

Research Article

***Cymbopogon citratus* and NaNO₂ Behaviours in 3.5% NaCl-Immersed Steel-Reinforced Concrete: Implications for Eco-Friendly Corrosion Inhibitor Applications for Steel in Concrete**

Joshua Olusegun Okeniyi ^{1,2}, **Abimbola Patricia Idowu Popoola** ²,
and **Elizabeth Toyin Okeniyi**³

¹Mechanical Engineering Department, Covenant University, Ota, Nigeria

²Chemical and Metallurgical Engineering Department, Tshwane University of Technology, Pretoria, South Africa

³Petroleum Engineering Department, Covenant University, Ota, Nigeria

Correspondence should be addressed to Joshua Olusegun Okeniyi; joshua.okeniyi@covenantuniversity.edu.ng

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This paper studies behaviours of *Cymbopogon citratus* leaf-extract and NaNO₂, used as equal-mass admixture models, in 3.5% NaCl-immersed steel-reinforced concrete by nondestructive electrochemical methods and by compressive-strength improvement/reduction effects. Corrosion-rate, corrosion-current, and corrosion-potential constitute electrochemical test-techniques while compressive-strength effect investigations followed ASTM C29 and ASTM C33, in experiments using positive-controls for the electrochemical and compressive-strength studies. Analyses of the different electrochemical test-results mostly portrayed agreements on reinforcing-steel anticorrosion effects by the concentrations of natural plant and of chemical admixtures in the saline/marine simulating-environment and in the distilled H₂O (electrochemical positive control) of steel-reinforced concrete immersions. These indicated that little amount (0.0833% cement for concrete-mixing) of *Cymbopogon citratus* leaf-extract was required for optimal inhibition efficiency, $\eta = 99.35\%$, on reinforcing-steel corrosion, in the study. Results of compressive-strength change factor also indicated that the 0.0833% *Cymbopogon citratus* concentration outperformed NaNO₂ admixture concentrations also in compressive-strength improvement effects on the NaCl-immersed steel-reinforced concrete. These established implications, from the study, on the suitability of the eco-friendly *Cymbopogon citratus* leaf-extract for replacing the also highly effective NaNO₂ inhibitor of steel-in-concrete corrosion in concrete designed for the saline/marine service-environment.

1. Introduction

Corrosion of reinforcing-steel by chloride ion ingress into concrete from saline (via artificial deicing salt usage in temperate regions) or marine (via natural seawater from coastal areas) environments is a major degradation mechanism affecting steel-reinforced concrete durability [1–4]. This is because chloride ion breaks the thin film of passive oxide layer protecting reinforcing-steel in the highly alkaline concrete pore environment, which, until the aggressive chloride ion ingress, had kept the steel embedment depassivated [5–7]. Chloride-induced corrosion of reinforcing-steel in

concrete is essentially problematic because chloride ion promotes and accelerates the corrosion reaction via formation of intermediate product but without the chloride ion being consumed through the reaction process [8, 9]. The steel-reinforced concrete degradation ensues from rust by-product of the embedded steel corrosion which is expansive within the concrete, thus causing hoop stress that leads to cracks, spalling, delamination, and loss of load-bearing integrity of the structural member [10–14]. This could lead to insidious failure of the steel-reinforced concrete structure culminating in economic losses, especially, in the bid to avert catastrophic injury to life and property via costly repairs,

rehabilitation, and maintenances of the corrosion-damaged structure [15, 16]. These engender interests globally from construction stakeholders, researchers, and governments on how corrosion-induced problems could be mitigated, and it is such that costly budgets are allocated in many countries to corrosion related issues alone [15, 17–19].

Techniques proffered for mitigating chloride-induced steel-in-concrete corrosion include use of steel or concrete surface coating, stainless steel, fibre reinforced polymer encasement, cathodic protection, electrochemical chloride extraction, and corrosion inhibitors [3, 19–25]. Among these techniques, the use of corrosion inhibitors attracts much preference due to its economically lower cost, labour saving, and ease of applications, all combined with its relative effectiveness at mitigating corrosion of steel embedded in concrete [20, 26–30]. Applications of corrosion inhibitors can take the form of admixture into freshly cast concrete or it can be applied unto the surface of already cast concrete structures as migratory corrosion inhibitors (MCIs) [31–33]. While each of these has its advantages, admixtures are applied to fresh steel-reinforced concrete during casting for delaying the corrosion initiation process, while MCIs could be used for rehabilitation of steel-reinforced concrete which have had its embedded steel corroded [34]. By this, MCI needs to penetrate or diffuse through the concrete for reaching the reinforcing-steel-rebar to be effective at suppressing the corrosion of the metal [31, 33].

The problem with corrosion inhibiting admixture usage depends on the fact that admixture substances that have been known to be effective in inhibiting chloride-induced reinforcing-steel corrosion in concrete include compounds of nitrites and of chromates [26, 28, 30, 35, 36]. The challenges from using these substances are that they are environmentally hazardous due to their toxicity and lethality to living beings/organs, even as they also exhibit ability to cause hereditarily inheritable health conditions [15, 37–39]. These challenges are causing increasing restrictions in many countries on their usage [15, 38–40]. The additional problem from this includes the fact that these compounds constitute highly effective corrosion inhibitors such that replacement for them is difficult [41, 42]. Research tests are required for novel corrosion inhibitor proposition that will be environmentally friendly, nontoxic, and nonhazardous to the environmental ecosystem.

