Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 15 (8): 1083-1092, 2015
ISSN 1812-5654

RESEARCH ARTICLE OPEN ACCESS

DOI: 10.3923/jas.2015.1083.1092

Evaluation and Analyses of *Rhizophora mangle* L. Leaf-Extract Corrosion-Mechanism on Reinforcing Steel in Concrete Immersed in Industrial/Microbial Simulating-Environment

[1]Joshua Olusegun Okeniyi, [1,2]Cleophas Akintoye Loto and [2]Abimbola Patricia Idowu Popoola
[1]Department of Mechanical Engineering, Covenant University, Ota, Nigeria
[2]Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

ARTICLE INFO
Article History:
Received: May 25, 2015
Accepted: July 30, 2015

Corresponding Author:
Joshua Olusegun Okeniyi
Department of Mechanical Engineering,
Covenant University, Ota, Nigeria

ABSTRACT

Test-data from electrochemical monitoring methods were obtained from *Rhizophora mangle* L. leaf-extract admixed steel-reinforced concretes for detailing mechanism of the extract on steel-rebar corrosion in 0.5 M H_2SO_4 (simulating industrial/microbial environment). These electrochemical test-measurements, including corrosion potential, corrosion current and corrosion rate, were subjected to the analyses of probability distributions as per ASTM G16-95 R05 through the Kolmogorov-Smirnov goodness-of-fit test-statistics. Results showed that corrosion rate exhibited correlations with function of the natural plant-extract concentration and compact series of the inverse electrochemical noise resistance; the ratio of standard deviations of corrosion potential and corrosion current. Both the experimental and the correlated-prediction model identified *Rhizophora mangle* L. leaf-extract admixture concentrations that exhibited inhibition efficiency performance of $\eta > 70\%$ on steel-rebar corrosion in the acidic test-medium. The adsorption isotherm modelling of the experimental and the predicted electrochemical test-results exhibited good agreements by following the Langmuir and Flory-Huggins isotherm fittings. In addition, the study identified physisorption as the prevalent corrosion-protection mechanism of the steel-rebar by the plant extract through both of the experimental and the correlated-prediction models of adsorption isotherm analyses.

Key words: Electrochemical steel-rebar corrosion, industrial/microbial simulating environment, eco-friendly plant-extract inhibitor, correlation analyses, adsorption isotherm analyses, corrosion-protection mechanism

INTRODUCTION

Steel-reinforcement corrosion in concrete due to attacks of aggressive agents in the service-environments of the steel-reinforced concrete is a global problem to building structures and infrastructure stakeholders (Jiang and Jin, 2013; Okeniyi *et al*., 2013a; Tang *et al*., 2012). Such attacks, among other possible sources, could ensue from acid rain due to the combination of SO_2 with atmospheric water (Tang *et al*., 2012; Tommaselli *et al*., 2009) in industrial environments or from the activities of sulphur-reducing bacteria, e.g., *Thiobacilli* spp. (Shing *et al*., 2012; De Muynck *et al*., 2009; Hewayde *et al*., 2007), in microbial/sewage environments. Both of these sources are potent at producing sulphuric acid that could both attack concrete and render the steel-rebar embedment susceptible to corrosion degradation. For these reasons, studies deliberate on improving resistance of concrete (De Muynck *et al*., 2009; Hewayde *et al*., 2007) as well as of the embedded reinforcing steel in the concrete to sulphuric acid attack (Okeniyi *et al*., 2014a; Gerengi *et al*., 2013). For both of these protection methods, many of the cited studies have identified the use of admixtures in concrete as an effective and economical protection system against corrosion degradation of steel-reinforced concrete.

In spite of these, problems ensue from the use of admixtures for inhibiting concrete steel-reinforcement corrosion in aggressive environment. One of these include the fact that traditional inhibitors that are well known for inhibiting steel-rebar corrosion in acidic environment suffer the drawbacks that they could be toxic and hazardous to the environmental ecosystem (Okeniyi *et al*., 2014b; Yadav *et al*., 2013). For these reasons, restriction against their use is increasing in many countries thus necessitating research for alternative environmentally-friendly replacement (Okeniyi *et al*., 2013b; Patel *et al*., 2013; Yadav *et al*., 2013; Fu *et al*., 2010). However, this lead to the other problem that adequate monitoring and requisite interpretations would be required to ascertain the performance effectiveness of alternative substances for the hazardous but highly effective traditional inhibitors. This is problematic from the view, posited in studies, that while known electrochemical methods exhibiting good relations to the technical and financial scope of non-destructive electrochemical testing provide information on what is ongoing in concrete, none gives the whole story (Birbilis and Cherry, 2005). Suggested approach for tackling these include combining different electrochemical test-techniques for complimenting one another (Gulikers, 2010; Song and Saraswathy, 2007) even as test-data from them could also be subjected to further analyses for obtaining more meaningful conclusion on effectiveness performance (Birbilis and Cherry, 2005).

These constitute motivations by which this study deliberates on the analyses of test-data from three different electrochemical techniques, obtained from *Rhizophora mangle* L. leaf-extract admixed steel-reinforced concrete in H_2SO_4 medium, for evaluating corrosion-mechanism. The use of *Rhizophora mangle* L. leaf-extract was considered in this study due to its identification in literature that extract from this natural plant exhibited no sign of toxicity to living organisms (Perera *et al*., 2010). This is therefore, potent as a green inhibitor with additional advantages of renewability and cost effectiveness (Mangai and Ravi, 2013). The modelling of electrochemical corrosion and inhibition by this natural plant will be based on the analyses of the corrosion potential, corrosion current and corrosion rate for detailing performance of the extract on steel-rebar corrosion in the industrial/microbial simulating-environment.

