

## Investigating the Corrosion Mechanism of *Morinda lucida* Leaf Extract Admixtures on Concrete Steel Rebar in Saline/Marine Simulating Environment

*Joshua Olusegun Okeniyi<sup>1,\*</sup>, Cleophas Akintoye Loto<sup>1,2</sup>, Abimbola Patricia Idowu Popoola<sup>2</sup>*

<sup>1</sup>Mechanical Engineering Department, Covenant University, Ota 112001, Nigeria

<sup>2</sup>Chemical, Metallurgical and Materials Engineering Department, Tshwane University of Technology, Pretoria 0001, South Africa

\*E-mail: [joshua.okeniyi@covenantuniversity.edu.ng](mailto:joshua.okeniyi@covenantuniversity.edu.ng)<mailto:jpshim@kunsan.ac.kr>

Received: 25 May 2015 / Accepted: 10 September 2015 / Published: 4 November 2015

In this paper, measurements of corrosion test data from steel reinforced concrete samples immersed in 3.5% NaCl, for simulating saline/marine environment, were analysed for investigating corrosion mechanism by *Morinda lucida* leaf extract admixtures on the steel rebar. Corrosion potential as per ASTM C876-95 R99, corrosion current by zero resistance ammeter and corrosion rate from linear polarization resistance instrument were subjected to the Weibull probability distribution as per Kolmogorov-Smirnov goodness of fit criteria. From this, electrochemical noise resistance was modelled through the ratio of Weibull standard deviation of corrosion potential to that of Weibull standard deviation of corrosion current after which the modelled noise resistance and the plant extract concentration were correlated with the corrosion rate. Results from these analyses of electrochemical test data showed that excellent correlation, of  $R = 98.07\%$ , Nash-Sutcliffe Efficiency = 96.18% and ANOVA  $p$ -value = 0.0456, exists between the corrosion rate as a function of the plant extract concentration and the noise resistance. The correlation model obtained exhibited good agreements with experimental results in inhibition efficiency performance of the admixture on steel reinforcement corrosion in the test medium. By these, 3.333 g/L *Morinda lucida* (per volume of concrete mixing water) exhibited optimal inhibition efficiency,  $\eta = 90.59 \pm 2.52$  (by correlation prediction) or  $\eta = 89.27 \pm 3.94$  (by experimental model), on the concrete reinforcing steel corrosion in the study. Adsorption isotherm fittings of the correlation prediction and experimental results showed that they both followed the Langmuir isotherm, which indicated physical adsorption (physisorption) as the prevalent mechanism of *Morinda lucida* leaf extract on the concrete steel rebar.

**Keywords:** reinforcing steel in concrete; corrosion protection; NaCl medium; natural plant extract inhibitor; corrosion inhibition modelling; corrosion mechanism modelling

## 1. INTRODUCTION

Concrete steel reinforcement (steel rebar) corrodes when the thin passive oxide layer from the highly alkaline,  $\text{pH} > 12$ , by-product of cement paste hydration, which protects the rebar from corrosion attacks, is destroyed by chloride ion in the service environment of the steel reinforced concrete [1–3]. The chloride ion, necessary for reinforcing steel corrosion, ingress through concrete onto the steel rebar surface from service environments of steel reinforced concrete structures and infrastructures such as artificial saline, from de-icing salt, or natural marine, from coastal region [4–9]. The steel rebar, thus rendered susceptible to corrosion attack, produces rusts which are expansive within the concrete such that the hoop stress from the expansion leads to cracks, delamination and spalling of the concrete [5,8–10]. Averting catastrophic loss of structural integrity of the steel reinforced concrete structure requires huge budgets for costly maintenance and repair globally [9,11].

These constitute reasons researchers and construction stakeholders employ anticorrosion methods [2,12–13] for ensuring durability of steel reinforced concrete, which has been identified as the most widely used construction material and the second most widely consumed material after water [14]. Out of the many known anticorrosion methods, the use of corrosion inhibitor admixtures has been identified in literature as one of the most effective techniques that is also economical and easy to apply for mitigating steel reinforcement corrosion in chloride contaminated medium [1,3,6,15]. Inhibitors that had been found effective in studies at inhibiting reinforcing steel corrosion can be broadly classified as inorganic and organic [16–17], and from these, the use of organic inhibitors are being preferred because of the toxicity and hazardousness of many of the inorganic inhibitors. Among the organic inhibitors, extracts from natural plant combine the advantages of non-toxicity and environmentally friendliness with renewability and high inhibition effectiveness on reinforcing steel corrosion in chloride contaminated medium [6,18]. These advantages are making them the preferred choice of study and applications for inhibiting corrosion of steel in aggressive media [18–19].

However, evaluating effectiveness and mechanism of inhibitor on concrete steel rebar corrosion requires use of electrochemical monitoring techniques for indicating how the inhibitor mitigates reinforcing steel corrosion [1,20–21]. Well known electrochemical techniques for monitoring steel rebar corrosion in concrete include the open circuit potential, the electrochemical (macrocell or galvanic) corrosion current and the corrosion rate measurement techniques. However, these techniques were identified with the problem that though each of the technique gives some information on the corrosion process, none of the methods tells the complete story [22]. For example, the open circuit potential can neither be used for indicating rate of corrosion nor for representing absolute corrosion activity [20,23–24]. In addition to these, each of these electrochemical corrosion monitoring techniques portends:

- Different advantages and disadvantages over one another [20,25];
- Distinct levels of simplicity and/or technicality of being undertaken [26]; and
- Disparate requirements of the scope finance for the routine inspections essential for the monitoring that could be sufficient for ascertaining reinforcing steel corrosion through the use of any of the techniques [21–22].

