RHIZOPHORA MANGLE L. LEAF BIOCHEMICAL CHARACTERIZATION: NATURAL-GREEN TOTAL-CORROSION INHIBITION PROSPECT ON CONCRETE STEEL-REINFORCEMENT IN 3.5% NaCl

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Graphical abstract
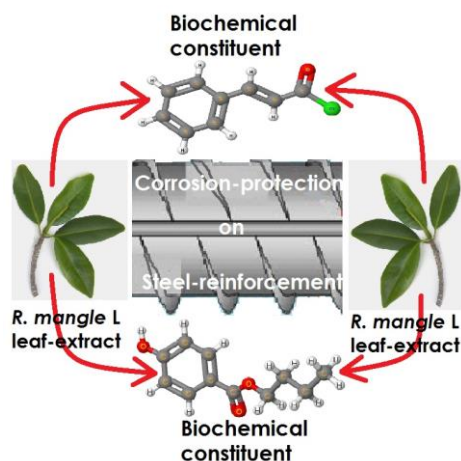
Abstract

Effective corrosion-protection by plant-extract on metals, in aggressive service-environment, is dependent on the biochemical constituents of which the natural plant is made-up. This paper investigates biochemical characterization of inorganic and organic constituents of *Rhizophora mangle* L. leaf for gaining insight on its steel-reinforcement corrosion mitigating prospect in NaCl-immersed concretes. Employed for the study include atomic absorption spectroscopy (AAS), Fourier transform infrared (FT-IR) spectroscopy and phytochemical screening techniques. Total-corrosion effect was also studied from steel-reinforced concrete samples, having different concentrations of the leaf-extract as admixture, and which were immersed in 3.5% NaCl (simulating saline/marine environment). AAS analyses indicated highest inorganic constituents n *Rhizophora mangle* L. leaf as iron, Fe = 10,316.17 µg/g, and the least as cadmium, Cd = 6.2019 µg/g, but with neither chromium (Cr) nor lead (Pb). From the leaf-extract, also, FT-IR analyses indicated organic constituents of aromatic chained compounds rich in lone-paired/π-electrons as well as nitrogen, oxygen and sulphur-bearing ligands exhibiting coordinate affinity with iron in reinforcing-steel. Characterization by phytochemical analyses depicted that the leaf-extract contains tannins, alkaloids, phlobatannins, steroids, saponins, and glycosides. Tested corrosion-inhibition prospects, using the leaf-extract, indicated reduced steel-reinforcement total-corrosion effects that correlated with the extract admixture concentrations employed in the 3.5% NaCl-immersed steel-reinforced concretes.

Keywords: *Rhizophora mangle* L. leaf, natural-plant material, concrete steel-reinforcement, total-corrosion analyses, biochemical characterization procedures, organic/inorganic bio-constituent analyses, saline/marine simulating-environment

1.0 INTRODUCTION

Chloride induced corrosion of reinforcing-steel in concrete is a major deterioration factor that affects service-life/durability of steel-reinforced concrete, one of the most widely used construction material for global physical infrastructure [1, 2]. Chloride ion ingress into steel-reinforced concrete from service-environments, including marine, in the form of coastal seawater, or saline, from de-icing salt usage, where it breaks the passive film of thin oxide layer usually protective of the steel-rebar in the concrete pore structure [1, 3, 4]. Rust, the by-product from reinforcing steel corrosion, is expansive within the concrete, and by this it causes hoop stresses that lead to cracks, delamination and spalling of the steel-reinforced concrete structure [1, 5]. These could lead to insidious premature failure of steel-reinforced concrete members, with attendant financial losses, if not averted through repairs, maintenance or replacement. However, the repairs, maintenance or replacement of corrosion deteriorated steel-reinforced structures are also cost-intensive such that they make up major portion of fiscal construction budget in many countries [6].

It is accepted that chloride induced corrosion could be controlled through several methods including use of cathodic protection, electrochemical chloride extraction, surface coatings, water-proofing membrane, galvanized/stainless steel-rebar and corrosion inhibitors. Among these, the use of corrosion inhibitors attracts preference due to its many advantages including comparably lower cost, ease of application, labour saving and yet highly effective technique for steel-reinforcement corrosion protection [1, 3]. However, a very serious challenge ensues from the use of synthetic compounds that have shown anticorrosive effectiveness and this include the fact that many of the synthetic compounds exhibit toxicity to living organs of human beings and hazardousness to the environmental ecosystem [5, 7, 8]. For these reasons research activities are being geared towards use of green, environmentally-friendly natural substitutes as corrosion inhibitors in the stead of the toxic and hazardous synthetic compounds [9, 10].

Extracts from plants are natural products that constitute environmentally-friendly biocompatible heteroatoms. These are rich in non-bonded lone-pair and π electrons, which are potent at inhibiting metallic corrosion through adsorption and electron donation to the metal [9, 11, 12]. By these properties, natural compounds found in plant extract are able to displace adsorbed water molecules from metallic surface and, thus, prevent a major reaction mechanism instigating metallic corrosion attacks in aggressive environments [12, 13, 14]. Among many plant extracts that had been studied by researchers on metallic corrosion inhibition, extracts from *Rhizophora* spp (mangrove) have been identified

with positive prospects of metallic corrosion protection in acidic and neutral chloride contaminated media [15, 16, 17]. However, unlike synthetic compounds that are of known chemical formula/structures, insights into understanding factors, such as chain lengths, bonding, aromatic/conjugate etc [12], contributing to inhibiting actions of plant extracts may only be attained through their requisite characterization [13, 14]. But while characterization study have been done on leaf from *Morinda lucida* in [13] and from *Phyllanthus muellerianus* in [5, 14], extract from which positive inhibition on rebar corrosion had also been exhibited [5, 12, 18, 19], no such report exists for *Rhizophora mangle* L. (red mangrove) leaf-extract. This paper, therefore, investigates characterization of the organic and inorganic biochemical constituents of *Rhizophora mangle* L. leaf, especially, for gaining insight into the prospect of the extract as a natural-green corrosion inhibitor of steel-reinforcement embedded in concrete designed for the saline/marine environment.