MATERIALS AND METHODS

Preparation of plant leaf-extract: Leaves of *Rhizophora mangle* L. (*Rhizophoraceae*) Euphorbiaceae, collected fresh from Ehin-more, Nigeria and identified at Forestry Herbarium Ibadan, Nigeria (FHI No. 109501), were dried under shade and blended into powder. Plant extract solution was then obtained from the blended powder using CH_3OH (methanol), from Sigma Aldrich®, as solvent in a condenser equipped soxhlet extractor (Okeniyi *et al*., 2014c; Hameurlaine *et al*., 2010). The plant extract solution was then concentrated into paste over water bath, which was then used as admixture in mixing water for concrete casting, as per ASTM C192/192M-02 (ASTM., 2005c), from 0 g dm^{-3} (or g L^{-1}) for the blank samples in increment of 1.6667 g dm^{-3} up to 8.3333 g dm^{-3}. These total six variations of admixture designs.

Steel reinforced concrete samples: The steel-reinforced concrete samples were cast in duplicates (Dup) having similar admixtures such that 12 steel-reinforced samples were studied in the experimental work. The deformed steel used as rebar specimen in each concrete is of 12 mm diameter. This steel-rebar has elemental composition: C = 0.273%, Mn = 0.780%, Si = 0.403%, Cu = 0.240%, Cr = 0.142%, Ni = 0.109%, P = 0.039%, S = 0.037%, Mo = 0.016%, Co = 0.0086%, Nb = 0.0083%, Sn = 0.0063%, Ce = 0.0037%, V = 0.0032%, while Fe = the % balance. Specimens of 190 mm steel-rods cut from this were subjected to similar surface preparations according to standard procedures prescribed in ASTM G109-99a (ASTM., 2005d) and described by Okeniyi *et al*. (2014b, c) and Muralidharan *et al*. (2004). From each rod of specimens, 150 mm was centrally embedded in 100×100×200 mm concrete casting such that 40 mm of each steel-rod protruded out of the concrete. These protrusions find usefulness as connectors for the electrochemical corrosion monitoring techniques that were employed in the study.

Setup of electrochemical monitoring experiment: Each sample of steel-reinforced concretes was partially immersed in bowls containing test-solution of 0.5 M H_2SO_4 (Sigma Aldrich®) for simulating industrial/microbial service-environments of concretes (Okeniyi *et al*., 2013b; Gerengi *et al*., 2013; Shing *et al*., 2012). Electrochemical corrosion test-monitoring were then obtained from each concrete sample for 89 days experimental period. The electrochemical test-monitoring techniques employed in the study are (Okeniyi *et al*., 2013c, 2014d; Song and Saraswathy, 2007; Broomfield, 2002).

Half-Cell Potential (HCP) versus $Cu/CuSO_4$ electrode (CSE), Model 8-A, obtained from Tinker and Rasor®, that was measured through high impedance digital multimeter as per ASTM C876-91 R99 (ASTM., 2005a; Okeniyi *et al*., 2013c, 2014a, e; Omotosho *et al*., 2014).

Electrochemical Cell Current (ECC) versus CSE that was measured through Zero Resistance Ammeter (ZRA), Model ZM3P obtained from Corrosion Service® (McCarter and Vennesland, 2004; Jaggi *et al*., 2001).

Corrosion Rate (CR) by linear polarization resistance that was measured through three-electrode LPR Data Logger, Model MS1500L obtained from Metal Samples® (Sastri, 2011).

Statistical analyses of measured corrosion test-data: According to standard procedure prescribed in ASTM G16-95 R04 (ASTM., 2005b) and in Roberge (2003), measured corrosion test-data was subjected to the Normal and the Weibull probability distribution functions (pdf's). Also, the compatibility of the scatter of each variable of electrochemical corrosion test-data, to each of the statistical distribution function models was studied using the Kolmogorov-Smirnov goodness-of-fit (K-S GoF) test-statistics (Okeniyi *et al*., 2014d; Ajayi *et al*., 2013; Okeniyi and Okeniyi, 2012; Roberge, 2003). This was done to heed warning from ASTM G16-95 R04 (ASTM., 2005b) on the need to avoid grossly erroneous conclusion that could be accrued from describing corrosion test-data by a distribution that the test-data were not statistically distributed. The parameters, e.g., mean and standard deviation, for each statistical distribution model were estimated, from the dataset of electrochemical test-variables obtained per specimen of steel-reinforced concrete sample using formulas detailed in (Okeniyi *et al*., 2014c; Haynie, 2005).

Model-estimation of noise resistance (R_n): The statistical distribution of better-fit for the HCP and ECC find usefulness for the estimation of the noise resistance that was obtained through the ratio of the standard deviation of the HCP to the standard deviation of the ECC test-data. This could be expressed by the equation (Okeniyi *et al*., 2014b, c; Eden, 2000; Kelly *et al*., 1996):

$$R_n = \frac{\sigma_{HCP}}{\sigma_{ECC}} \tag{1}$$

Model-estimations of surface coverage and inhibition efficiency: The statistical distribution of better-fit of the CR test-data also find usefulness for the estimations of surface coverage (θ) and inhibition efficiency (η) performance of *R. mangle* L. leaf-extract admixture on the reinforcing steel corrosion in the concrete samples using the relationships (Okeniyi, 2014; Alagbe *et al*., 2006):

$$\theta = \frac{CR_{\text{Blank sample}} - CR_{\text{Admixed sample}}}{CR_{\text{Blank sample}}} \tag{2}$$

$$\eta = \frac{CR_{\text{Blank sample}} - CR_{\text{Admixed sample}}}{CR_{\text{Blank sample}}} \times 100 \tag{3}$$

RESULTS AND DISCUSSION

Results from the distribution modelling of electrochemical test-variables: The mean values of electrochemical corrosion test-data, HCP, ECC and CR, obtained from the probability distribution fittings, by the Normal and by the Weibull distributions, are plotted in Fig. 1. The HCP and ECC plots, Fig. 1a and b, also include plots of standard deviations from the mean values of these electrochemical corrosion test-variables. In addition, linear plots where included in Fig. 1a for corrosion risk interpretations as per ASTM C876-91 R99 (ASTM., 2005a) and (Zamora *et al*., 2009) and in Fig. 1c for corrosion rate criteria according to literature (Soylev *et al*., 2007; Bungey *et al*., 2006).