In spite of the foregoing, it had been identified from [22] that requisite analyses of data from these electrochemical monitoring techniques can lead to more meaningful conclusions instead of the presentation of alternative approach for replacing them. For instance, meaningful results on corrosion inhibition and corrosion mechanism of the extract of a natural plant admixture on concrete steel reinforcement in NaCl medium was obtained from modelling analyses of electrochemical measurements obtained from the concretes [2]. However, though extract from the leaf of *Morinda lucida* has been identified for medicinal usage and which exhibited no toxicity effect on living organs [27], there is paucity of study on the mechanism of corrosion protection ability of this plant on concrete steel rebar. For specific instance and motivation, reported work by Bharathi et al [28] had deliberated on the mechanism of corrosion protection effect by *Morinda citrifolia* L. leaves extract, a plant of the same genus with *Morinda lucida* but of a different epithet (the *citrifolia* refers to leaves similar to *Citrus* genus, *lucida* refers to shining/glistering/reflecting leaves), on aluminium immersed in hydrochloric acid (HCl). However, the novelty in the present paper is based on the fact that no reported work in literature has studied the mechanism of corrosion protection by the leaf extract of *Morinda lucida* on reinforcing steel embedment in concrete immersed in NaCl medium. Therefore, this study employs analyses of the electrochemical performance of *Morinda lucida* leaf extract on steel rebar corrosion for investigating the corrosion mechanism of the leaf extract on steel reinforcement in concrete immersed in 3.5% NaCl medium, simulating saline/marine environment.

## 2. EXPERIMENTAL

### 2.1. Experimental materials

Methanolic extract from the leaf of *Morinda lucida* (*M. lucida*) was obtained according to standard procedure described in [29]. Different concentrations of the extract, per volume of concrete mixing water, were used as admixture in replicates of freshly cast steel reinforced concrete slabs. The replicated design of these *M. lucida* admixed concentrations are as presented in Table 1. Casting of the steel reinforced concrete specimens, each of 0.002 m<sup>3</sup> by volume, were as prescribed by ASTM C192/192M-02 [30] and described in [31].

**Table 1.** Concentrations of *M. lucida* leaf extract admixed in steel reinforced concrete specimens.

Specimen No	Concentration, $\rho$ , (per volume of concrete mixing water)	Specimen No	Concentration, $\rho$ , (per volume of concrete mixing water)
1	0 g/L <i>M. lucida</i> (Ctrl) <sup>a</sup>	2	0 g/L <i>M. lucida</i> (Ctrl_Rep) <sup>a</sup>
3	1.667 g/L <i>M. lucida</i>	4	1.667 g/L <i>M. lucida</i> _Rep
5	3.333 g/L <i>M. lucida</i>	6	3.333 g/L <i>M. lucida</i> _Rep
7	5.0 g/L <i>M. lucida</i>	8	5.0 g/L <i>M. lucida</i> _Rep
9	6.667 g/L <i>M. lucida</i>	10	6.667 g/L <i>M. lucida</i> _Rep
11	8.333 g/L <i>M. lucida</i>	12	8.333 g/L <i>M. lucida</i> _Rep
<sup>a</sup> Replicates of Control specimens			

The casting formulation of 300 kg/m<sup>3</sup> cement, 890.6 kg/m<sup>3</sup> river sand, 1106.3 kg/m<sup>3</sup> granite stones of maximum size 19 mm and 149.7 kg/m<sup>3</sup> water, implying water-cement ratio of 0.499, was

employed. The reinforcing steel specimen embedded in each slab of concrete sample was of 150 mm long from which 90 mm was centrally embedded in the concrete while the remaining 40 mm protrusion was painted with glossy paint and was used for electrochemical connection. This rod of steel reinforcement was of 12 mm diameter and it has elemental composition in % of: 0.273 C, 0.780 Mn, 0.403 Si, 0.240 Cu, 0.142 Cr, 0.109 Ni, 0.039 P, 0.037 S, 0.016 Mo, 0.0086 Co, 0.0083 Nb, 0.0063 Sn, 0.0037 Ce, 0.0032 V and the balance Fe.

Each steel reinforced concrete specimen was immersed longitudinally in a bowl containing 3.5% NaCl solution, for simulating saline or marine environment [16,32], with the test solution made up to just below the protruding reinforcing steel in the concrete but without touching it. For maintaining the corrosive test medium, the NaCl test solution was replenished every three weeks in the bowl of each concrete sample immersion [28,33–34].

## 2.2. Experimental measurements of electrochemical test data

Electrochemical test data of reinforcing steel corrosion were obtained from each steel reinforced concrete specimen in five days interval for 40 days and thereafter in seven days interval for the following seven weeks. This totals 89 days for the corrosion setup experiment. For each day of experimental measurement, three different electrochemical measurements, by three different measuring instruments, were obtained from each steel reinforced concrete specimen for monitoring the reinforcing steel corrosion. These experimental test techniques employ the use of:

- Corrosion potential (*CP*) measurement by the technique of open circuit potential (OCP) versus Cu/CuSO<sub>4</sub> electrode (CSE), Model 8-A obtained from Tinker & Rasor®, through instrumental usage of a high impedance digital multimeter as prescribed by ASTM C876-91 R99 [35–38];
- Corrosion current (*CC*) measurement by the technique of macrocell current versus the CSE through instrumental usage of a zero resistance ammeter (ZRA), Model ZM3P obtained from Corrosion Service® [26,33,39];
- Corrosion rate (*CR*) measurements by the technique of linear polarization resistance (LPR) through instrumental usage of a 3-electrode LPR Data Logger, Model MS1500L obtained from Metal Samples® [35,40–41].

## 2.3. Statistical analyses and modelling of experimental data

Modelling of experimental data of electrochemical measurements were initiated by first subjecting each variable of corrosion test measurements to the statistical distribution analysis, as per ASTM G16-95 R04 [42], of the Weibull distribution [35,43–45]. For this, test data compatibility to the Weibull model was ascertained by the Kolmogorov-Smirnov goodness of fit statistics [35,45–47].

