internal Corrosion, www.mdpi.com/journal/energies, (Retrieved, 16/10/2016).

Khadom, A. A.,Yaro, A. S. andKadhum, A. H. (2010), Corrosion Protection Evaluation of Buried Pipeline using Organic Coating, ChileanJ. Chem. Soc 55:150-152.

Nwoye, C.I., Simeon, N., Ebere, A.,Awo, N. and Ndubuisi, I. (2013), Predictability of Al-Mn Alloy Exposure Time Based On Its As-Cast Weight And Corrosion Rate in Sea Water Environment, Journal of Minerals And Materials Characterization and Engineering, I(3), 307-314.

Nwoye, C. I. (2008), C-Nikbran Data Analytical Memory (Software).

Nwigbo, M.N., Beredam, J. N. and Ejimofor, R. A. (2017), Corrosion Rate Model for Mild Steel in Hydrochloric Acid, Int. J. Eng. and Modern Tech., 3(2), 1 – 6.

Rosa, V., Judith, A., Ana, M. and Enrique, V. (2013), Effect of Surface Coatings on The Corrosion of Reinforced Concrete In Acid Environments, Int. J. Electrochemical Science 8(2) 118322-118346

Samuel A.O.,Okon, E.,Uchenna, B. C. and Maduka, R.(2013), Evaluation of Corrosion Behavior of Galvanized Steel in Acqueous media, J. Chem. Tech. 3:1-9.

Suleiman, K., Peter, A., Monday, S. and MacJohn, T.O. (2013), Evaluation of Weeds Extract on the Corrosion protection of Galvanized Steel in HCl acid. J. chemistry, 3(2),1142- 1150.

Talo, E., Susan, M. and Ziga, K. (2013), Prediction of Corrosion Rate Data using Statistical Methods, Bull.Electrochem., 17, 205-211.