Thus, the Kolmogorov-Smirnov goodness-of-fit test-statistics of the scatter of the electrochemical test-data like the Normal and Weibull pdf's are plotted in Fig. 2, in which α = 0.05 linear plot for directly interpreting dataset not following the pdf's was also included. This shows that while only the HCP and ECC datasets of the 8.3333 g dm^{-3} *R. mangle* L. admixture were not distributed like the Normal pdf, only the CR dataset of the 0 (blank)_Dup sample comes from the Normal pdf, according to the K-S GoF test-criteria at α = 0.05. This indicates that HCP and ECC datasets of 11 out of the 12 steel-reinforced concrete samples studied distributed like the Normal pdf, but CR datasets of 11 out of the 12 steel-reinforced concrete samples used for the experiments were not distributed like the Normal pdf. In comparison, all the datasets of electrochemical test-variables, i.e., HCP, ECC and CR, from all the 12 steel-reinforced concrete samples followed the Weibull pdf models as per the K-S GoF test-statistics at α = 0.05 level of significance. This support use of the Weibull probability distribution function as the descriptive statistics for detailing the prevailing corrosion condition in the steel-reinforced concrete samples immersed in the industrial/microbial simulating-environment being studied.

Correlation modelling analyses for corrosion rate and noise resistance: The distribution of the electrochemical test-variables, obtained from the steel-reinforced concrete specimens, like the Weibull pdf model facilitates application of Eq. 1 for evaluating the noise resistance R_n from the Weibull standard deviation models of HCP and ECC. The plot of this model of noise resistance is plotted with the corrosion rate, in ranking order of corrosion rate for the H_2SO_4-immersed steel-reinforced concrete specimens in Fig. 3. The expectation from the plotting from this figure was that the samples with the higher-valued R_n would be attended with low corrosion rate while sample with the lower-valued R_n would exhibit high corrosion rate. This would have found agreement with Kelly *et al*. (1996) where R_n values tracked linear polarization resistance just as it had been established in other reported

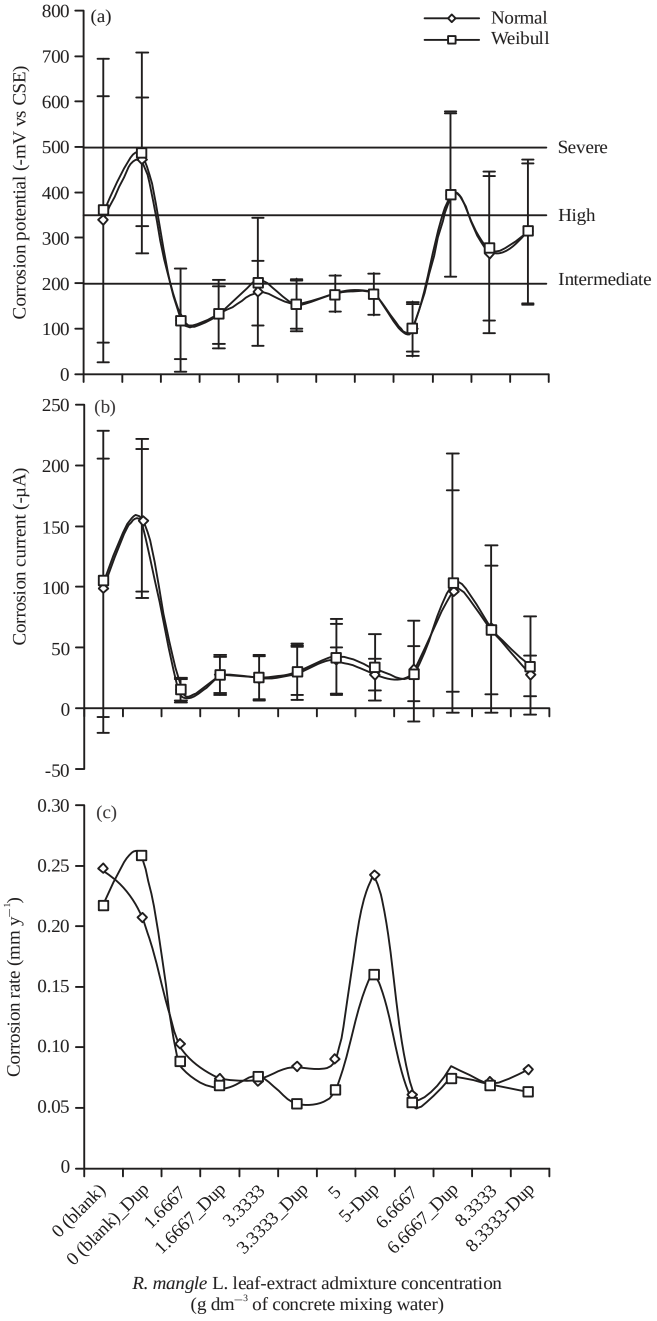

Fig. 1(a-c): Results of the distribution models of electrochemical corrosion test-variables (a) Mean and standard deviations of HCP with linear plots of corrosion risks as per ASTM C876-91 R99 (ASTM., 2005a), (b) Mean and standard deviations of ECC and (c) Corrosion rate with corrosion criteria classification as prescribed by Soylev *et al.* (2007) and Bungey *et al*. (2006)

works (Okeniyi *et al.*, 2014b, c). However, this form of tracking is not very obvious from the R_n and CR plots in Fig. 3, where the noise resistance plots generally undulates about the ranked corrosion rate.