The compatibility of the experimental test data with the Weibull distribution fitting facilitate the use of the Weibull distribution model as the descriptive statistics for detailing measurements of central tendencies and of the dispersions of the scatter of electrochemical test data [42,47]. More specifically, the measurement of dispersion, i.e. the standard deviation, of the corrosion potential,  $\sigma_{CP}$ ,

and of the corrosion current,  $\sigma_{CC}$ , find usefulness for the modelling of noise resistance,  $R_n$ , for each steel reinforced concrete sample according to the expression [2,20,39]:

$$R_n = \frac{\sigma_{CP}}{\sigma_{CC}} \quad (1)$$

This estimation from Equation (1) then facilitates investigation of how the Weibull mean model of corrosion rate, from the LPR monitoring technique, correlates with the natural plant admixture concentration,  $\rho$ , and the estimated noise resistance from the open circuit potential and macrocell current techniques [2]. The modelling efficiency of the resultant correlation fitting model, a model of how well the correlation could predict the experimental results, were studied through the usage of correlation coefficient,  $R$ , and Nash-Sutcliffe efficiency,  $NSE$ , which are respectively evaluated from [40,48–49]:

$$R = \frac{\sum_{i=1}^n (o - \bar{o}) \cdot (p - \bar{p})}{\sqrt{\sum_{i=1}^n (o - \bar{o})^2} \times \sqrt{\sum_{i=1}^n (p - \bar{p})^2}} \quad (2)$$

$$NSE = 1 - \frac{\sum_{i=1}^n (o - p)^2}{\sum_{i=1}^n (o - \bar{o})^2} \quad (3)$$

Where  $o$  and  $\bar{o}$  are the experimental and mean experimental model while  $p$  and  $\bar{p}$  are the predicted and the mean predicted (from the correlation) model, respectively, of electrochemical test variable. For interpreting estimations from Equation (2) and Equation (3) the modelling efficiency classification detailed in Coffey et al [50] was employed. Also, the one-way analysis of variance, ANOVA [2,32,35], between the dependent variable, corrosion rate, and the independent variables, the admixture concentration and noise resistance, was studied for the deduction of statistical significance, or otherwise, of the relationship by the correlation model.

#### 2.4. Corrosion inhibition and corrosion mechanism modelling

The experimental model and correlation prediction of corrosion rate find usefulness for modelling corrosion mechanism of *M. lucida* on reinforcing steel metal, in the study, which was initiated by evaluating the surface coverage,  $\theta$ , from [2,28,51]:

$$\theta = \frac{CR_{Ctrl} - CR_{admixed\ sample}}{CR_{Ctrl}} \quad (4)$$

Estimation of  $\theta$  from Equation (4) was then fitted to the Langmuir adsorption isotherm model given by [28,52–53]:

$$\frac{\rho}{\theta} = \frac{1}{K_{ads}} + \rho \quad (5)$$

Where  $K_{ads}$  is the equilibrium constant of the Langmuir adsorption model which could be applied for modelling the adsorption nature by using it for estimating the separation factor,  $R_L$ , from [53]:

$$R_L = \frac{1}{1 + K_{ads} CR_{Ctrl}} \quad (6)$$

From Equation (6),  $R_L > 1$  suggests unfavourable,  $R_L = 1$  suggests linear,  $0 < R_L < 1$  suggests favourable while  $R_L = 0$  suggests irreversible adsorption [2,51,53].

Corrosion mechanism of *M. lucida* on metallic surface was also modelled using the value of  $K_{ads}$  for estimating Gibbs free energy of adsorption through usage of the relationship [51,54]:

$$\Delta G_{ads}^\circ = -2.303RT \log(55.5K_{ads}) \quad (7)$$

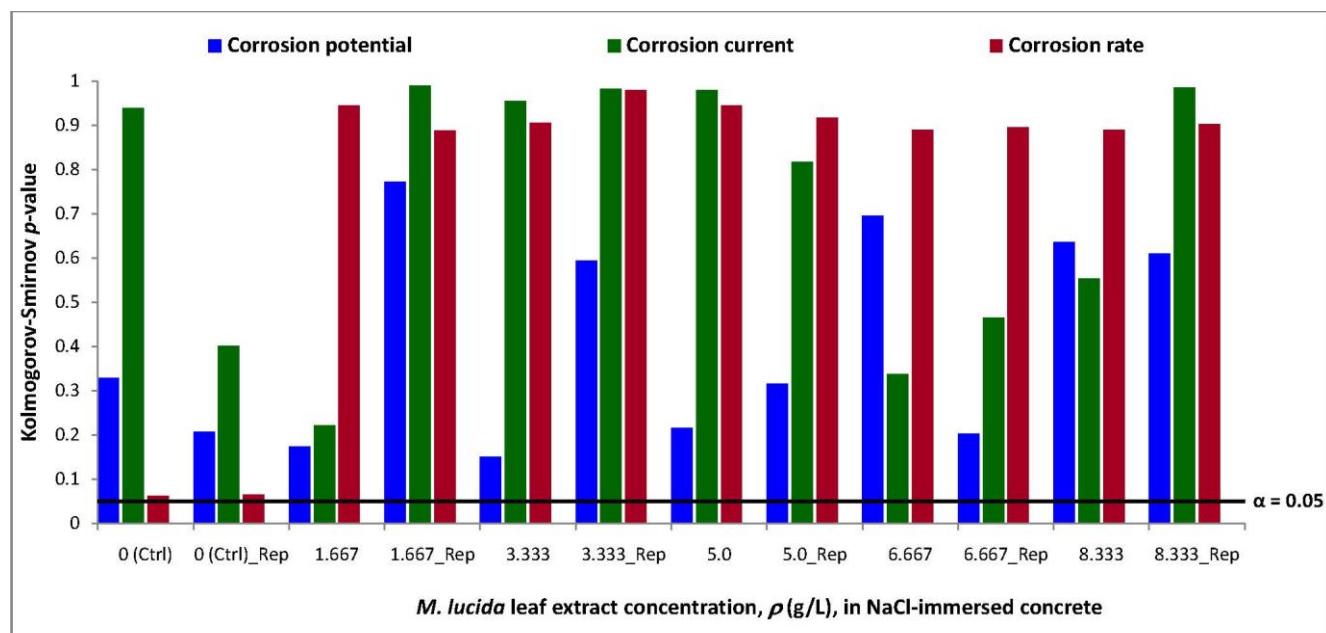
From which  $R$  (the molar gas constant) = 8.314 J/mol·K,  $T$  (the absolute temperature) = 300K and 55.5 is the concentration of water in solution expressed in molar. Values of  $\Delta G_{ads}^\circ$  more positive than -40 kJ/mol suggest prevalence of physical adsorption (physisorption), i.e. electrostatic interactions between the charged molecules and metal, while values of  $\Delta G_{ads}^\circ$  more negative than -40 suggests prevalence of chemical adsorption (chemisorption) [2,51,54].