Sodium nitrite (NaNO_2) is a compound that had exhibited high effectiveness, in the literature, at inhibiting reinforcing-steel corrosion in chloride-contaminated environment [34, 35, 43, 44]. The high effectiveness of NaNO_2 at inhibiting reinforcing-steel corrosion in diverse environments has made it suitable for use in comparative study on other corrosion inhibiting prospects for carbon steel/steel in concrete, especially substances that could exhibit better environmental compatibility [27, 45–47]. *Cymbopogon citratus* (*C. citratus*) *Poaceae*, or lemongrass, is an essential-oil yielding, perennial plant used for beverage and medicinal purposes, in parts of the world, due to its antioxidant, antimicrobial, anti-inflammatory, anticarcinogenic, antihypertensive, and many other healthy/beneficial bioactive effects [48, 49]. Studies have shown that extract from *C. citratus* leaf is rich in

biocompatible phytoconstituents and heteroatoms of organic ligands that could exhibit affinity for iron in steel [50, 51]. Yet, these cited works have employed *C. citratus* leaf-extract for inhibiting reinforcing-steel corrosion in acidic sulphate medium and carbon steel in produced water. But unlike other plant-extracts that had been used in studies as “green” inhibitors of steel corrosion in NaCl-immersed concrete [52–55], there is dearth of studies on *C. citratus* leaf-extract usage for inhibiting chloride-induced reinforcing-steel corrosion. No report in the literature has investigated the comparison between anticorrosion effects from *C. citratus* and from NaNO_2 on reinforcing-steel embedment in concrete. Specific motivation for the usage of *C. citratus* in the present study follows from the consideration that some of the “green” plant-extracts from the cited works [53] have also been employed for inhibiting acidic sulphate induced reinforcing-steel corrosion [37, 56, 57]. Definitely, further investigation is required on the performance of *C. citratus* and also on reinforcing-steel corrosion in NaCl environment of steel-reinforced concrete immersion, because a substance that inhibited corrosion in a medium may not necessarily do so in another medium. This paper, therefore, studies the corrosion behaviours of *C. citratus* leaf-extract and NaNO_2 on the corrosion of reinforcing-steel in concrete immersed in 3.5% NaCl medium (saline/marine simulating-environment). Also, because using admixtures exhibit potency of changing concrete properties [58, 59], especially, via strength improvement/reduction [60], the compressive-strength effects of *C. citratus* and NaNO_2 admixtures on the studied steel-reinforced concrete were also investigated.

2. Materials and Methods

2.1. Experimental Materials

2.1.1. Plant-Extract and Chemical Materials for Steel-Reinforced Concrete Admixture. As detailed in [50], *C. citratus* used for the study had been freshly cut from Idiroko road, Canaanland, Ota, Nigeria, identified with FHI number 109497 by a professional Determinavit, dried at 20°C in well aerated room employing a 5-ton air-conditioning facility. This drying method was to forestall getting the phytochemical bioconstituents in the plant from getting denatured by the heat of tropical sun. The dried leaves were ground into smaller bits before being wrapped in Whatman paper that was placed in a condenser-equipped soxhlet extractor employing CH_3OH (methanol) as solvent [61]. The methanolic extract thus obtained was concentrated into the pasty form of *C. citratus* leaf-extract used in the present study for steel-reinforced concrete admixture.

All chemicals used for the study were of Analytical Reagent (AR) grade. These include NaNO_2 and NaCl that were both obtained from Eurostar Scientific®, CH_3OH from Sigma Aldrich®, and isopropyl alcohol (used hereafter for constituting conducting fluid) from J.T. Baker®.

2.1.2. Reinforcing-Steel, Concrete Block, and Admixture Materials. Commercial grade reinforcing-steel rod used for the study was of 12 mm diameter and has elemental composition:

0.27% C, 0.40% Si, 0.78% Mn, 0.04% P, 0.04% S, 0.14% Cr, 0.11% Ni, 0.02% Mo, 0.24% Cu, 0.01% Co, 0.01% Nb, 0.01% Sn, and the balance Fe. From this reinforcing-steel rod, 190 mm lengths of samples were cut before each sample was subjected to precorrosion experiment surface preparation, which was uniform for each steel sample, as per ASTM G109-07(2013) [62] and the literature [63].

Formulation used for the concrete casting was 300 kg/m³ Ordinary Portland Cement, 890.6 kg/m³ sand from River Ogun, Nigeria, 1106.3 kg/m³ granite passing 19 mm sieve, and 149.7 kg/m³ portable water, which makes the water-cement ratio = 0.499 [62, 64]. Each of the cast concrete types was of size 100 mm × 100 mm × 200 mm into which 150 mm of reinforcing-steel sample was centrally embedded during the concrete block casting [64]. The protrusion of 40 mm remaining on the reinforcing-steel serves for electrochemical test-measurement connection and this was painted with glossy paint immediately after concrete casting.