This form of undulating model of noise resistance about the ranking of corrosion rate exemplified the position upheld in ASTM G16-95 R04 (ASTM., 2005b). In that ASTM standard, it had been stated that corrosion test-results are potent at exhibiting values that deviate in a more or less random way from expected values for the condition that are present in the corrosive system. The prescription proffered by that standard for attaining better approximations to the expected values include the necessity of statistical analyses for determining associations that could exist between variables

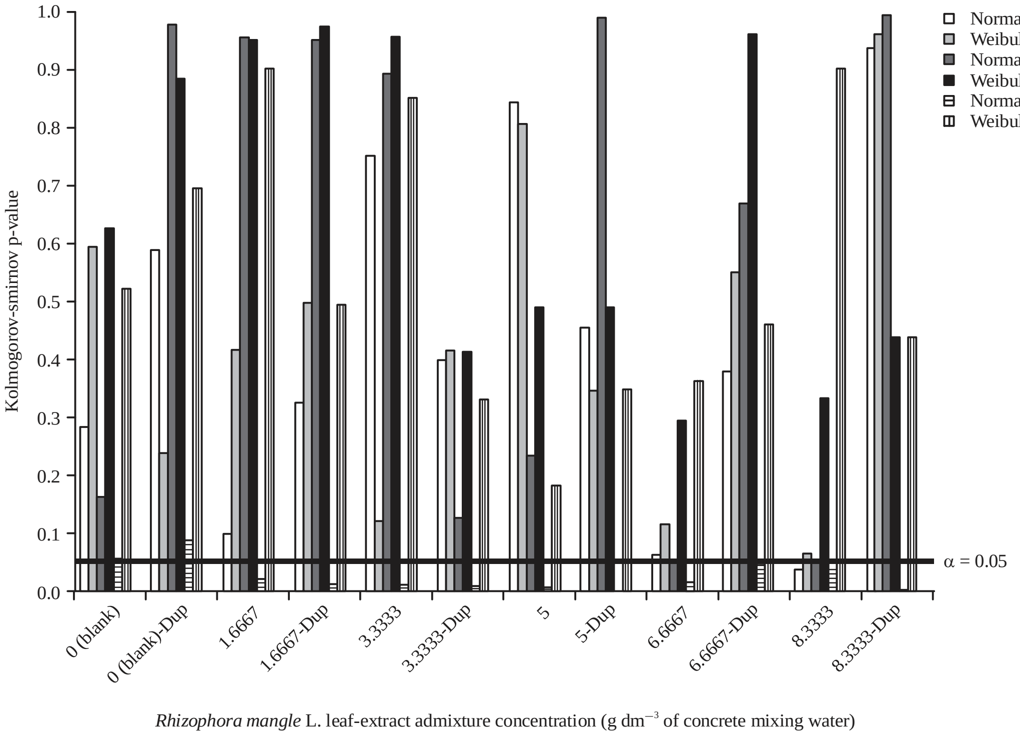

Fig. 2: Kolmogorov-Smirnov goodness-of-fit test-statistics for the distribution of electrochemical corrosion test-variables like the Normal and the Weibull pdf's

Table 1: Numerical values of the constant coefficients a_j in the correlation Eq. 4

j	a_j
0	0.218973019
1	-0.064731161
2	0.615572061
3	-7.419904795
4	34.46328554
5	-77.02145672
6	82.7975318
7	-34.24703428

Table 2: ANOVA for the correlation fitting model in Eq. 4

Source of variations	df	SS	MS	F	p-value
Regression	7	0.0463	0.0066	4.0836	0.0960
Residual	4	0.0065	0.0016		
Total	11	0.0528			

and developing quantitative expressions relating variables. Based, on this, several correlation fitting models were applied to the corrosion rate CR as dependent variable and the noise resistance R_n as well as the *R. mangle* L. admixture concentration ρ as the independent variable. From the analyses, it was observed that the CR exhibited a relationship with the independent variables that can be written in the compact form:

$$CR = a_0 + a_1\rho + e^{\rho V}.\sum_{j=2}^{7} a_j \times 10^{3j}\left(1/R_n\right)^j \qquad (4)$$

where, V is the volume of concrete mixing water which is a constant = 1.2 dm^3 ≡ 1.2 L. The constant coefficients a_j in j = 0, 1, 2, …, 7 have the numerical values given in Table 1.

For the correlation fitting in Eq. 4, correlation coefficient, r = 93.66% and Nash-Sutcliffe efficiency, NSE = 87.72%. By these modelling criteria, the correlation fitting model in Eq. 4 classifies to the "very good" model efficiency, according to the model efficiency interpretations from literature (Okeniyi *et al*., 2013c, 2014d; Coffey *et al*., 2013). Also, as specified by ASTM G16-95 R04 (ASTM., 2005b), the correlation fitting model facilitates estimation of confidence interval from the relationships of the measured variables and this was obtained from analysis of variance (ANOVA) for the fitting model, which is presented in Table 2. From the table, the ANOVA p-value = 0.0960 which bear indication that it cannot be rejected that there is statistically significant relationship between the correlated dependent variable CR and the independent variables ρ and R_n within 90.40% confidence interval.