2.0 METHODOLOGY

2.1 Experimental Materials

2.1.1 Rhizophora mangle L. Leaf Material

Fresh leaves of *Rhizophora mangle* L. (*R. mangle* L.) *Rhizophoraceae*, were collected from Ehin-more, Ilaje ese-odo area of Ondo State, Nigeria. The leaves were identified at the Forestry Herbrium, Ibadan (FHI), Nigeria and a sample of it, which was labelled FHI No. 109501 (as voucher number) was deposited at the Herbarium. The fresh leaves were dried under cover in an aerated room that was maintained at 20°C, for ensuring crisp-drying of the leaves for easy pulverisation [15, 20].

2.1.2 Steel-reinforcement Material

Steel-reinforcement material used for test of corrosion prospect in the study is of 12 mm diameter. The elemental composition for this reinforcing steel material includes: 0.273% C, 0.780% Mn, 0.240% Cu, 0.403% Si, 0.142% Cr, 0.109% Ni, 0.039% P, 0.037% S, 0.0086% Co, 0.0083% Nb, 0.0063% Sn, 0.0037% Ce, 0.0032% V, 0.016% Mo, while the remainder is Fe. For concrete rebar embedment, the steel was cut into 190 mm rods of specimen, from which 150 mm of the steel rod was embedded in the concrete while the protruding 40 mm was painted, after concrete casting, with anticorrosive paint and it was used for corrosion monitoring connection. Each rods of steel-rebar was given the same surface preparation that follows standard prescriptions from ASTM G109-99a [21].

2.2 Experimental Procedures Biochemical Characterization

Atomic Absorption Spectroscopy (AAS) characterization of inorganic constituent, i.e. heavy metal, from *R. mangle* L. leaf that had been subjected to requisite pre-AAS preparations described in [11, 14] was done through use of the S Series, AA Spectrometer from Thermo Electron Corporation® (Waltham, Massachusetts). The pre-AAS preparation was done via ashing a portion of the dried and then pulverized *R. mangle* L. leaves through use of a model CD-1700X High Temperature Muffle Furnace® (Chida®, Zhengzhou, Henan, China) that was heated up to 500°C before being maintained for 2 hrs at this temperature. This procedure yields an ash content of 8.45% for the *R. mangle* L. leaf. Then, overnight soaking of 0.25 g of the ashed material followed in 5 ml of 1:1 nitric-perchloric acid mixture, and this was heated in a reflux condenser to 150°C temperature at which it was maintained for 1 hr before gradual temperature increase to 235 °C. This heating at 235 °C was maintained again for 2 hr, for observing the occurrence of dense fume. Cooling to 100 °C then followed, via removing of the mixture from the heating block, after which 1:1 HCl solution was added before further heating was continued until obtaining white fumes and, thereafter, colourless solution. Then, pouring into 100 ml flask, of the colourless solution, followed and washing five times with water, with the washing added to the flask each time, before making up with water to the 100 ml mark of the flask's volume. This was concluded by filtering the resulting solution for obtaining the filtrate that was analyzed using the S Series, AA Spectrometer (from Thermo Electron Corporation®), which employs Hollow Cathode Lamps, for AAS test-analyses.

Investigation of the organic bio-constituents of *R. mangle* L. leaf was followed by employing two methods on the extract of the leaf; the FT-IR spectrum and phytochemical screening analyses [11, 14]. The leaf-extract used was obtained through concentration, over water-bath, of the extraction solution from a condenser equipped soxhlet extractor employing CH_3OH (methanol) as solvent and in which the pulverised *R. mangle* L leaf powder in Whatman filter paper had been placed.

The FT-IR (Fourier Transform Infra Red Spectrophotometer) spectrum for the organic bio-constituent study from *R. mangle* L. leaf-extract was obtained through the KBr pelleting of the leaf-extract mounted on the Perkin-Elmer® FT-IR Spectrum BX System (from Waltham, Massachusetts, USA). The FT-IR spectrum, obtained from this instrumentation, was then rendered to the Euclidean (computer-based) Search of Fluka library by the Perkin-Elmer® equipment. This facilitated generation of the Euclidean Search hit-list of organic compounds that the instrument could identify from the FT-IR spectrum through the Fluka library that had been integrated with the Perkin-Elmer® FT-IR Spectrum BX system.

Characterization by phytochemical screening method was initiated by thoroughly mixing 2 g of the *R. mangle* L. leaf extract in distilled water and using the distilled water to make up the obtained solution up to 20 ml. From the ensuing solution, test-procedures for the presence, or otherwise, of different phyto-constituents were carried out as detailed in literature [11, 14, 22], which include:

- Test for tannins: was carried out by boiling 0.4 ml of the *R. mangle* L. leaf-extract solution in 5ml water followed by filtering and adding a few drops of 0.1% $FeCl_3$ and, from this, the colouration of brownish-green or blue-black was observed.
- Test for phlobatannins: was carried out by boiling a portion of the *R. mangle* L. leaf-extract solution in 1% HCl from which precipitation of red coloured deposit was observed.
- Test for saponins: was carried out by boiling 0.4ml of the *R. mangle* L. leaf-extract solution with an equal-part distilled water in a water bath followed by filtering and then shaking the filtrate vigorously for stable persistent froth, which was then mixed with 3 drops olive oil before shaking vigorously again for observing the formation of emulsion.
- Test for flavonoids: was carried out by heating 0.4 ml of the *R. mangle* L. leaf-extract solution with 2 ml ethyl acetate over steam bath for 3 min before steeping the mixture and then shaking 0.4 ml of the filtrate with 0.1 ml dilute ammonia solution and from this the coloration of yellow was observed.
- Test for steroids: was carried out by adding 0.4 ml of acetic anhydride to 0.1 g of the *R. mangle* L. leaf-extract and following this with the addition of 0.4 ml H_2SO_4 for observing change of colouration to blue (or green) from violet.
- Test for terpenoids (Salkowski test): was carried out by mixing 1 ml of the *R. mangle* L. leaf-extract solution with 0.4 ml chloroform and carefully adding 0.6 ml concentrated H_2SO_4 in order to form a layer from which colouration of reddish-brown was observed.
- Test for glycosides (Keller-Killani test): was carried out by treating 0.5 ml of the *R. mangle* L. leaf-extract solution with 0.2 ml of glacial acetic acid into which a drop of $FeCl_3$ solution had been added and which had also been under-laid with 1 ml concentrated H_2SO_4 for observing brown ring and/or violet ring below the brown ring or green ring through the thin layer.
- Test for alkaloids: was carried out by adding 10 ml of water to the *R. mangle* L. leaf-extract solution and from this, 1 ml was then taken into which was added 2 drops of Wagner's reagent (Iodo-potassium iodide was obtained through dissolution of 0.2 g iodine and 0.6 g KI in 1 ml of water) for observing brown or reddish-brown precipitate.

2.3 Experimental Procedures for Total-corrosion Testing

The total-corrosion test-analysis employs the use of macrocell current measurements from a total of 12 steel-reinforced concrete samples, each of size 100mm × 100mm × 200mm. Ten of the steel-reinforced concrete samples were admixed, during casting of the fresh concrete as prescribed in ASTM C192/192M-02 [23], with different *R. mangle* L. leaf-extract concentrations, ranging from 0.00 g/L (for the control samples) up to 6.67 g/L, in increment of 1.67 g/L of the concrete mixing water. As illustrated in [24], each of these ten steel-reinforced concrete samples was immersed longitudinally in bowls containing 3.5% NaCl test-solution, for simulating saline/marine environment [25]. The remaining two steel-reinforced concrete samples were not admixed with *R. mangle* L. leaf-extract, but they were immersed (also longitudinally) in bowls containing distilled water, these are hereafter referred to as "0.00 g/L [control in Water]" samples. These "0.00 g/L control in Water" steel-reinforced concrete samples constitute positive control samples. In this study, they find special usefulness for ascertaining that the corrosion test measurements from the samples immersed in the corrosive environment, i.e. the 3.5% NaCl, ensue from the corrosiveness of the environment of their immersion alone rather than from other unaccounted environmental factor [5].

In each of the bowls, the 3.5% NaCl test-solution was made up to just below the protruding steel-rebar from the concrete but without allowing the test-solution to touch the steel-reinforcement. Then, macrocell current were measured, versus Cu/CuSO4 reference electrode, using the zero resistance ammeter (Corrosion Service®) in five days interval for 40 days and, thereafter, in seven days intervals for seven weeks. These totaled n = 16-point measurements in the 89-day period of experiment. From these, total-corrosion, Tc (C), estimations via the macrocell current i (A) was as per the standard formula from ASTM G109- 99a [11, 14, 21]:

$$Tc_k = Tc_{k-1} + \left[\left(t_k - t_{k-1} \right) \times \left(i_k + i_{k-1} \right)/2 \right]; \; k = 2, 3, ..., n \quad (1)$$

where: t is the time (s) between the present (k_{th}) and the previous, $(k-1)$th, macrocell current measurements i_k at time t_k, and i_k - 1, at time t_k - 1.

3.0 RESULTS AND DISCUSSION

3.1 Results of Heavy Metals from AAS Study

Results of AAS test for heavy metals, i.e. inorganic constituents, from the *R. mangle* L. leaf in the study are tabulated in Table 1. These results show that the studied *R. mangle* L. leaf does not contain Lead (Pb) and Chromium (Cr). Also, the concentration of Nickel (Ni) and Cadmium (Cd) in the *R. mangle* L. were lower than the Ecological Soil Screening Levels (Eco-SSLs) [11, 14], set for plants by USEPA [27, 28]. In

contrast to these, concentration of copper (Cu) in the studied *R. mangle* L. leaf was above the Eco-SSL for plant, set at 70 μg/g in [29]. However, it is worth noting the Cu concentration obtained in this study was still within the range of acceptable values, 32 μg/g ≤ set EcoSSL ≤ 251 μg/g, from which geometric mean of the set Eco-SSL was computed in [29]. The concentration of Cu in *R. mangle* L. showed that the plant have sufficiency of this constituent that it needs for oxidation, photosynthesis, as well as for protein and carbohydrate metabolism [29]. The studied *R. mangle* L. leaf was highest in iron (Fe) constituent, which indicates ability of the plant to absorb Fe that it needs for growth, chlorophyll formation as well as enzymes functioning for the mechanism of the plant's respiration (photosynthesis) [30]. Also, this high Fe concentration bare implication that the environment wherein the studied plant has grown was not toxic with heavy metals that could have made the *R. mangle* L. leaf for the study, to be Fe-deficient [11, 30].