2.1.3. Admixture/Concrete Block Design. Two sets of steel-reinforced concrete samples were cast for this study. The first set includes steel-reinforced concrete samples into which equal-mass model of different concentrations of *Cymbopogon citratus* leaf-extract and NaNO₂ admixtures were mixed as per ASTM C192/192 M-16a [65]. In these samples, the equal-mass model for each type of admixture ranged from 0.00% (for the blank) in increment of 0.083% up to 0.4167% relative to cement proportion for the concrete casting [66]. These 11 steel-reinforced concrete samples are for corrosion immersion testing in 3.5% NaCl medium. Also included among the first set of steel-reinforced concrete samples is another 0.00% blank sample but for immersion in distilled water environment, tagged blank (H₂O) hereafter, to serve as positive control for the electrochemical experiment. It is worth noting that all steel-reinforced concrete samples in this first set were cured in curing room for 28 days [67, 68], as per ASTM C192/192 M-16a [65]. The second set of steel-reinforced concrete samples includes three samples that were cast in similar manner to the samples for electrochemical experiment (the first set) but with 0.00% admixture and which were cured in water for 28 days [11, 41, 69]. These samples of the second set are not subjected to electrochemical corrosion monitoring but are employed in the study as control samples for the compressive-strength testing according to the specification from ASTM C267-01(2012) [70].

2.2. Experimental Procedures

2.2.1. Electrochemical Corrosion Test-Procedures. The set of steel-reinforced concrete samples for electrochemical corrosion tests was immersed in bowls containing their requisite corrosion testing medium. This implies that the samples having *C. citratus* leaf-extract or NaNO₂ admixtures and a blank sample (without admixture) were immersed in 3.5% NaCl medium, well known as saline/marine simulating-environment [71, 72]. The remaining blank sample, for positive control, was immersed in distilled H₂O, for ascertaining the relative corrosiveness of the other blank sample

immersed in the 3.5% NaCl by the electrochemical corrosion testing.

From each of these steel-reinforced concrete samples, applied electrochemical corrosion monitoring procedures include measurements of

- (i) corrosion-potential (CP) versus Cu/CuSO₄ electrode (CSE) from Tinker & Rasor® via high impedance (10 MΩ) multimeter from MASTECH Equipment® according to ASTM C876-15 [73],
- (ii) corrosion-current (CC) versus the CSE using Zero Resistance Ammeter (ZRA) from Corrosion Service® [34, 45];
- (iii) Corrosion-rate (CR) using the 3-electrode LPR Data Logger from Metal Samples®, whereby saturated calomel electrode (SCE) from EDT direct-ION® is the reference, brass plate is auxiliary, and the reinforcing-steel embedded in concrete is the working electrode [11, 45]: For giving readout of the corrosion-rate directly, this LPR instrument nulls the potential difference between the reference and working electrodes before increasing current flow between the auxiliary and working electrodes. The ratio $\Delta V/\Delta I$, from the shifted working electrode potential (ΔV) relative to the reference electrode by the polarizing current (ΔI), is then used by the LPR instrument to compute the directly readout corrosion-rate on the instrument [15].

Each of these electrochemical test-measurements was taken in five-day interval for the first 40 days and thereafter in seven-day interval for the next eight weeks. This measurement design, which spanned 96-day period of electrochemical experiment, culminates in 17 data points for each electrochemical test-technique for the study. As prescribed in ASTM C876-15 [73], good electrical contact for electrochemical tests was ensured by using a water-retentive conducting sponge between the electrochemical testing probes and the steel-reinforced concrete samples. Contact solution used for prewetting this water-retentive sponge, before electrochemical measurements, was constituted of drinkable tap water to which small portions of isopropyl alcohol and of a local detergent (for improving wetting characteristics) were added [73].

2.2.2. Compressive-Strength Testing of Steel-Reinforced Concrete Samples. The steel-reinforced concrete samples for the electrochemical experiments were subjected to compressive-strength testing after the 96-day postcorrosion medium immersion testing by following the prescription from ASTM C39/C39 M-17b [74] and as detailed in [41, 46]. For this compressive-strength testing, the Model YES 2000, hydraulically powered, compression testing machine, from Eccles Technical Engineering Ltd®, England, was used. Also subjected to compressive-strength testing are the compressive-strength control samples (the second set of steel-reinforced concrete samples) that were cured in water for 28 days. The compressive-strength of the samples for electrochemical experiments was then compared to the averaged

compressive-strength of these control samples immersed in water as described in [68, 69] and according to the prescription from ASTM C267-01(2012) [70].

2.3. Analyses Procedures for Measured Experimental Data

2.3.1. Statistical Analyses and Test of Fitting Significance. Datasets of electrochemical measurements for each test-variable from the steel-reinforced concrete samples were subjected to the statistical analyses of the Normal and Weibull probability distribution fitting models. According to ASTM G16-13 [75], mean/average values from these models better approximate the expected value of corrosion condition prevalent in the corrosion test-system compared with the randomly deviating singly measured electrochemical testing. Thus, we recall that the Normal and Weibull probability distribution model equations, for test-data x of corrosion test-variable measurement, are, respectively, of the following forms [44, 76]:

$$f(x)_N = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\mu_N)^2}{2\sigma_N^2}\right], \quad (1)$$

$$f(x)_W = \left(\frac{k}{c}\right)\left(\frac{x}{c}\right)^{k-1} \exp\left[-\left(\frac{x}{c}\right)^k\right]. \quad (2)$$