Inhibition efficiency performance and modelling of adsorption mechanisms: The application of Eq. 3 to the experimental and correlation predicted models of CR facilitates estimation of inhibition efficiency performance that was averaged over each of the duplicated samples of steel-reinforced concrete admixed with *R. mangle* L. leaf-extract. The results of the averaged inhibition efficiency

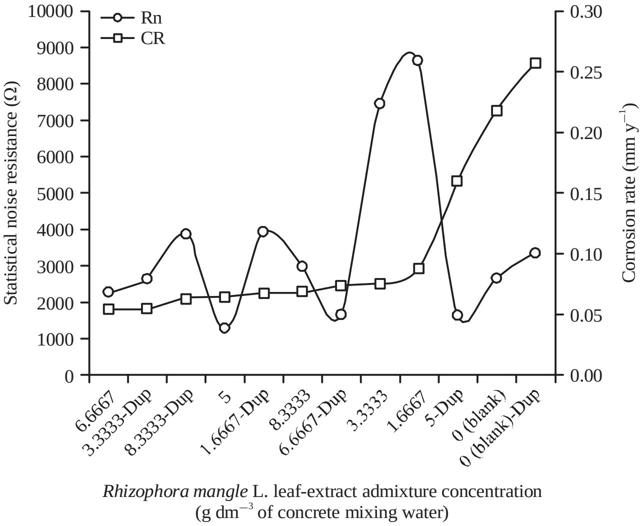

Fig. 3: Plots of noise resistance and corrosion rate in ranking order of corrosion rate performance of *P. muellerianus* admixtures in concrete samples

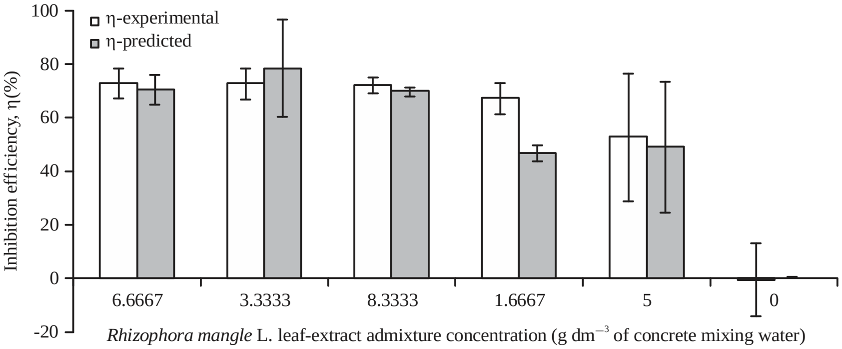

Fig. 4: Experimental and correlation prediction model of *R. mangle* L. leaf-extract effectiveness at inhibiting steel-rebar corrosion in H_2SO_4-immersed concrete

models estimations are plotted in ranking order of *R. mangle* L. leaf-extract effectiveness at inhibiting concrete steel-rebar corrosion in Fig. 4, for the experimental and correlation prediction model.

From the figure, 6.6667 g dm^{-3} *R. mangle* L. leaf-extract admixture exhibited optimal inhibition effectiveness, η = 72.87±5.49% by the experimental model. By the correlation prediction model the inhibition effectiveness of the 6.6667 g dm^{-3} *R. mangle* L. leaf-extract admixture at η = 70.55±5.34% falls short that of the 3.3333 g dm^{-3} *R. mangle* L. leaf-extract admixture that exhibited η = 78.42±18.32%. By the experimental model, three *R. mangle* L. leaf-extract admixtures, the 6.6667, the 3.3333 and 8.3333 g dm^{-3} concentrations, exhibited η>70% inhibition effectiveness. In comparison, only two *R. mangle* L. leaf-extract admixtures, the 6.3333 and the 3.3333 g dm^{-3} concentrations, exhibited η>70% inhibition effectiveness by the correlation prediction model; the inhibition efficiency by the 8.3333 g dm^{-3} admixture just fall short with η = 69.64±1.58%. These inhibition efficiency models find comparisons with the range of inhibition efficiency performance that were reported in literature (Tommaselli *et al*., 2009) for steel-reinforcement corrosion in acidic medium in the presence of inorganic chemical inhibitors. These bare suggestions of the suitability of *R. mangle* L. leaf-extract admixture for inhibiting steel-rebar corrosion in concrete designed for the industrial/microbial environments that were simulated by the corrosive medium used in this study.

Applications of the surface coverage Eq. 2 to the experimental and correlation predicted data facilitate modelling of the electrochemical test-results to different models of adsorption isotherms of the Langmuir, Flory-Huggins, Frumkin and Freundlich. Among these, the experimental and predicted result followed the Langmuir and the Flory-Huggins adsorption isotherm models given, respectively as (Okeniyi, 2014; Okeniyi *et al*., 2014c; Foo and Hameed, 2010; Eddy and Mamza, 2009).

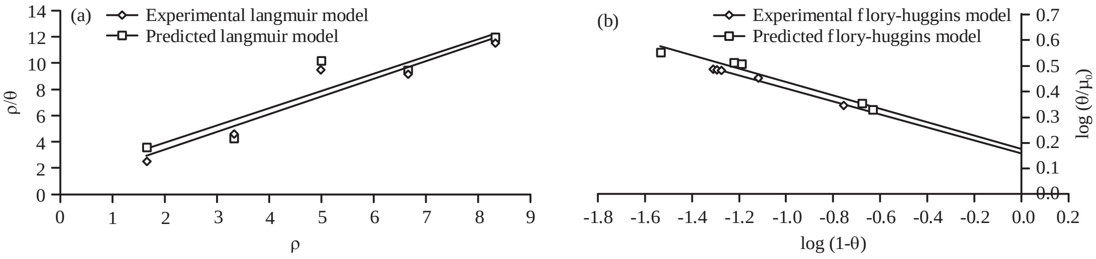

Fig. 5: Fittings of experimental and predicted electrochemical corrosion performance of *R. mangle* L. leaf-extract to adsorption isotherm models for H_2SO_4-immersed concrete steel-reinforcement (a) Langmuir isotherm model and (b) Flory-Huggins isotherm model

Table 3: Estimated parameters from the adsorption isotherm fittings of experimental and predicted data