Table 1 Results of AAS testing of inorganic constituents from *R. mangle* L. leaf

Inorganic Constituent	Concentration (μg/g)
Ni	6.682
Cd	6.2019
Cu	100.41
Pb	-
Cr	-
Fe	10,316.17

3.2 FT-IR Analyses of *R. mangle* L. Leaf-extract

Figure 1 shows the FT-IR spectra obtained from the *R. mangle* L. leaf-extract characterization. From the figure, O–H (free) stretching absorption of alcohol/phenol could be inferred at 3729.48 cm^{-1} with fingerprint vibrations of O–H in-plane bending at 1329.37 cm^{-1} and O–H out-of-plane bend at 707.91 cm^{-1} [14, 31]. Also, aromatic 1° amine overlap was suggested from the two peaks at 3729.48 cm^{-1} and 3401.57 cm^{-1}. This suggestion followed from the asymmetric and symmetric N–H stretching vibrations respectively at 3729.48 cm^{-1} and 3401.57 cm^{-1} with fingerprints of NH$_2$ scissoring at 1558.16 cm^{-1}, C–N stretching at 1149.39 cm^{-1} and 1059.19 cm^{-1} [31], and NH$_2$ out-of-plane wagging at 707.91 cm^{-1}. The absorptions at 2334.58 cm^{-1}, 1835.20 cm^{-1}, and at 1688.82 cm^{-1} respectively bare indications of –N=C=S stretching of isothiocyanate, C=O stretching of acyl halides and the carbonyl stretching of aryl ketones. The fingerprints of C–O–H bending at 1408.85 cm^{-1} and hydrogen-bonded O–H out-of-plane bending at 891.66 cm^{-1} support the assignment of the absorption at 1558.16 cm^{-1} to the C=O vibration of carboxylic acid salt (i.e. carboxylates) [31]. By the foregoing, only the absorption at 1485.85 cm^{-1} has not been assigned. This vibration actually suggests the C–H bend of methylene bridge ligand that potentially

finds usefulness as skeletal backbone vibration for many of the functional groups that had, thus, been identified [26, 31].
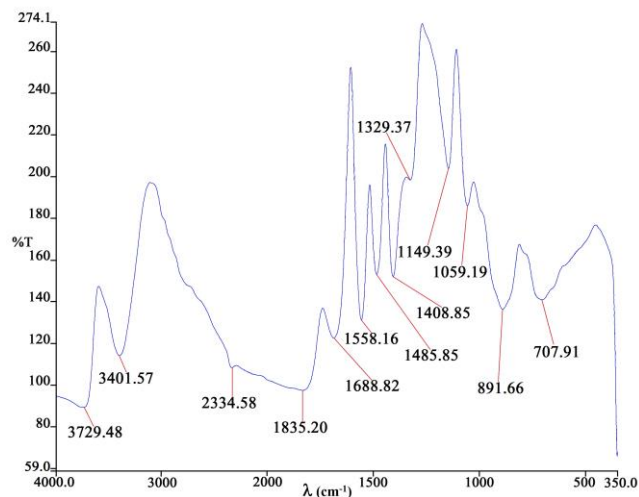

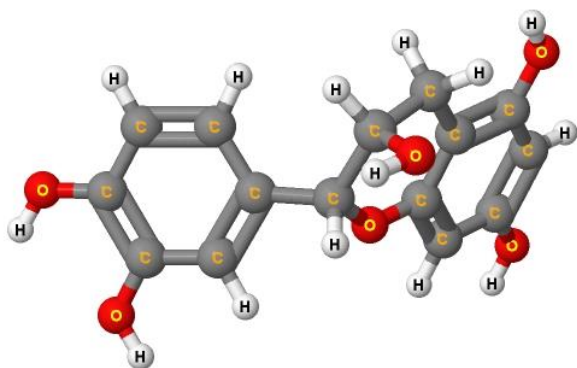**Figure 1** FT-IR spectra of *R. mangle* L. leaf-extract

These indications of absorbed ligands from the FTIR spectra of *R. mangle* L. find corroborations from suggested organic compounds by the Euclidean search hit-list of the Perkin-Elmer instrument, based on reference database of the Fluka library. These compounds are represented in their 3-D optimized structures in Figure 2.
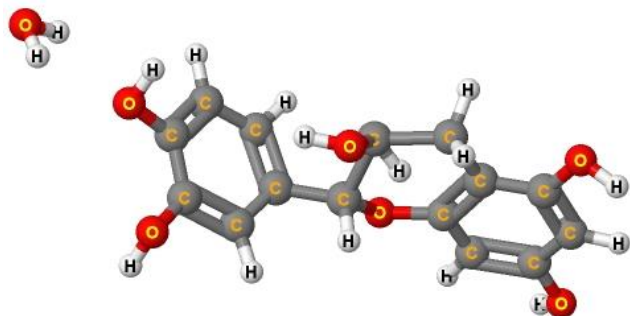

a.   (+–)-Catechin
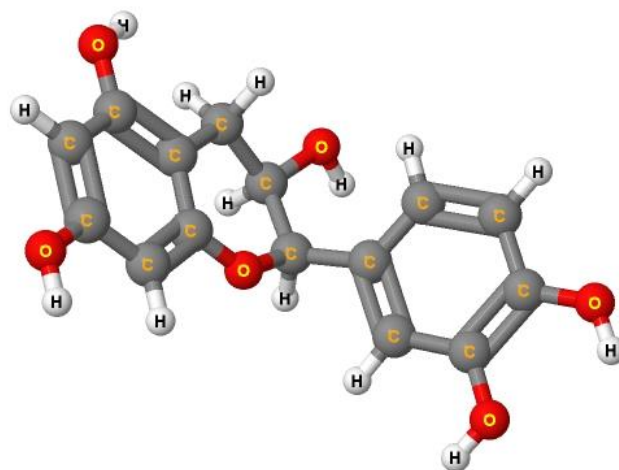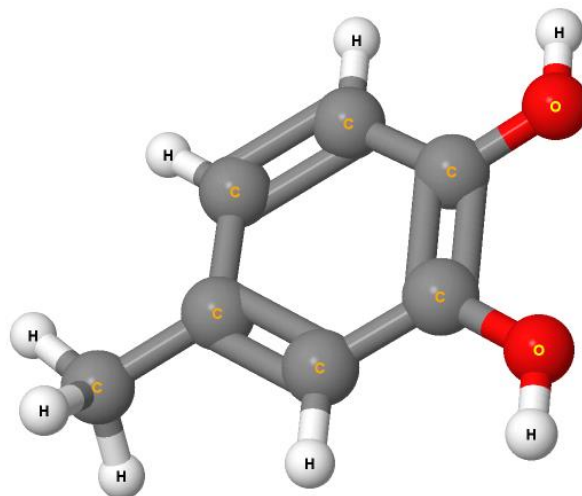