Also, the experimental and prediction models of the surface coverage,  $\theta$ , find usefulness for estimating corrosion inhibition efficiency,  $\eta$ , through usage for each of the models, of the formula [51-52,55]:

$$\eta = \theta \times 100 \equiv \frac{CR_{Ctrl} - CR_{admixed\ sample}}{CR_{Ctrl}} \times 100 \quad (8)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Compatibility of electrochemical test data to the Weibull distribution model

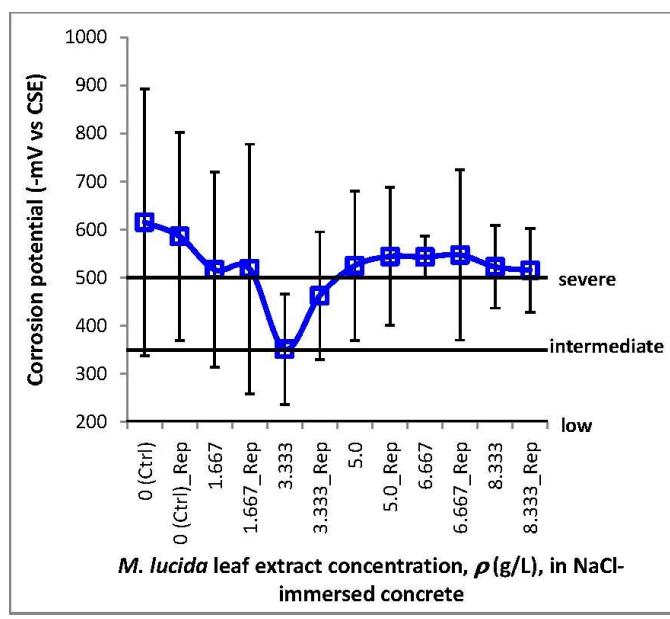


**Figure 1.** Kolmogorov-Smirnov goodness of fit tests of electrochemical test data compatibility with the Weibull distribution for the steel reinforced concrete specimens.

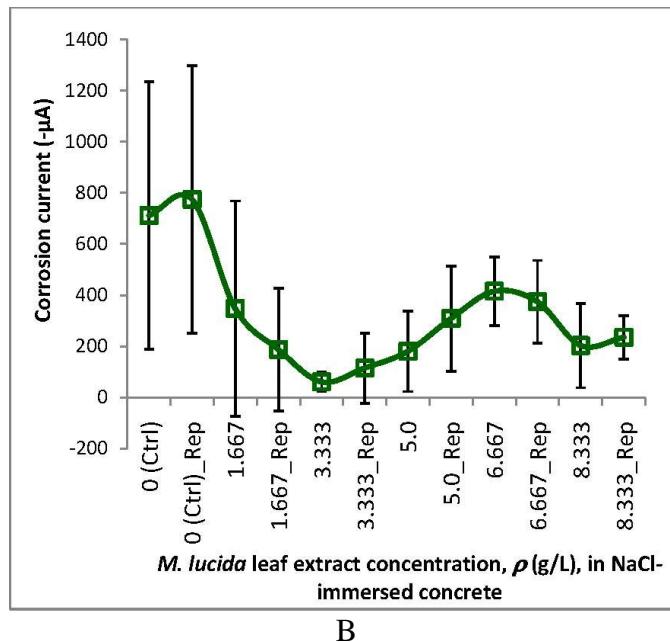
The plot of Kolmogorov-Smirnov goodness of fit testing of the compatibility to the Weibull distribution model, of the electrochemical test responses obtained from the steel reinforced concrete specimens, is shown in Figure 1. From the figure, the  $p$ -value of Kolmogorov-Smirnov goodness of fit test results range from 0.062 obtained from the “0 Ctrl” steel reinforced concrete specimen up to 0.99 obtained from the “1.667\_Rep” specimen. That the  $p$ -values from the goodness of fit test results are greater than the  $\alpha = 0.05$  significant level, the linear plot in Figure 1, for all the steel reinforced concrete specimens studied, indicates that the electrochemical test data from each of the specimens comes from the Weibull distribution. This satisfies the set criteria by the standard specification of ASTM G16-95 R04 [42], as well as the prescription from [47], for using the Weibull distribution as the descriptive statistics for detailing the electrochemical performance of the NaCl-immersed steel reinforced concretes.

### 3.2. Statistical distribution model of electrochemical test data

The statistical distribution modelled results of the electrochemical test data of corrosion potential and corrosion current are shown, respectively in Figure 2(a) and Figure 2(b) as the Weibull mean $\pm$ standard deviation models of these corrosion test variables. Linear plots of corrosion potential interpretation as per ASTM C876-91 R99 [38] are also included in Figure 2(a). It could be noted from the figure that corrosion potential ranged from  $351.41\pm 115.26$  –mV (CSE) obtained from the 3.333 g/L *M. lucida* admixed specimen to  $615.90\pm 277.51$  –mV (CSE) from the “0 Ctrl” specimen. This finds pattern like the corrosion current that ranged from  $60.90\pm 37.68$  – $\mu$ A also from the 3.333 g/L *M. lucida* admixed specimen to  $523.59\pm 0.59$  – $\mu$ A from the “0 Ctrl” specimen.