	Experimental model		Predicted model	
Isotherm parameters	Langmuir	Flory-huggins	Langmuir	Flory-huggins
K_{ads}	1.5721	1.1719	0.7761	1.1925
r (%)	95.35	99.58	92.74	98.76
R_L (separation factor)	0.7270		0.8547	
ΔG^o_{ads} (kJ mol^{-1})	-25.6693	-23.9819	-21.6150	-24.0819

$$\frac{\rho}{\theta} = \frac{1}{K_{Lang}} + \rho \tag{5}$$

$$\text{L og}\left(\frac{\theta}{\mu_0}\right) = \log K_{FH} + n_{FH} \log\left(1-\theta\right) \tag{6}$$

where, K_{Lang} and K_{FH} are the equilibrium constants (K_{ads}) of the Langmuir and Flory-Huggins desorption-adsorption process, respectively; n_{FH} is the Flory-Huggins model exponent; while $\mu_0 \equiv CR_{blank}$. The plots of these adsorption isotherm models followed by the test-results in this study are presented in Fig. 5, in which plots of the Langmuir model are in Fig. 5a and plots of the Flory-Huggins models are in Fig. 5b. The estimated requisite parameters from the isotherm fitting models, which are useful for interpreting the fitting performance, are presented in Table 3. These include estimation of the free energy of adsorption ΔG^o_{ads}, using the Gibbs-Helmotz equation and the separation factor, R_L, a dimensionless constant for indicating adsorption nature of *R. mangle* L. leaf-extract on steel-rebar surface. These parameters are, respectively given by Okeniyi *et al*. (2014b, c), Foo and Hameed (2010) and Eddy and Mamza (2009) as:

$$\Delta G^o_{ads} = 2.303\ RT \log\left(55.5 K_{ads}\right) \tag{7}$$

$$R_L = \frac{1}{1+K_{ads}\mu_0} \tag{8}$$

The parameters estimated from the fitting performances of the Langmuir and the Flory-Huggins isotherm models of electrochemical corrosion test-results showed that the predicted models followed both isotherm models than the experimental models. This was well indicated by the K_{ads} and correlation coefficients of the predicted model that were higher than those of the experimental model by the fitting isotherm functions. In spite of these, however, both experimental and correlated fitting models bare agreements on the basis that the adsorption of *R. mangle* L. leaf-extract on the rebar surface is favourable from the separation factor models R_L values from Table 3 that satisfy the condition $0<R_L<1$. Also, the experimental and the correlation prediction models exhibited agreements in the negative values of ΔG^o_{ads} which suggest spontaneity of the adsorption process and stability of the adsorbed layer on the reinforcing steel surface. In addition, further agreements between the experimental and the correlated models was fostered by the values of ΔG^o_{ads} which is around -20 kJ mol^{-1} and that suggest prevalent physical adsorption (physisorption) as the mechanism of *R. mangle* L. adsorption on the rebar.

By these results, it is established in this study that the performance of *R. mangle* L. leaf-extract admixture indicates the natural plant extract as an effective inhibitor of steel-rebar corrosion in concrete designed for the industrial/microbial, environments. That the plant-extract has been identified in biochemical studies as non-toxic also bare indication that its effectiveness at inhibiting concrete steel-rebar corrosion in the acidic medium is potent with the additional advantage that the plant extract is an environmentally-friendly inhibitor.

CONCLUSION

Corrosion mechanism of *R. mangle* L. leaf-extract admixture on reinforcing steel in concrete has been evaluated through analyses of experimental and correlation predictions from the steel-reinforced samples immersed in industrial/microbial simulating environment. The conclusions from the study include:

- The datasets of electrochemical corrosion monitoring come from the Weibull distribution function according to the Kolmogorov-Smirnov goodness-of-fit statistics at $\alpha = 0.05$ level of significance, thus supporting preference of the Weibull pdf for detailing prevailing corrosion condition in the experimental steel-reinforced concrete specimens
- Although the noise resistance undulates about the performance ranking of corrosion rate, correlation analyses portrayed that the corrosion rate model from the *R. mangle* L. admixed steel-reinforced concrete samples bear relationship with the *R. mangle* L. admixture concentration and the inverse function of noise resistance model with correlation coefficient, R = 93.66% and Nash-Sutcliffe efficiency, NSE = 87.72%, which indicated "very good" model efficiency and ANOVA p-value = 0.0960 that suggest statistically significant relationship at 90.40% confidence interval
- By the experimental model of electrochemical test-results, the 6.6667 g dm^{-3} R. mangle L. leaf-extract exhibited optimal inhibition efficiency, $\eta = 72.87\pm5.49\%$, on concrete steel-rebar corrosion in the corrosive medium tested, while both the experimental and correlation prediction models identified, in agreements, admixtures with inhibition efficiency performance of $\eta>70\%$ that is within the range of effectiveness performance by inorganic inhibitors that where reported in literature
- Both experimental and correlated prediction models of electrochemical corrosion test-results from the steel-reinforced concrete samples exhibited agreements by following adsorption isotherm modelling of the Langmuir and of the Flory-Huggins isotherms, with correlation coefficients, r>90%, even as both isotherm models bare suggestions of physical adsorption (physisorption), for the experimental and predicted test-results, as the prevalent mechanism of the *R. mangle* L. leaf-extract adsorption on steel-rebar surface
- By these results, it is established in this study that the performance of *R. mangle* L. leaf-extract admixture indicates the natural plant extract as an effective inhibitor of steel-rebar corrosion in concrete designed for the industrial/microbial, environments that is also potent with the additional advantage that the plant extract is an environmentally-friendly inhibitor of steel-reinforcement in the acidic medium

REFERENCES

ASTM., 2005a. Standard test method for half-cell potentials of uncoated reinforcing steel in concrete. ASTM C876-91 R99, ASTM International, Conshohocken, PA., USA.

ASTM., 2005b. Standard guide for applying statistics to analysis of corrosion data. ASTM G16-95 R04, ASTM International, Conshohocken, PA., USA.