b.   (+)-Catechin hydrate

c.   (–)-Epicatechin
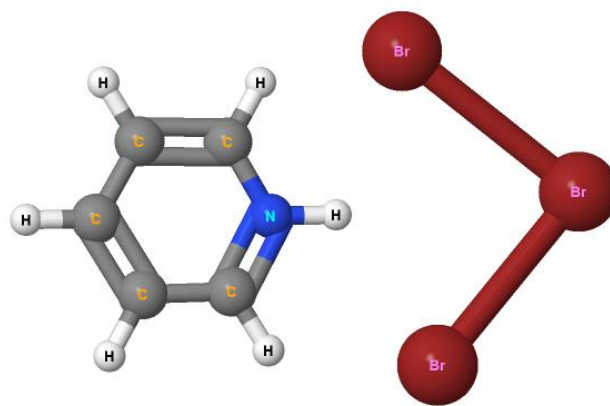
d.   Pyridine hydrobromide perbromide
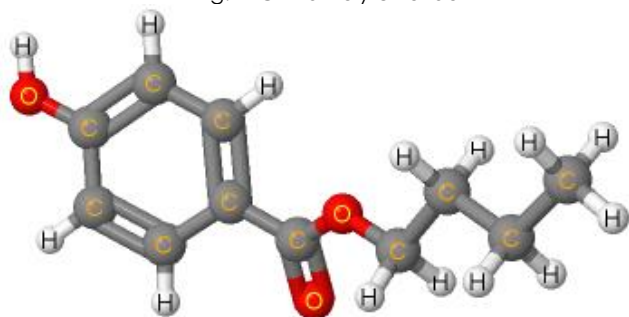

e.   4-methylcatechol
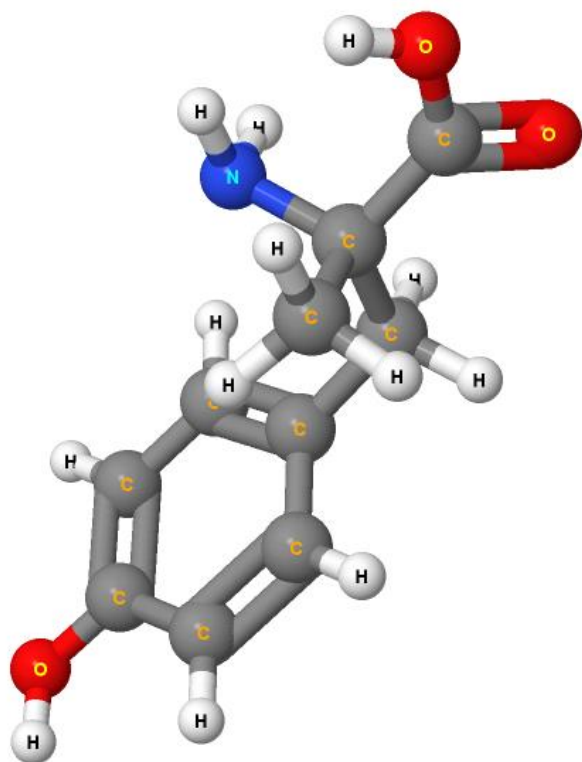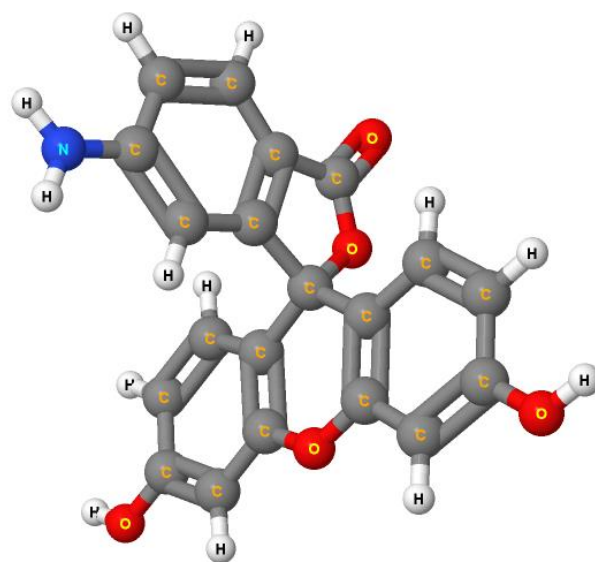
f.   Alpha-methyl-DL-tyrosine
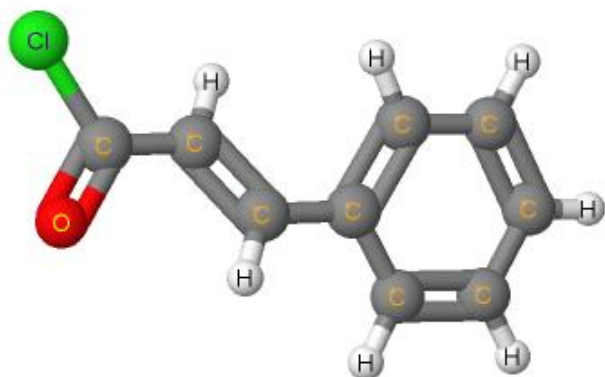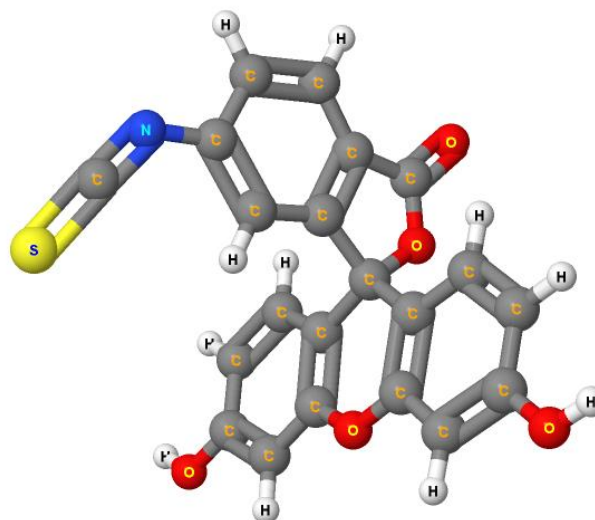

g.   Cinnamoly chloride

h.   Butyl 4-hydroxybenzoate

i.   5-Aminofluorescein

j.   Fluorescein isothiocyanate

Figure 2 Euclidean search hit-list compounds from FT-IR analyses of *R. mangle* L. leaf-extract