For (1), μ_N and σ_N are the location parameter (also the mean) and the scale parameter (also the standard deviation) of the Normal distribution model, while, in (2), k and c are the shape and scale parameters of the Weibull distribution. For the $n = 17$ data points of corrosion test-measurements making up each dataset of x , the Normal mean, μ_N , is directly obtainable from the location parameter of the Normal distribution as [76, 77]

$$\mu_N = \frac{1}{n} \sum_{i=1}^n x_i. \quad (3)$$

In contrast, the mean value of datasets of x can only be obtained after estimations of the Weibull shape (k) and scale (c) parameters. For estimating these parameters, the linear form of the Weibull cumulative function, $F(x)$, as per ASTM Manual MNL20 [77], was employed with the randomly distributed median rank approximation $F(x_i)$ for plotting position. These two functions, respectively, assume the following form [77, 78]:

$$\ln\{-\ln[1-F(x)]\} = c \ln x - c \ln k, \quad (4)$$

$$F(x_i) = \frac{i-0.3}{n+0.4}. \quad (5)$$

The computed k and c values are then used for evaluating Weibull mean, μ , from

$$\mu_W = c\Gamma\left(1 + \frac{1}{k}\right). \quad (6)$$

Also, it is a requirement of ASTM G16-13 [75] that describing the scatter of corrosion test-data should necessarily employ

the descriptive statistics followed by the data. For ascertaining this condition for the empirical, $F^*(x)$, and the theoretical, $F(x)$, corrosion test-data distributions by the Normal and Weibull model, the Kolmogorov-Smirnov goodness-of-fit (K-S GoF) test was used, at $\alpha = 0.05$ significance level of test-criteria, via the statistics [79]:

$$D_n = D(x_1, \dots, x_n) = \sup_{-\infty < x < \infty} |F^*(x) - F(x)|. \quad (7)$$

2.3.2. Inhibition Efficiency Analysis. The evaluated mean of corrosion-rate from the distribution fitting the data better, $\mu_{\text{distribution}}$, is used for modelling inhibition efficiency by the *C. citratus* and NaNO_2 admixture concentrations relative to the blank sample in the steel-reinforced concrete. This modelling of corrosion-inhibition behaviours uses the following formula [45, 47, 51]:

$$\eta = \frac{\mu_{\text{distribution,blank}} - \mu_{\text{distribution,admixed}}}{\mu_{\text{distribution,blank}}} \times 100. \quad (8)$$

2.3.3. Analysis for Admixture's Compressive-Strength Effect on Concrete. The compressive-strength effect of each admixture concentration on steel-reinforced concrete was analysed using the compressive-strength change factor $\text{CSCF}_{(\%)}$ modelling formula [68–70]:

$$\text{CSCF}_{(\%)} = \frac{f'_{c_{u,28}} - f'_{c_{\text{post-corrosion}}}}{f'_{c_{u,28}}} \times 100. \quad (9)$$

3. Results and Discussions

3.1. Modelled Results of Corrosion Test-Data by Statistical Analyses. The statistical analyses by the Normal and Weibull distributions led to the mean/average of corrosion test-results plotted in Figure 1, wherein statistical models of corrosion-potential are plotted in Figure 1(a), corrosion-current in Figure 1(b), and corrosion-rate in Figure 1(c). For direct-plotting interpretation purpose, linear plots of corrosion risk probability as per ASTM C876-15 [73] are included in Figure 1(a) as well as those of typical rate of corrosion classification for steel in concrete as per [80, 81].

Easily observable from the plots in Figure 1 is the patterning alike of the curves from the electrochemical test-results, not only along the statistical models of test-data by the different distributions but also across the different corrosion test-techniques employed. However, the pattern of the mean corrosion-potential values across the steel-reinforced concrete for electrochemical experiment appears to exhibit the most mode of amplification, followed by that of the corrosion-current, while that of the corrosion-rate is highly damped. It is opined that this high amplification of corrosion test-response observed from the corrosion-potential makes this electrochemical test-technique useful as an initial testing method for assessing probability of corrosion risk in steel-reinforced concrete before further tests [15, 81]. This supports the usage of corrosion-potential technique as a rapid approach of indicating corrosion propagation ahead of its causative damage, as detailed in [15].