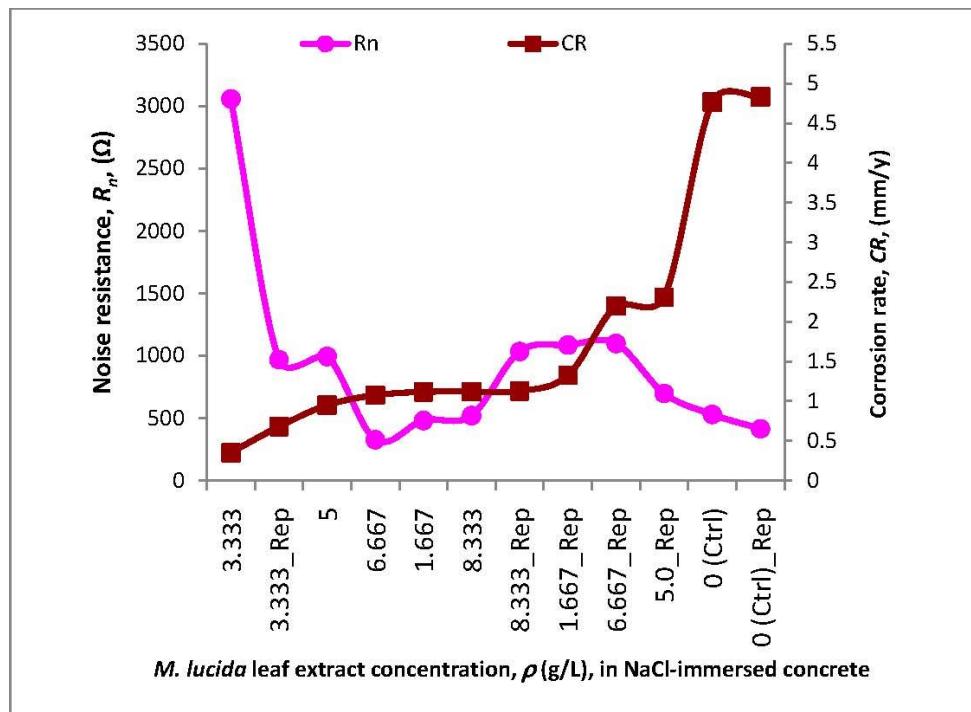


A



**Figure 2.** Weibull mean±standard deviation models of (a) corrosion potential (b) corrosion current.

Application of Equation (1) to the standard deviation models of the corrosion potential and the corrosion current gives the noise resistance,  $R_n$ , which is plotted in Figure 3 along with the Weibull mean model of corrosion rate, in ranking order of the corrosion rate.



**Figure 3.** Noise resistance model and Weibull mean of corrosion rate from the NaCl-immersed steel reinforced concrete specimens.

It could be observed from Figure 3 that, with just some few fluctuations, high values of noise resistance were attended by low values of corrosion rate and vice versa. This could be noted from the mirror like lateral inversion image of the noise resistance plot that was assumed by the corrosion rate plot in Figure 3. That the noise resistance values could track linear polarization resistance (LPR), which is known to exhibit inverse proportionality with corrosion rate, has been reported by Kelly et al in [56]. This bare implication of the existence of relationship between the noise resistance and corrosion rate, though the form taken by such relationship may be influenced by the type of material, corrosion inhibiting substance and the corrosive medium/environment [2,29].

### 3.3. Correlation modelling of corrosion rate and noise resistance

Investigation of several correlation fitting models between the corrosion rate,  $CR$ , as the dependent variable and the noise resistance,  $R_n$ , as well as the admixed concentration,  $\rho$ , of *M. lucida* in the steel reinforced concrete specimen taken as the independent variables gave the relationship:

$$CR = 620.38 - 26.90\rho + 53649.15(1/R_n) + 580.85\rho^2 - 45474.96(1/R_n)^{1/2} - 1222.26\rho^3 + 38449.20(1/R_n)^{1/3} + 668.57\rho^5 - 12245.59(1/R_n)^{1/5} \quad (9)$$

This correlation fitting expression can be expressed in compact form as:

$$CR = (a_0 + b_0) + \sum_{\lambda=1}^{5} \left( a_{\lambda} \rho^{\frac{1}{\lambda}} + b_{\lambda} (1/R_n)^{\frac{1}{\lambda}} \right) \quad (10)$$

From which it is worth noting that  $a_4 = b_4 = 0$ . Applications of Equation (2) and Equation (3) to this correlation fitting model indicate that  $R = 98.07\%$  and  $NSE = 96.19\%$ . Subjecting these fitting efficiency models to the modelling efficiency classification from Coffey et al [50] showed that the correlation fitting model interprets to excellent modelling efficiency,  $NSE > 90\%$ , of the electrochemical performance from the NaCl-immersed steel reinforced concrete specimens.

The results of analysis of variance of the correlation fitting model in Equation (9), represented in compact form in Equation (10), are presented in Table 2. This showed that the ANOVA  $p$ -value = 0.0456 which implies that the inference that the correlation fitting model represented statistically significant relationship between the correlated and the independent variables cannot be rejected within 95% confidence interval.

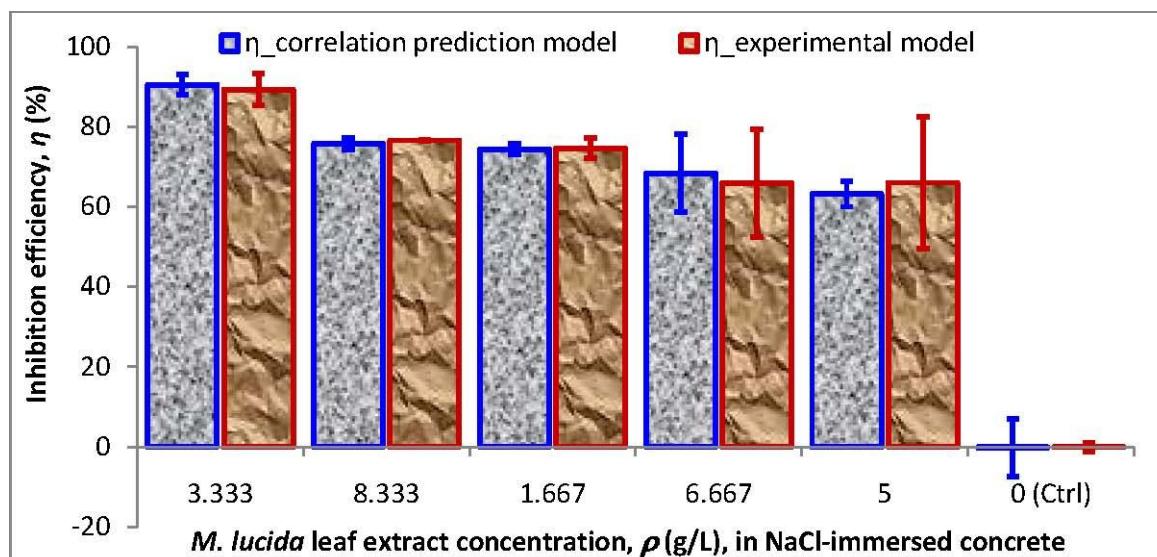
**Table 2.** Analysis of variance (ANOVA) for the correlation fitting model in Equation (9).