ASTM., 2005c. Standard practice for making and curing concrete test specimens in the laboratory. ASTM C192/192M-02, ASTM International, West Conshohocken, PA., USA.

ASTM., 2005d. Standard test method for determining the effects of chemical admixtures on the corrosion of embedded steel reinforcement in concrete exposed to chloride environments. ASTM G109-99a, ASTM International, Conshohocken, PA., USA.

Ajayi, O.O., R.O. Fagbenle, J. Katende, S.A. Aasa and J.O. Okeniyi, 2013. Wind profile characteristics and turbine performance analysis in Kano, North-Western Nigeria. Int. J. Energy Environ. Eng., Vol. 4. 10.1186/2251-6832-4-27

Alagbe, M., L.E. Umoru, A.A. Afonja and O.E. Olorunniwo, 2006. Effects of different amino-acid derivatives on the inhibition of NST-44 mild steel corrosion in lime fluid. J. Applied Sci., 6: 1142-1147.

Birbilis, N. and B.W. Cherry, 2005. Monitoring the corrosion and remediation of reinforced concrete on-site: An alternative approach. Mater. Corrosion, 56: 237-243.

Broomfield, J.P., 2002. Corrosion of Steel in Concrete: Understanding, Investigation and Repair. CRC Press/Taylor and Francis Group, Boca Raton, FL., USA., ISBN-13: 9780203475287, Pages: 264.

Bungey, J.H., S.G. Millard and M.G. Grantham, 2006. Testing of Concrete in Structures. 4th Edn., CRC Press/Taylor and Francis Group, Boca Raton, FL., USA., ISBN-13: 978-0415263016, Pages: 352.

Coffey, R., S. Dorai-Raj, V. O'Flaherty, M. Cormican and E. Cummins, 2013. Modeling of pathogen indicator organisms in a small-scale agricultural catchment using SWAT. Hum. Ecol. Risk Assess.: Int. J., 19: 232-253.

De Muynck, W., N. De Belie and W. Verstraete, 2009. Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete. Cem. Concr. Compos., 31: 163-170.

Eddy, N.O. and P.A.P. Mamza, 2009. Inhibitive and adsorption properties of ethanol extract of seeds and leaves of *Azadirachta indica* on the corrosion of mild steel in H_2SO_4. Portugaliae Electrochimica Acta, 27: 443-456.

Eden, D.A., 2000. Electrochemical Noise. In: Uhlig's Corrosion Handbook, Revie, R.W. (Ed.). 2nd Edn., John Wiley and Sons, New York, USA., ISBN-13: 9780471157779, pp: 1227-1238.

Foo, K.Y. and B.H. Hameed, 2010. Insights into the modeling of adsorption isotherm systems. Chem. Eng. J., 156: 2-10.

Fu, J.J., S.N. Li, L.H. Cao, Y. Wang, L.H. Yan and L.D. Lu, 2010. L-Tryptophan as green corrosion inhibitor for low carbon steel in hydrochloric acid solution. J. Mater. Sci., 45: 979-986.

Gerengi, H., Y. Kocak, A. Jazdzewska, M. Kurtay and H. Durgun, 2013. Electrochemical investigations on the corrosion behaviour of reinforcing steel in diatomite-and zeolite-containing concrete exposed to sulphuric acid. Constr. Build. Mater., 49: 471-477.

Gulikers, J., 2010. Statistical interpretation of results of potential mapping on reinforced concrete structures. Eur. J. Environ. Civil Eng., 14: 441-466.

Hameurlaine, S., N. Gherraf, A. Benmnine and A. Zellagui, 2010. Inhibition effect of methanolic extract of *Atractylis serratuloides* on the corrosion of mild steel in H_2SO_4 medium. J. Chem. Pharma. Res., 2: 819-825.

Haynie, F.H., 2005. Statistical Treatment of Data, Data Interpretation and Reliability. In: Corrosion Tests and Standards: Application and Interpretation, Baboian, R. (Ed.). 2nd Edn., ASTM International, West Conshohocken, PA, pp: 83-88.

Hewayde, E., M.L. Nehdi, E. Allouche and G. Nakhla, 2007. Using concrete admixtures for sulphuric acid resistance. Proc. ICE-Constr. Mater., 160: 25-35.

Jaggi, S., H. Bohni and B. Elsener, 2001. Macrocell corrosion of steel in concrete-experimental and numerical modelling. Proceedings of the European Corrosion Congress, September 30-October 4, 2001, Riva del Garda, Italy.

Jiang, G. and W. Jin, 2013. Quantitative distribution of rebar corrosion sensor in reinforced concrete T-beam bridge. Inform. Technol. J., 12: 6837-6840.

Kelly, R.G., M.E. Inman and J.L. Hudson, 1996. Analysis of Electrochemical Noise for Type 410 Stainless Steel in Chloride Solutions. In: Electrochemical Noise Measurement for Corrosion Applications, Kearns, J.R., J.R. Scully, P.R. Roberge, D.L. Reichert and J.L. Dawson (Eds.). ASTM International, USA., ISBN-13: 9780803120327, pp: 101-113.

Mangai, S.A. and S. Ravi, 2013. Comparative corrosion inhibition effect of imidazole compounds and of *Trichodesma indicum* (Linn) R. Br. on C38 steel in 1 M HCl medium. J. Chem. 10.1155/2013/527286

McCarter, W.J. and O. Vennesland, 2004. Sensor systems for use in reinforced concrete structures. Constr. Build. Mater., 18: 351-358.

Muralidharan, S., V. Saraswathy, S.P.M. Nima and N. Palaniswamy, 2004. Evaluation of a composite corrosion inhibiting admixtures and its performance in Portland pozzolana cement. Mater. Chem. Phys., 86: 298-306.