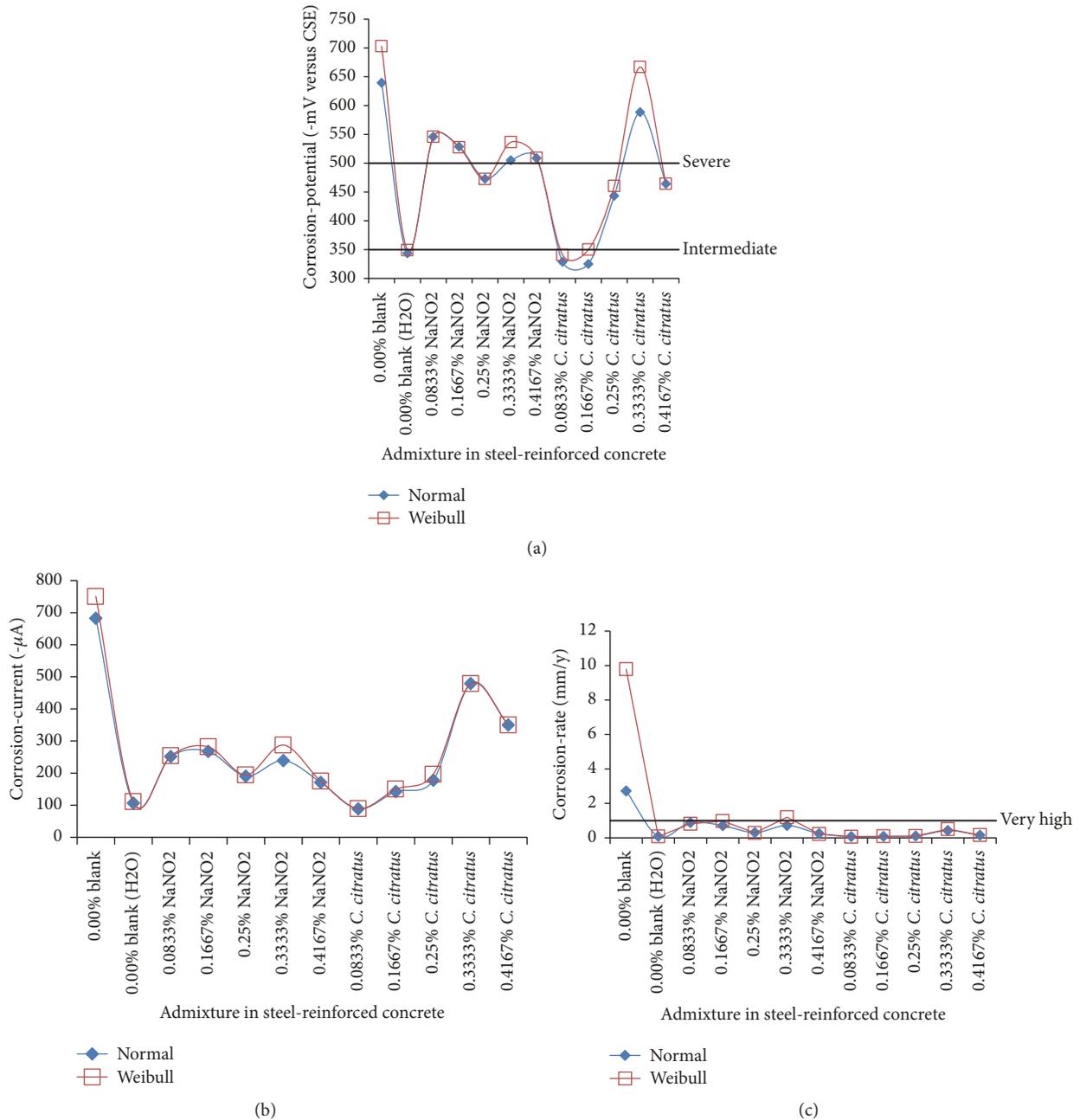


FIGURE 1: Results of statistical analyses of the Normal and Weibull distribution models detailing mean/average corrosion test-responses from electrochemical monitored steel-reinforced concrete samples: (a) corrosion-potential, (b) corrosion-current, and (c) corrosion-rate.

Thus, the probability of corrosion risks from the modelled results of corrosion-potential is well corroborated by the dissolution model of the iron in the reinforcing-steel in concrete to which the corrosion-current is proportional, according to [82]. Both the corrosion risk probability and the dissolution activity models culminated in the corrosion-rate observed in the steel-reinforced concrete samples having NaNO₂ or *C. citratus* admixtures as well as the 0.00% blank (the NaCl-immersed control) and the blank (H₂O) samples. From these considerations, it could be noted that the corrosion-rate in the 000% blank sample ranged very well above the

“very high” corrosion-rate delineation, which represents a severe condition of corrosion test-system. This follows the designation of preferred practice for laboratory corrosion tests by [83] and is corroborated by the identification of 3.5% NaCl solution as a medium with higher corrosion-rate on carbon steel in [71]. In contrasts, the blank (H₂O) sample exhibited comparatively much lower corrosion-rate than the 0.00% blank (in NaCl) and, also, than the “very high” corrosion-rate delineation. These two high and low data points of corrosion conditions lend credence to the inference that both the NaNO₂ chemical and *C. citratus*

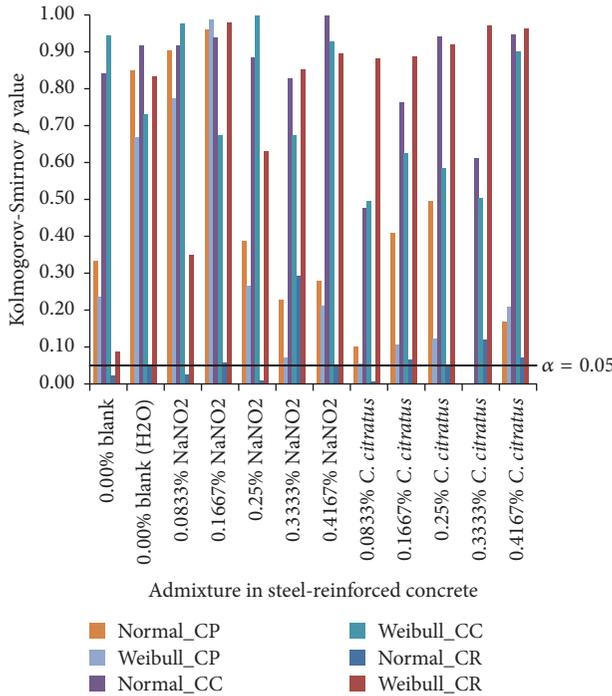


FIGURE 2: Kolmogorov-Smirnov goodness-of-fit tests of corrosion datasets scattering like the Normal and the Weibull distribution.

leaf-extract exhibited corrosion reductions in the reinforcing-steel embedded in the 3.5% NaCl-immersed concrete studied.