Source of variations	df	SS	MS	F	p-value
Regression	8	23.6836	2.9604	9.4662	0.0456
Residual	3	0.9382	0.3127		
Total	11	24.6218			

### 3.4. Corrosion inhibition efficiency modelling

Corrosion inhibition efficiency modelling, through application of Equation (8) to the experimental model of *CR* and the correlation prediction model of *CR*, and that were averaged between each replicate of *M. lucida* leaf extract admixed concretes is presented in Figure 4. These inhibition efficiency models are plotted in ranking order of *M. lucida* leaf extract admixture performance in the NaCl-immersed steel reinforced concrete specimens.

From the figure, it could be noted that both the experimental and the correlation prediction models identified the 3.333 g/L of *M. lucida* leaf extract admixture with optimal effectiveness performance at inhibiting reinforcing steel corrosion in the NaCl-immersed steel reinforced concretes. The 3.333 g/L *M. lucida* leaf extract admixture exhibited corrosion inhibition efficiency  $\eta = 90.59 \pm 2.52$  by the correlation prediction model while, by the experimental model the admixture exhibited  $\eta = 89.27 \pm 3.94$ . Also, the correlation prediction and the experimental models exhibited continuance of agreements in the performance ranking of the 8.333 g/L and that of the 1.667 g/L *M. lucida* leaf extract admixture on the inhibition of reinforcing steel corrosion in the study.



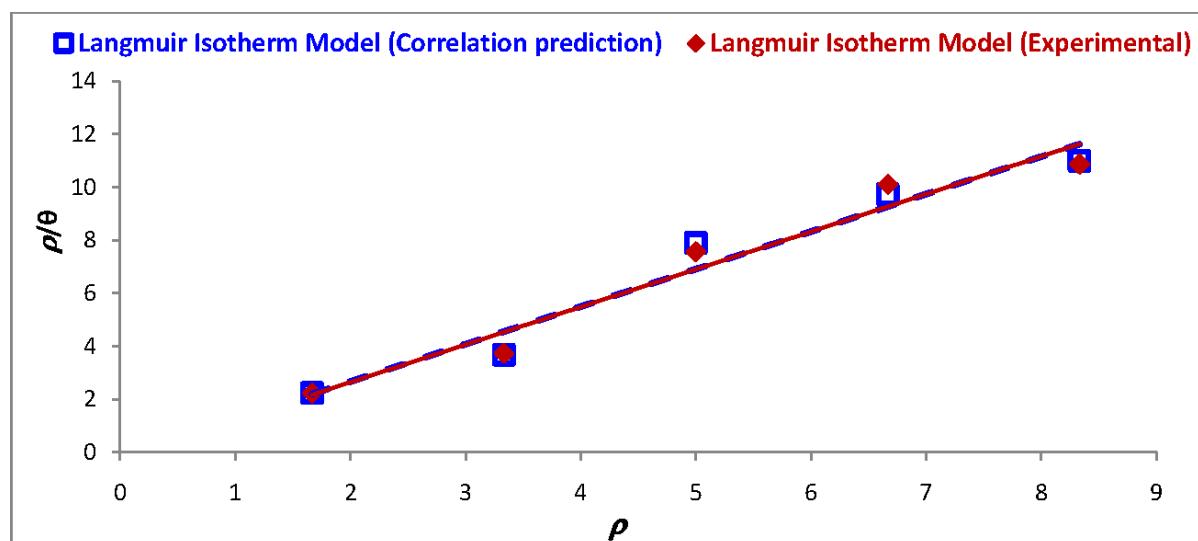
**Figure 4.** Experimental and correlation prediction models of corrosion inhibition efficiency by *M. lucida* leaf extract admixture in NaCl-immersed steel reinforced concrete

The only slight disagreement was observed with the 6.667 g/L *M. lucida* leaf extract admixture which the correlation prediction model identified with better inhibition efficiency,  $\eta = 68.39 \pm 9.77$ , than that of  $\eta = 63.20 \pm 3.17$  that was predicted for the 5 g/L *M. lucida* leaf extract admixture. In contrast to this, the 5 g/L *M. lucida* leaf extract admixture exhibited better inhibition efficiency,  $\eta = 66.03 \pm 16.39$ , by the experimental model, than the inhibition efficiency of  $\eta = 65.92 \pm 13.51$  modelled experimentally for the 6.667 g/L *M. lucida* leaf extract admixture. These discrepancies could be due to the high deviations from the expected values that characterised the experimental models of corrosion inhibition efficiency performance which was tempered by the correlation prediction model, especially for these two concentrations of leaf extract admixture.

### 3.5. Corrosion mechanism modelling

Plots from the rendering of the surface coverage,  $\theta$ , evaluations, through the applications of Equation (4) to the correlation prediction and experimental models of corrosion rate, to the fitting of the Langmuir adsorption isotherm in Equation (5) are shown in Figure 5. Also, the estimated fitting efficiency and evaluated parameters from the Langmuir model of correlated and experimental data are presented in Table 3.