From the figure, it could be deduced that the *R. mangle* L. leaf-extract from this study is indicated as constituting the first four organic compounds listed in Figure 2 in similarity with the Euclidean search hit list constituents suggested for *Morinda lucida* leaf-extract that was reported in [11]. These organic compounds in Figure 2a to Figure 2d and the compounds identified in Figure 2f and Figure 2j are six compounds that were also suggested as being constituted in *Phyllanthus muellerianus* leaf-extract in the study reported in [5]. By these therefore, it could be inferred that *R. mangle* L. leaf-extract exhibited four and six organic compounds that are respectively different from compounds indicated for *Phyllanthus muellerianus* leaf-extract in [5] and from *Morinda lucida* leaf-extract in [11].

The compounds indicated for *R. mangle* L., in Figure 2, are constituted of 10 aromatic, an S– (sulphur), a Br– (bromide), a Cl– (chloride), 4 N– (nitrogen) and 9 O– (oxygen) containing hetero-atoms. All these hetero-atom compounds are abundant in ligands of non-bonded lone-pairs and π electrons that are known to exhibit ability to adsorb, through interactions between charged molecules, unshared electron pairs or π electrons in the ligands, with the iron (Fe) in reinforcing steel [32]. The coordinate link of electron transfer, from this affinity of the ligands with iron in steel-rebar, displaces water molecules from the metallic surface, and, by such prevention of a major corrosion instigating reaction mechanism, inhibits steel-rebar corrosion in aggressive environments [13, 32].

3.3 Phytochemical Characterization of *R. mangle* L. Leaf-extract

Presented in Table 2 are the results of phytochemical characterization of *R. mangle* L. leaf-extract. The table showed that *R. mangle* L. leaf-extract is constituted of six out of the eight phyto-constituents tested.

Table 2 Results of phytochemical characterization of *R. mangle* L. leaf-extract

Phytochemical	Status in leaf-extract[1]
Tannins	+
Phlobatannins	+
Alkaloids	+
Saponins	+
Flavonoids	−
Glycosides	+
Steroids	+
Terpenoids	−

[1] Present ≡ +; Absent ≡ −

The presence of tannins in *R. mangle* L. leaf-extract exhibited agreements with findings of this phytochemical constituent in other species of *Rhizophora* species (spp.) in reported works by other researchers [16, 17]. For specific instances, *Rhizophora apiculata* obtained from forests in Malaysia was found to contain tannins [16, 17], although the part of the plant employed in those studies was the bark, instead of the leaf of *R. mangle* L. in this present case. In spite of this, however, it is worth noting that tannins that were extracted from *Rhizophora apiculata* exhibited corrosion inhibition effectiveness on steel material in acidic chloride (dilute HCl) environment, in the study reported in [17]. In similar manner, the extracted tannins from *Rhizophora apiculata* in [16] mitigated rusted steel corrosion in 3.5% NaCl medium, the same environment employed for the steel-reinforcement corrosion testing in this study.

The phytochemical test-results in Table 2 also show that *R. mangle* L. leaf-extract is constituted of glycosides, which is a biologically-compatible (green) glycoside from the natural source unlike the synthesized form of glycoside in [25]. However, it is still worth noting that the synthesized glycoside in [25] effectively mitigated carbon steel corrosion in 3.5% NaCl medium, the same environment of test-immersion for steel-reinforced concrete in this study.

On a closer scrutiny of the FT-IR spectrum obtained from the synthesized glycoside in [25], it could be observed that the spectrum in that study exhibited some form of similarities in comparison with the FT-IR spectrum obtained from *R. mangle* L. leaf-extract in this study. Both of the spectra obtained from [25] and from Figure 1 in this study exhibited the C-H bend vibration of methylene bridge at 1484 cm^{-1} in [25] or at 1485.85 cm^{-1} in this study, as a central skeletal backbone of absorbed ligands. From this, the vibrations find patterns one towards the other although they were shifted leading to their being assigned to different ligands as per the dictates of FT-IR assignment rules. Thus the CH_2 stretching at 2948 cm^{-1} and 2890 cm^{-1} in [25] patterned after the 3729.48 cm^{-1} and 3401.57 cm^{-1}, in this study, which were suggested for aromatic amines. This is just as the C–C stretch at 1463 cm^{-1} in that report patterned after the C–O–H bending at 1408.85 cm^{-1} from the *R. mangle* L. FT-IR spectrum in this work. In addition, the C–O stretching at 1070–1140 cm^{-1} finds counterparts of C–N stretching at 1149.39 cm^{-1} and 1059.19 cm^{-1} from this study. These FT-IR pattern from the synthesized glycoside in [25] with that from *R. mangle* L. leaf-extract engender suggestions that the observed shifts in the vibration frequencies would, most probably, be due to the other ligands of biologically/naturally formulated constituents present in the leaf-extract material but that were not present in the synthesized glycoside.

Along with the patterning of FT-IR spectra, finding of anticorrosion effects was exhibited in [25] by the synthesized glycoside, a type of phyto-constituent that was also obtained in its biologically-formulated natural form from *R. mangle* L. leaf-extract in this study. These engender indications that *R. mangle* L. leaf-extract exhibit positive prospect of being suitable as a natural-green inhibitor of reinforcing steel corrosion in the saline/marine simulating-environment.