It is also notable from Figure 1 that the statistical distribution fitting of corrosion test-data by the Weibull exhibited agreements with fitting from the Normal model but with some overpredictions of corrosion test-results, in each of the three corrosion test-techniques. These forms of test-results disparities necessitate compatibility testing of dataset scattering like one distribution or the other as designated in ASTM G16-13 [75]. Based on these statistical distribution compatibility tests, Figure 2 therefore presents the Kolmogorov-Smirnov goodness-of-fit test-results on the distribution of each of the corrosion test-techniques like the Normal and the Weibull distribution. Also for direct-plotting interpretation the linear plot of $\alpha = 0.05$ level of significance is included in Figure 3 for ascertaining dataset following the distribution models of study from the figure.

From the goodness-of-fit plotting in Figure 3, it could be deduced that datasets of corrosion-potential and corrosion-current from the studied steel-reinforced concrete samples followed the Normal distribution, because K-S p values for these samples are > 0.05 . These results find agreement with indication from [77] that corrosion-potential may scatter like the Normal distribution. However, five (out of the studied twelve) datasets of corrosion-rate, two from the NaNO_2 , two from the *C. citratus* admixture concentrations, and the 0.00% blank sample (in NaCl), did not scatter like the Normal distribution, for they have K-S p values < 0.05 . In contrast to these results, all the dataset of corrosion-potential, corrosion-current, and corrosion-rate in this study scattered like the Weibull distribution by having K-S p values > 0.05 . This

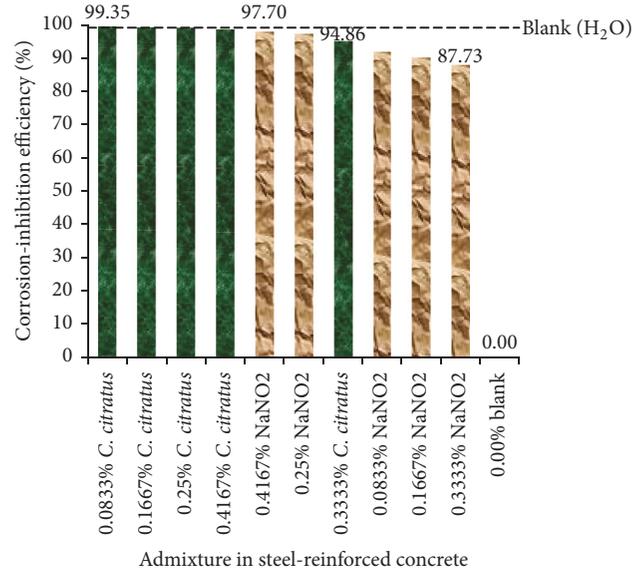


FIGURE 3: Ranking of inhibition efficiency performance of *C. citratus* leaf-extract and NaNO_2 admixtures on reinforcing-steel corrosion in concrete samples studied.

following Weibull probability distribution model, a Type III extreme value distribution of minima, by the corrosion test-data implies that the corrosion test-data in the study exhibited behaviour of failure culminating data [77]. These considerations, therefore, support use of the Weibull distribution as the descriptive statistics for detailing the corrosion test-results in this study.

3.2. Inhibition Efficiency Performance of *C. citratus* Leaf-Extract and NaNO_2 Admixtures. The results of inhibition efficiency on reinforcing-steel corrosion, obtained by subjecting the Weibull mean of corrosion-rate to (8), are plotted in Figure 3, according to the ranking order of *C. citratus* leaf-extract and NaNO_2 admixture performance. While the inhibition efficiency modelling was relative to the 0.00% blank sample (in NaCl), according to (8), the model of efficiency by the blank (H_2O) positive control relative to the NaCl-immersed control was also included as a linear plot in Figure 3. From the figure, it could be observed that NaNO_2 chemical exhibited confirmation as an excellent inhibitor of concrete reinforcing-steel corrosion in chloride-contaminated medium by the optimal 0.4167% NaNO_2 admixture in this study having $\eta = 97.70\%$. The least performance by the NaNO_2 admixture concentrations employed was by the 0.3333% NaNO_2 having $\eta = 87.73\%$. Studies have documented that nitrite exhibits this highly effective corrosion performance on steel-rebar due to its ability to form chloride ion-blocking protective film on the reinforcing-steel, in cooperation with the hydroxyl ion [28, 34]. This form of passive layer could be less porous and more compact such that it could shift the corrosion-potential towards more electropositive direction while it mitigates corrosion effects in chloride-contaminated environment [34].