Interpretation of the fitting efficiency as per the model efficiency classification from Coffey et al [50] indicates that both correlation prediction and experimental models were fitted excellently,  $NSE > 90\%$ , by the Langmuir adsorption isotherm. The values of the correlation coefficient,  $R = 97.94\%$ , and of the Nash-Sutcliffe efficiency,  $NSE = 96.93\%$ , were the same, correct to 2 decimal places, for the correlation prediction and for the experimental models.



**Figure 5.** Langmuir adsorption isotherm models of correlation prediction and experimental test results

**Table 3.** Fitting efficiency and estimated parameters from the Langmuir adsorption isotherm models.

Description	Item	Correlation prediction	Experimental model
<b>Fitting efficiency</b>	$R$ (%)	97.94	97.94
	$NSE$ (%)	95.93	95.93
<b>Isotherm parameters</b>	$K_{ads}$	6.2724	5.1435
	$R_L$	0.0322	0.0389
	$\Delta G_{ads}^\circ$	-33.6178	-32.4780

For both the correlation prediction and the experimental models, the values of the separation factor,  $R_L$ , were in the range  $0 < R_L < 1$ , which suggests favourable adsorption, while the negative

value of the Gibbs free energy of adsorption indicates spontaneity of the adsorption-desorption process. Also, that the values of  $\Delta G_{ads}^\circ$  are more positive than  $-40$  kJ/mol, for both correlation prediction and experimental models, indicates physical adsorption (physisorption) was the prevalent mechanism of *M. lucida* leaf extract adsorption on the reinforcing steel surface.

#### 4. CONCLUSIONS

In this study, the mechanism of corrosion protection has been modelled from the electrochemical performance of *M. lucida* leaf extract admixture in NaCl-immersed steel reinforced concrete specimens. From the study, the conclusions that could be drawn include

- Test data of electrochemical test responses from the steel reinforced concrete specimens come from the Weibull distribution model according to the Kolmogorov-Smirnov goodness of fit test criteria, at  $\alpha = 0.05$  significant level;
- High values of noise resistance models were attended by low values of corrosion rate and vice versa, with just some few fluctuations, thus suggesting existence of relationship between the corrosion rate obtained from the LPR technique and the noise resistance evaluated from the ratio of standard deviation of corrosion potential to the standard deviation of the corrosion current;
- The corrosion rate exhibited excellent correlation with the function of the *M. lucida* leaf extract admixture concentration and the noise resistance model with correlation coefficient  $R = 98.07\%$  and the Nash-Sutcliffe efficiency  $NSE = 96.19\%$  and ANOVA  $p$ -value = 0.0456;
- The correlation prediction model find agreements with the experimental model by which both models identified the 3.333 g/L *M. lucida* leaf extract admixture, per volume of concrete mixing water, with the optimal inhibition efficiency model,  $\eta = 90.49 \pm 2.52$  by the correlation prediction model) and  $\eta = 89.27 \pm 3.94$  by the experimental model;
- The correlation prediction and the experimental models both followed, with equal values of excellent model fitting efficiencies  $R = 97.94\%$  and  $NSE = 95.93\%$ , the Langmuir adsorption isotherm which indicates:
  - Favourable adsorption by values of  $R_L$  which ranged between  $0 < R_L < 1$ ;
  - Spontaneity of the adsorption-desorption process by the negative values of  $\Delta G_{ads}^\circ$ ; and
  - Physical adsorption (physisorption) as the prevalent mechanism of *M. lucida* leaf extract adsorption on the reinforcing steel surface in the NaCl-immersed steel reinforced concrete specimens studied.

#### References

1. N. Etteyeb, L. Dhouibi, H. Takenouti, E. Triki, *Cem. Concr. Compos.* 55 (2015) 241
2. J.O. Okeniyi, C.A. Loto, A.P.I. Popoola, *Trans. Indian Inst. Met.* 67 (2014) 959.
3. L. Yohai, M. Vázquez, M. B. Valcarce, *Electrochim. Acta* 102 (2013) 88
4. J.O. Okeniyi, A.P.I. Popoola, C.A. Loto, O.A. Omotosho, S.O. Okpala, I.J. Ambrose, *Adv. Mater. Sci. Eng.* 2015 (2015) 1