Okeniyi, J.O. and E.T. Okeniyi, 2012. Implementation of kolmogorov-smirnov p-value computation in visual basic®: Implication for Microsoft Excel® library function. J. Stat. Comput. Simul., 82: 1727-1741.

Okeniyi, J.O., I.J. Ambrose, I.O. Oladele, C.A. Loto and P.A.I. Popoola, 2013a. Electrochemical performance of sodium dichromate partial replacement models by triethanolamine admixtures on steel-rebar corrosion in concretes. Int. J. Electrochem. Sci., 8: 10758-10771.

Okeniyi, J.O., I.O. Oladele, I.J. Ambrose, S.O. Okpala, O.M. Omoniyi, C.A. Loto and A.P.I. Popoola, 2013b. Analysis of inhibition of concrete steel-rebar corrosion by $Na_2Cr_2O_7$ concentrations: Implications for conflicting reports on inhibitor effectiveness. J. Cent. South Univ., 20: 3697-3714.

Okeniyi, J.O., O.M. Omoniyi, S.O. Okpala, C.A. Loto and A.P.I. Popoola, 2013c. Effect of ethylenediaminetetraacetic disodium dihydrate and sodium nitrite admixtures on steel-rebar corrosion in concrete. Eur. J. Environ. Civil Eng., 17: 398-416.

Okeniyi, J.O., 2014. $C_{10}H_{18}N_2Na_2O_{10}$ inhibition and adsorption mechanism on concrete steel-reinforcement corrosion in corrosive environments. J. Assoc. Arab Univ. Basic Applied Sci., (In Press). 10.1016/j.jaubas.2014.08.004

Okeniyi, J.O., C.A. Loto and A.P. Popoola, 2014a. Electrochemical performance of *Phyllanthus muellerianus* on the corrosion of concrete steel-reinforcement in industrial/microbial simulating-environment. Portugaliae Electrochimica Acta, 32: 199-211.

Okeniyi, J.O., C.A. Loto and A.P.I. Popoola, 2014b. *Morinda lucida* effects on steel-reinforced concrete in 3.5% NaCl: Implications for corrosion-protection of wind-energy structures in saline/marine environments. Energy Procedia, 50: 421-428.

Okeniyi, J.O., C.A. Loto and A.P.I. Popoola, 2014c. Electrochemical performance of *Anthocleista djalonensis* on steel-reinforcement corrosion in concrete immersed in saline/marine simulating-environment. Trans. Indian Inst. Met., 67: 959-969.

Okeniyi, J.O., I.J. Ambrose, S.O. Okpala, O.M. Omoniyi, I.O. Oladele, C.A. Loto and P.A.I. Popoola, 2014d. Probability density fittings of corrosion test-data: Implications on $C_6H_{15}NO_3$ effectiveness on concrete steel-rebar corrosion. Sadhana, 39: 731-764.

Okeniyi, J.O., O.A. Omotosho, O.O. Ajayi and C.A. Loto, 2014e. Effect of potassium-chromate and sodium-nitrite on concrete steel-rebar degradation in sulphate and saline media. Construct. Build. Mater., 50: 448-456.

Omotosho, O.A., C.A. Loto, O.O. Ajayi, J.O. Okeniyi and A.P.I. Popoola, 2014. Investigating potassium chromate and aniline effect on concrete steel rebar degradation in saline and sulphate media. Int. J. Electrochem. Sci., 9: 2171-2185.

Patel, N.S., S. Jauhariand, G.N. Mehta, S.S. Al-Deyab, I. Warad and B. Hammouti, 2013. Mild steel corrosion inhibition by various plant extracts in 0.5 M sulphuric acid. Int. J. Electrochem. Sci., 8: 2635-2655.

Perera, L.M.S., A. Escobar, C. Souccar, M.A. Remigio and B. Mancebo, 2010. Pharmacological and toxicological evaluation of *Rhizophora mangle* L., as a potential antiulcerogenicdrug: Chemical composition of active extract. J. Pharmacogn. Phytother., 2: 56-63.

Roberge, P.R., 2003. Statistical Interpretation of Corrosion Test Results. In: ASM Handbook: Corrosion: Fundamentals, Testing and Protection, Cramer, S.D. and B.S. Covino (Eds.). 10th Edn., ASM International, USA., ISBN-13: 978-0871707055, pp: 425-429.

Sastri, V.S., 2011. Green Corrosion Inhibitors: Theory and Practice. John Wiley and Sons, New York, USA., ISBN-13: 978-0470452103, Pages: 328.

Shing, C.K., C.M.L. Wu, J.W.J. Chen, C.S. Yuen and R.Y. C. Tsui, 2012. A review on protection of concrete for sewage installations and an accelerated test on protection systems. HKIE Trans., 19: 8-16.

Song, H.W. and V. Saraswathy, 2007. Corrosion monitoring of reinforced concrete structures-A review. Int. J. Electrochem. Sci., 2: 1-28.

Soylev, T.A., C. McNally and M. Richardson, 2007. Effectiveness of amino alcohol-based surface-applied corrosion inhibitors in chloride-contaminated concrete. Cem. Concr. Res., 37: 972-977.

Tang, Y., G. Zhang and Y. Zuo, 2012. The inhibition effects of several inhibitors on rebar in acidified concrete pore solution. Constr. Build. Mater., 28: 327-332.

Tommaselli, M.A.G., N.A. Mariano and S.E. Kuri, 2009. Effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components. Constr. Build. Mater., 23: 328-333.

Yadav, M., S. Kumar and P.N. Yadav, 2013. Development of ecofriendly corrosion inhibitors for application in acidization of petroleum oil well. J. Chem. 10.1155/2013/618684

Zamora, M.A.B., D.N. Mendoza, H.H. Zamora and F.A. Calderon, 2009. Monitoring of corrosion potential and mechanical resistance of contaminated concrete exposed to a chlorinated environment. Portugaliae Electrochimica Actam, 27: 237-246.