However, in spite of these highly effective performances exhibited by the NaNO_2 admixtures, the *C. citratus* leaf-extract concentrations exhibited higher inhibition efficiency performance than each of their counterparts of equal-mass NaNO_2 admixtures. From the ranking order of inhibition efficiency, four out of the five *C. citratus* leaf-extract concentrations outperformed all the NaNO_2 admixture concentrations for the study and this is such that just the 0.4167% and the 0.25% NaNO_2 admixtures outperformed the 0.3333% *C. citratus*. Thus, even though this 0.3333% *C. citratus* leaf-extract exhibited the least inhibition efficiency performance among the natural plant-based admixture in this study, this inhibition efficiency is still as high as $\eta = 94.86\%$. By the ranking order of admixture performance on reinforcing-steel corrosion in the studied saline/marine model-environment, the overall, optimal admixture in the study is the 0.0833% *C. citratus* leaf-extract admixture, which exhibited $\eta = 99.35\%$.

The high effectiveness of *C. citratus* concentrations could be attributed to its composition of S-, N-, and O-containing organic ligands that are rich in lone pairs and π -electrons [50] and which are known to have affinity for iron in reinforcing-steel [84]. For instance, Euclidean search hit-list, based on the Fluka® library, of the Fourier Transform Infrared (FTIR) spectroscopy analysis of *C. citratus* leaf-extract, fully expatiated in the cited study [50], indicated that constituents of this plant-extract include

- (i) $\text{C}_4\text{H}_{10}\text{O}_2\text{S}$ (thiodiethylene glycol),
- (ii) $\text{C}_{15}\text{H}_{14}\text{O}_6$ (catechin),
- (iii) $\text{C}_{15}\text{H}_{14}\text{O}_6$ (epicatechin),
- (iv) $\text{C}_{15}\text{H}_{16}\text{O}_7$ (catechin hydrate),
- (v) $\text{C}_{24}\text{H}_{40}\text{O}_4$ (deoxycholic acid),
- (vi) $\text{C}_2\text{H}_6\text{OS}$ (2-mercaptoethanol),
- (vii) $\text{C}_7\text{H}_5\text{ClO}_3$ (3-chloroperoxybenzoic acid),
- (viii) $\text{C}_7\text{H}_8\text{N}_2\text{S}$ (N-phenylthiourea),
- (ix) $\text{C}_6\text{H}_6\text{N}_2\text{O}_3$ (2-amino-4-nitrophenol),
- (x) $\text{C}_9\text{H}_9\text{HgNaO}_2\text{S}$ (sodium ethylmercurithiosalicylate).

As it was explained in [50], which rather involves H_2SO_4 , it is worth noting that *C. citratus* leaf-extract shares some of these indicated biochemical constituents in common with other plant-extracts that had inhibited chloride-induced corrosion of steel in concrete in studies [26, 85]. These eco-friendly and biocompatible phytoconstituents would have been capable of preferential interaction with the reinforcing-steel metal, which could have exhibited chloride attack prevention activity in a more multifaceted mechanisms than that obtainable from the NaNO_2 chemical. The cooperative synergism, instead of competitive, of the multiple biochemicals in *C. citratus* leaf therefore constitutes reasons why the *C. citratus* leaf-extract outperformed the rather single but highly effective NaNO_2 chemical both on equal-mass and in overall admixture performance. This form of synergistic corrosion-protection effect by different bioconstituents in a plant-extract is well supported from study using mild steel in direct-immersion experiment in acidic solution [86]

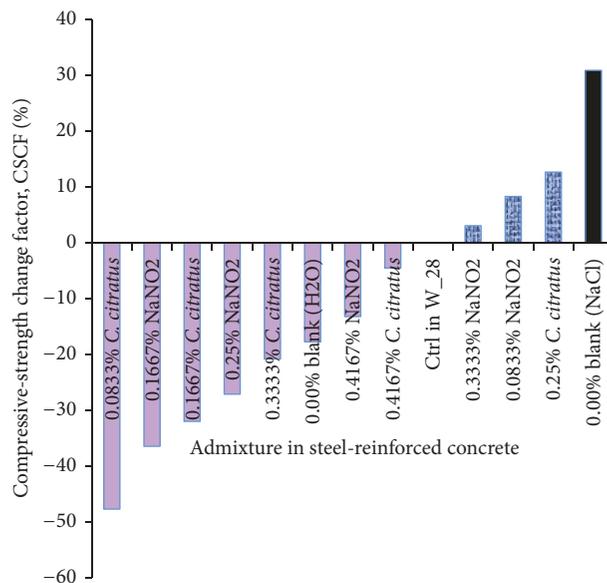


FIGURE 4: Ranking of compressive-strength change behaviour of studied admixtures.

wherein it was shown that the phytoconstituents adsorb on the steel material. However, just as was noted in that reported work in [86], the individual and the combined (synergistic) contributions of the bioconstituents in the plant-extracts exhibit extreme difficulties both in evaluations and in explanations. Thus, while studies of the nature reported in this work are indicative of the combined effects of the plant-extract bioconstituents, several standalone studies would be required for ascertaining individual contributions of each component on metallic corrosion in the tested-environment.

3.3. Compressive-Strength Change Behaviour of *C. citratus* and NaNO_2 Admixtures. Ranking order of the compressive-strength improvement performance by the *C. citratus* leaf-extract and NaNO_2 admixtures is presented in graphical plotting shown in Figure 4.