3.4 Steel-Reinforcement Total-corrosion Results and Analyses from *R. mangle* L. Leaf-extract Admixed Concrete

Figure 3 shows the results of total-corrosion effect investigation, from macrocell current modelling via equation (1), on the steel-reinforcements in duplicated concrete samples, admixed with different *R. mangle* L. leaf-extract concentrations, which were immersed in 3.5% NaCl medium as well as those in duplicated concrete samples that were immersed in distilled water.
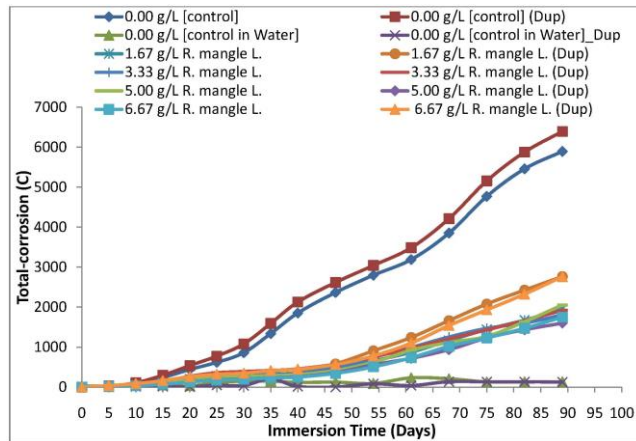
Figure 3 Plots of total corrosion test-results from steel-reinforced concrete samples having different concentrations of *R. mangle* L. leaf-extract (in duplicates) and which were immersed in 3.5% NaCl

The Figure 3 showed that total-corrosion estimations from the duplicates of NaCl-immersed 0.00 g/L control samples, i.e. without *R. mangle* L leaf-extract, portrayed higher rates of increments than the total-corrosion models from samples having the leaf-extract admixed in them. In comparison, the duplicate of 0.00 g/L [control in Water] samples consistently exhibited lower values of total-corrosion models compare to all the *R. mangle* L leaf-extract admixed and non-admixed samples that were immersed in the NaCl medium. Both the very high total-corrosion model from the normal control (0.00 g/L) in the NaCl and the very low total-corrosion model from the positive 0.00 g/L [control in Water] samples corroborate the fact that the NaCl test-environment employed constitutes a corrosive environment for the steel-rebar. This satisfies the precondition of severe condition of corrosion test-system identified as the preferred practice for efficient observation timing in laboratory corrosion tests [33, 34]. In addition to these, it could be deduced that the high total-corrosion models from the duplicate of NaCl-immersed 0.00 g/L control samples was being reduced in effect by the concentrations of *R. mangle* L. leaf-extract admixture in the other duplicates of NaCl-immersed steel-reinforced concrete samples. These reductions in total-corrosion models of the *R. mangle* L. leaf-extract admixed samples tend towards the lower values of total-corrosion obtained from the duplicate of 0.00 g/L [control in Water] samples that were immersed in non-corrosive (positive control) environment.

The plot of the variation of the modelled, post-experimental period, cumulative total-corrosion with the concentration of the *R. mangle* L. leaf-extract admixture in their duplicated samples of NaCl-immersed steel-reinforced concretes is shown in Figure 4. While this figure further shows how the admixture of *R. mangle* L. leaf-extract in the steel-

reinforced concrete samples culminated in cumulative total-corrosion reductions, it also indicates how the total-corrosion values obtained from samples with similar *R. mangle* L. admixture concentration exhibited agreements. Therefore, it could be observed from the figure that the duplicated samples admixed with 3.33 g/L *R. mangle* L. leaf-extract exhibited the best between-duplicate agreements (by exhibiting the lowest between-duplicate disparity), in the values of their cumulative total-corrosion models. The next set of samples following the 3.33 g/L in between-duplicate agreements of total-corrosion values includes the duplicate of 5.00 g/L *R. mangle* L. leaf-extract admixed samples. Careful observation of the plot in Figure 4 showed that the values of total-corrosion tend towards minimum at these 3.33 g/L and 5.00 g/L *R. mangle* L. leaf-extract concentrations that exhibited better between-duplicate total corrosion agreements than the other concentrations employed. These considerations engender interest on the mathematical analyses for the *R. mangle* L. leaf-extract concentration that could be employed in steel-reinforced concrete for obtaining the minimum total-corrosion, based on the experimental data from this study.
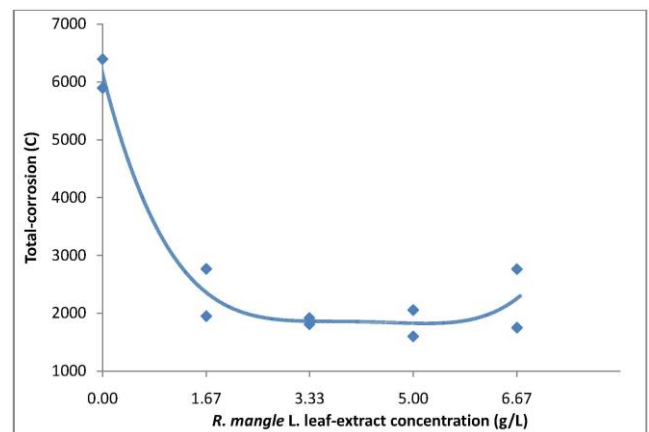

Figure 4 Plot of cumulative trend of total-corrosion with increasing *R. mangle* L. leaf-extract concentration in duplicated samples of 3.5% NaCl-immersed steel-reinforced concretes

On closer scrutiny, it could be noted that the curve in Figure 4 passes through the averaged points of the total-corrosion models for each set of the duplicates of steel-reinforced concrete samples. From this, the mathematical correlation between the total-corrosion, *Tc* (C), and the *R. mangle* L. leaf-extract concentration, ρ (g/L), could be expressed, in compact form, as

$$Tc = \sum_{\lambda=0}^{4} a_\lambda \rho^\lambda \qquad (2)$$

where a_λ {λ = 0, 1, …, 4} are non-dimensionless constants, which have the values and dimensional units that are presented in Table 3.