5. A. Rahimi, C. Gehlen, T. Reschke, A. Westendarp, *Int. J. Corros.* 2014 (2014) 1.
6. J.J. Shi, W. Sun, *Cem. Concr. Compos.*, 45 (2014) 166
7. P.C. Ryan, A.J. O'Connor, *Constr. Build. Mater.* 47 (2013) 1106
8. R. R. Aveldaño, N.F. Ortega, *Constr. Build. Mater.* 25 (2011) 630
9. S. Guzmán, J.C. Gálvez, J.M. Sancho, *Cem. Concr. Res.* 41 (2011) 893
10. B. Sanz, J. Planas, J.M. Sancho, *Eng. Fract. Mech.* 114 (2013) 26
11. S. Pour-Ali, C. Dehghanian, A. Kosari, *Corros. Sci.* 90 (2015) 239
12. E. Daigle, P. George, C. Gilmore, *Mater. Perform.* 54 (2015) 36
13. G. Mangaiyarkarasi, S. Muralidharan, *Procedia Eng.* 86 (2014) 615
14. W. V. Srubar III, *Cem. Concr. Compos.* 55 (2015) 103
15. F. -L. Fei, J. Hu, J. -X. Wei, Q. -J. Yu, Z. -S. Chen, *Constr. Build. Mater.* 70 (2014) 43
16. J. O. Okeniyi, O. A. Omotosho, O. O. Ajayi, C. A. Loto, *Constr. Build. Mater.* 50 (2014) 448
17. X. Zhou, H. Yang, F. Wang, *Corros. Sci.* 54 (2012) 193
18. S.A. Asipita, M. Ismail, M.Z. Abd Majid, Z.A. Majid, C. Abdullah, J. Mirza, *J. Clean Prod.* 67 (2014) 139
19. S.A. Mangai, S. Ravi, *J. Chem.* 2013 (2013) 1
20. H. -W. Song, V. Saraswathy, *Int. J. Electrochem. Sci.* 2 (2007) 1
21. J.P. Broomfield, *Corrosion of steel in concrete: Understanding, investigation and repair*, Taylor, Francis, NY (2003)
22. N. Birbilis, B.W. Cherry, *Mater Corros.* 56 (2005) 237
23. J. Gulikers, *Eur. J. Environ. Civ. Eng.* 14 (2010) 441
24. N.S. Berke, M.C. Hicks, *Cem. Concr. Compos.* 26 (2004) 191
25. J.H. Bungey, S.G. Millard, M.G. Grantham, *Testing of Concrete in Structures*, 4th edition, Taylor, Francis, NY (2006)
26. W.J. McCarter, Ø. Vennesland, *Constr. Build. Mater.* 18 (2004) 351
27. T. Oduola, I. Bello, G. Adeosun, A.-W. Ademosun, G. Raheem, G. Avwioro, *N. Am. J. Med. Sci.* 2 (2010) 230
28. K. Bharathi, S. Lakshmi, S. Geetha, *J. Chem. Pharm. Res.* 5 (2013) 187
29. J.O. Okeniyi, C.A. Loto, A.P.I. Popoola, *Port. Electrochim. Acta* 32 (2014) 199
30. ASTM C192/192M-02, *Standard practice for making and curing concrete test specimens in the laboratory*, ASTM International, West Conshohocken, PA
31. J.O. Okeniyi, O.M. Omoniyi, S.O. Okpala, C.A. Loto, A.P.I. Popoola, *Eur. J. Environ. Civ. Eng.* 17 (2013) 398
32. M.M. Mennucci, E.P. Banczek, P.R.P. Rodrigues, I. Costa, *Cem. Concr. Compos.* 31 (2009) 418
33. J.O. Okeniyi, I.O. Oladele, I.J. Ambrose, S.O. Okpala, O.M. Omoniyi, C.A. Loto, A.P.I. Popoola, *J. Cent. South Univ.* 20 (2013) 3697
34. S. Muralidharan, V. Saraswathy, S. P. Merlin Nima, N. Palaniswamy, *Mater. Chem. Phys.* 86 (2004) 298
35. J.O. Okeniyi, I.J. Ambrose, S.O. Okpala, O.M. Omoniyi, I.O. Oladele, C.A. Loto, P.A.I. Popoola, *Sadhana – Acad. Proc. Eng. Sci.* 39 (2014) 731
36. S. K. Verma, S. S. Bhaduria, S. Akhtar, *The Sci World J.* 2014 (2014) 1
37. M.A.B. Zamora, D.N. Mendoza, H.H. Zamora, F.A. Calderón, *Port. Electrochim. Acta* 27 (2009) 237
38. ASTM C876–91 R99, *Standard test method for half-cell potentials of uncoated reinforcing steel in concrete*, ASTM International, West Conshohocken, PA
39. R.W. Revie, Editor. *Uhlig's Corrosion Handbook – second edition* (2000). Chapter 69: D.A. Eden, “Electrochemical noise” 1227
40. J. O. Okeniyi, I.J. Ambrose, I. O. Oladele, C.A. Loto, P.A.I. Popoola, *Int. J. Electrochem. Sci.* 8 (2013) 10758

41. V.S. Sastri, *Green Corrosion Inhibitors: Theory and Practice*, John Wiley & Sons, Inc, Hoboken, NJ (2011)
42. ASTM G16-95 R04, *Standard guide for applying statistics to analysis of corrosion data*, ASTM International, West Conshohocken, PA
43. J.O. Okeniyi, O.S. Ohunakin, E.T. Okeniyi, *The Sci. World J.* 2015 (2015) 1
44. J.O. Okeniyi, C.A. Loto, A.P.I. Popoola, *Int. J. Electrochem. Sci.* 9 (2014) 4205
45. D. Izquierdo, C. Alonso, C. Andrade, M. Castellote, *Electrochim. Acta* 49 (2004) 2731
46. J.O. Okeniyi, E.T. Okeniyi, *J. Stat. Comput. Simul.* 82 (2012) 1727
47. S.D. Cramer, B.S. Covino Jr, Editors. *ASM Handbook vol 13A – Corrosion: Fundamentals, testing, and protection* (2003). P.R. Roberge, “Statistical interpretation of corrosion test results” 425
48. O.O. Ajayi, R.O. Fagbenle, J. Katende, S.A. Aasa, J.O. Okeniyi, *Int. J. Energy Environ. Eng.* 4 (2013) 1
49. T. Mandal, V. Jothiprakash, *ISH J. Hydraul. Eng.* 18 (2012) 20
50. R. Coffey, S. Dorai-Raj, V. O’Flaherty, M. Cormican, E. Cummins, *Hum. Ecol. Risk Assess.: An Int. J.* 19 (2013) 232
51. J.O. Okeniyi, *J. Assoc. Arab Univ. Basic Appl. Sci.* <http://dx.doi.org/10.1016/j.jaubas.2014.08.004>, (2014) 1
52. M.P. Chakravarthy, K.N. Mohana, *ISRN Corros.* 2014 (2014) 1
53. K.Y. Foo, B.H. Hameed, *Chem. Eng. J.* 156 (2010) 2
54. R. Karthikaiselvi, S. Subhashini, *J. Assoc. Arab Univ. Basic Appl. Sci.* 16 (2014) 74
55. J.O. Okeniyi, I.O. Oladele, O.M. Omoniyi, C.A. Loto, A.P.I. Popoola, *Can. J. Civ. Eng.* 42 (2015) 408
56. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, J.L. Dawson, Editors. *Electrochemical Noise Measurement for Corrosion Applications*, ASTM STP 1277 (1996). R. G. Kelly, M. E. Inman, J. L. Hudson, “Analysis of electrochemical noise for type 410 stainless steel in chloride solutions” 101

© 2015 The Authors. Published by ESG ([www.electrochemsci.org](http://www.electrochemsci.org)). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/>).