For the reason that the compressive-strength change factor plotted in Figure 4 was evaluated in (9) relative to the Ctrl in W_28 steel-reinforced concrete, it then follows that negative CSCF (%) indicates strength improvement while positive value of this parameter implies strength reduction. Thus, it could be noted from Figure 4 that the 0.00% blank (NaCl -immersed) sample exhibited the highest reduction in compressive-strength among the studied steel-reinforced concrete for this study. In addition to this, it is also worth noting that the 0.00 blank (H_2O) positive control of electrochemical steel-reinforced concrete exhibited higher compressive-strength, for its CSCF (%) is >0 , than the Ctrl in W_28. By these result models, the normal control immersed in the 3.5% NaCl test-solution and the positive control immersed in distilled water constitute two important data points for the compressive-strength comparisons.

On equal-mass basis of comparisons, the NaNO_2 admixture mostly surpassed their equal-mass *C. citratus* leaf-extract

admixture counterpart in compressive-strength improvement performance. The exceptions to these compressive-strength improvement behaviours are the 0.0833% *C. citratus* and the 0.3333% *C. citratus* leaf-extract concentrations that outperformed their NaNO₂ admixture counterparts in compressive-strength improvement effects. Actually, the compressive-strength change effect by the 0.0833% *C. citratus* leaf-extract admixture, CSCF = -47.67%, constitutes the utmost compressive-strength improvement on steel-reinforced concrete in this study. In comparison, the closely following 0.1667% NaNO₂ admixture, having CSCF = -36.42%, exhibited the highest compressive-strength improvement performance on steel-reinforced concrete among the NaNO₂ admixtures studied. Three *C. citratus* leaf-extract, compared to two NaNO₂, concentrations surpassed the blank (H₂O) in compressive-strength improvement performance, while the positive distilled H₂O-immersed control in turn surpassed the 0.4167% concentrations of the *C. citratus* and of the NaNO₂ admixtures in compressive-strength improvement performance. On the other side of compressive-strength change effects, two NaNO₂ admixtures and the 0.25% *C. citratus* admixture concentration exhibited compressive-strength reduction behaviour in the study.

Implications from these foregoing result observations include the following:

- (i) The highly effective improvement to the compressive-strength of steel-reinforced concrete by the 0.0833% *C. citratus* leaf-extract constitutes added advantage to the highly efficient performance on the inhibition of reinforcing-steel corrosion by this same admixture.
- (ii) The additional advantage from this 0.0833% *C. citratus* leaf-extract admixture includes the fact that it is the lowest concentration of the admixture design in this study.
- (iii) Thus, little amount of *C. citratus* leaf-extract would be required for effectively inhibiting steel-in-concrete corrosion in the chloride-contaminated service-environment of steel-reinforced concrete.
- (iv) The ultimate advantage follows from the consideration that the *C. citratus* leaf-extract is an eco-friendly material that, unlike its NaNO₂ counterpart of anticorrosion effect comparisons, is nontoxic and nonhazardous to the environmental ecosystem.

These behaviours of admixture performances in 3.5% NaCl-immersed steel-reinforced concrete, therefore, support the suitability of the *C. citratus* leaf-extract for the total-replacement of NaNO₂ chemical as inhibitor of reinforcing-steel corrosion in concrete designed for the saline/marine service-environment.

4. Conclusions

The behaviours by equal-mass basis of *C. citratus* and NaNO₂ on the corrosion of reinforcing-steel in concrete immersed

in 3.5% NaCl, test-solution for saline/marine simulating-environment, has been studied in this paper. Conclusions from the study therefore include the following:

- (i) Both the *C. citratus* leaf-extract and the NaNO₂ admixture concentrations efficiently mitigated the severe reinforcing-steel corrosion observed in the normal control of steel-reinforced concrete immersed in the 3.5% NaCl test-environment.
- (ii) On equal-mass consideration, most of the *C. citratus* leaf-extract admixture concentrations surpassed the also highly effective NaNO₂ admixture concentrations on the inhibition of concrete reinforcing-steel corrosion in the chloride-contaminated medium of study.
- (iii) While most of the NaNO₂ admixture concentrations for the study outperformed their equal-mass model of the *C. citratus* leaf-extract concentrations in compressive-strength improvement, 0.0833% *C. citratus* leaf-extract still surpassed all the admixture concentration design in the study as the admixture with the utmost compressive-strength improvement performance.
- (iv) The utmost compressive-strength improvement performance, CSCF = -47.67%, by the 0.0833% *C. citratus* leaf-extract was with the added advantage of optimal inhibition effectiveness performance, $\eta = 99.35\%$, on the corrosion of reinforcing-steel embedment in 3.5% NaCl-immersed steel-reinforced concrete by this same admixture.
- (v) These performances of behaviours indicate that just the little concentration of 0.0833% *C. citratus* is required for effective inhibition of chloride-induced steel-in-concrete corrosion with no loss but rather very good compressive-strength improvement advantage on its steel-reinforced concrete of admixture.
- (vi) The foregoing considerations as well as the being eco-friendly, nontoxicity, and nonhazardousness of *C. citratus* leaf-extract support suitability of this natural plant material for totally replacing NaNO₂ chemical as inhibitor of reinforcing-steel corrosion in steel-reinforced concrete designed for the saline/marine environment.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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