Table 3 Values and dimensional units of the coefficients a_λ in Equation (2)

λ	a_λ	Unit
0	6,144.4627	C
1	−4,243.3060	C/(g/L)
2	1,565.7031	C/(g/L)^2
3	−254.2192	C/(g/L)^3
4	15.2568	C/(g/L)^4

For this given correlation in Equation (2), the correlation coefficient, R = 98.06% and the Nash-Sutcliffe efficiency, NSE = 96.15%. These model fitting parameters indicate that the correlation fitting interprets to excellent model efficiency [5]. The analysis of variance for the given correlation fitting in Equation (2) is presented in Table 4 and this further shows that the p-value = 0.0010. By the p-value that is < 0.05, it could be deduced that the correlated relationship in Equation (2) between the dependent variable of total-corrosion, Tc (C), and the independent variable of *R. mangle* L. leaf-extract concentration, ρ (g/L), is statistically significant within 95% confidence interval.

Table 4 Analysis of variance for the correlation fitting expression in Equation (2)

Source of variations	df	SS	MS	F	p-value
Treatment	4	2.6900 × 10^7	6.7250 × 10^6	31.2288	**0.0010**
Residual	5	1.0767 × 10^6	2.1535 × 10^5		
Total	9	2.7977 × 10^7			

By denoting Equation (2) as $f(\rho)$, the truncation after the second term of the Taylor series expansion of the first derivative of $f(\rho)$ about a small increment, i.e. $f'(\rho + \Delta\rho)$, leads to the Newton-Raphson iteration formula [35], for the numerical solution of $f'(\rho)$ = 0, a minimum point of $f(\rho)$, that could be expressed as;

$$\rho_{k+1} = \rho_k - \frac{f'(\rho)}{f''(\rho)} \tag{3}$$

For this Newton-Raphson iterative procedure, ρ_0 = 4.1650 g/L, the average of 3.33 g/L and 5.00 g/L (i.e. *R. mangle* L. leaf-extract concentrations that exhibited better between-duplicate total-corrosion agreements than the others) was suggested as initial value. This gave the numerical solution of the equation $f'(\rho)$ = 0 as the value ρ = 5.2088 g/L, after the 23rd Newton-Raphson iterations.

This value ρ = 5.2088 g/L, the only real root of $f'(\rho)$ = 0 (for, by further mathematical investigation, the remaining two roots of $f'(\rho)$ = 0 are the complex conjugate 3.6441 ± j·0.2633), constitutes a stationary

point of minimum for $f(\rho)$, i.e. Equation (2). By this therefore, the value ρ = 5.2088 g/L is the analytical value of *R. mangle* L. leaf-extract concentration for the minimum total-corrosion that could be obtained from the NaCl-immersed steel-reinforced concrete. The substitution of this value into Equation (2) gives the minimum total-corrosion from the NaCl-immersed steel-reinforced concrete as $Tc_{(min)}$ = 1825.81 (C). This is a reduced total-corrosion in comparison to the experimental results from the duplicate of 0.00 g/L control samples in NaCl for which average Tc = 6144.46 ± 353.39 (C), as could be observed from Figure 4.

Moreover, it is worth noting that the minimum total-corrosion, $Tc_{(min)}$, obtained for the NaCl-immersed steel-reinforced concretes from the analytically estimated ρ = 5.2088 g/L., *R. mangle* L. leaf-extract concentration, still finds corroboration with experimental results from this study. This especially follows from the consideration that in the experimental results of cumulative total-corrosion plotted in Figure 4, increments of *R. mangle* L. leaf-extract concentration from 0.00 g/L to 5.00 g/L, by the incremental 1.67 g/L, have led to decreasing values of total-corrosion. In contrast to these, however, further increment of the *R. mangle* L. leaf-extract concentration from 5.00 g/L to 6.67 g/L rather culminated into increment of the total-corrosion from 1828.59 ± 321.65 (C) to 2257.90 ± 714.05 (C) in the experimental results. The analytical result therefore implies that the total-corrosion decreases first to $Tc_{(min)}$ = 1825.81 (C) for the slight increment of ρ from 5.00 g/L to 5.2088 g/L while further increment leads to the corresponding increase of the total-corrosion, thereafter.

It is therefore based on these analytical and experimental results, by which this study is establishing that *R. mangle* L. leaf exhibited positive prospect as a suitable natural-plant material for green/eco-friendly inhibition of steel-reinforcement corrosion in concrete immersed in the 3.5% NaCl medium. That this 3.5% NaCl medium are used in studies for simulating saline/marine environments leads to the implication from this study that extract from the *R. mangle* L. leaf will also be suitable as corrosion-inhibitor for steel-reinforcement embedded in concrete that had been designed for the saline/marine service-environment.

4.0 CONCLUSION

It was established from the biochemical characterization of *R. mangle* L. leaf in this study that this plant material is rich in inorganic/organic bio-constituents and ligands by which it could be suitable as a natural-green inhibitor of steel-reinforcement corrosion in corrosive environment. Further tests on total-corrosion effects in 3.5% NaCl-immersed steel-reinforced concretes that have different concentrations of *R. mangle* L. leaf-extract as

admixtures showed that the presence of the extract led to total-corrosion reduction of the steel-reinforcement in the admixed samples. The positive prospects from these results, which are corroborated by the experimental and analytical studies, support suitability of extract from *R. mangle* L. leaf as natural-plant material for green/ corrosion-inhibition of steel-reinforcement in concrete designed for saline/marine environment (simulated by the 3.5% NaCl in this work).

Acknowledgement

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