Anticorrosive Performance of *Mangifera indica* L. Leaf Extract-Based Hybrid Coating on Steel

Krishnapriya Karattu Veedu,†‡*, Thejus Peringattu Kalarikkal,†‡ Nithyaa Jayakumar,†‡ and Nishanth Karimbintherikkal Gopalan†,‡,‡‡

†Materials Science and Technology Division, CSIR-National Institute for Interdisciplinary Science and Technology (NIIST), Thiruvananthapuram 695019, India
‡Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

Supporting Information

ABSTRACT: Ecological awareness brought adequate innovations in the corrosion prevention technology in the last decade. Plant extracts are an interesting category among them, being the rich source of phytochemicals explored as corrosion inhibitors in various electrolytic media instead of toxic synthetic materials. Herein, the most ample tropical plant *Mangifera indica* L. leaf (MIL) extract was prepared, and its antioxidant ability has been utilized for corrosion prevention of commercial steel in 3.5 wt % NaCl environment. A rich source of polyphenol content provided excellent anticorrosive property. Corrosion prevention occurs by forming an insoluble organometallic complex between metal ions and functional groups in the antioxidants at the metal–electrolyte interface. A new simple strategy is adopted here to make bio-extract containing epoxy coating on steel. An MIL-precipitated amorphous silica hybrid is incorporated in epoxy coating. Electrochemical measurement demonstrated that the developed coating has a superlative corrosion inhibition efficiency of 99%. Thus, the present findings demonstrate a novel environmentally benign, efficient corrosion inhibitor for steel protection in saline media.

1. INTRODUCTION

In the last few decades, the concept of “Green” has immensely influenced all the areas of science and technology, where fascination for plant extracts as a metallic corrosion inhibitor has got significant attention. From 1960’s onward, a large number of synthetic organic compounds have been studied as anticorrosive materials in which heteroatoms such as C, N, O, and S were identified to be the prime reason for its corrosion inhibition ability. The selective adsorption of heteroatoms on the metal surface developed a metal–electrolyte interface barrier and prevented corrosion. However, most of these inhibitors were expensive, harmful to humankind, and nonbiodegradable. Therefore, more attention was given toward the development of naturally derived environmentally benign organic corrosion inhibitors. Apparently, every plant contains several active phytochemicals, and they are the ideal candidates to replace traditional toxic inhibitors. Reduced environmental hazards, easy availability, renewability, and simple extraction procedures made it the suitable one, and the intensity of works on different plant parts, such as seed, root, fruit, leaf, and so forth, on various metals in different electrolytic media reveals the significance of the go green policy in scientific endeavors. Literature reports suggest that plant extracts have excellent corrosion inhibition efficiency, especially leaf extract, because of the presence of the abundant source of phytochemicals compared to other parts. *Mangifera indica* L. is a major tropical fruit crop in India. It is reported that the methanol/ethanol extracts of various parts of mango are a rich source of bioactive compounds such as polyphenols, flavonoids, and xanthanones, among which antioxidant, anti-inflammatory, and allelopathic effects of polyphenols have been extensively studied. Rocha et al. observed the combined effect of mango and orange peel extracts for corrosion inhibition on carbon steel in the acidic medium over a concentration range of 200–600 ppm. They concluded that polar heterosides and hydroxyl groups are the leading cause of inhibition property. Even though the presence of oxidation-retarding components can enhance the anticorrosive property of mango leaf extracts, not much emphasis was given to it in the area of corrosion science. Apart from *Mangifera indica* L. leaf (MIL) extract, a lot of other plant extracts have been employed. However, an efficient anti-corrosive coat out of it is still limited. Zinc—*Cichorium intybus* leaf extract hybrid coat, *Gracilaria edulis* extract in epoxy coating, silane-treated *Mentha longifolia* coat, and soya alkyd nanocomposite coats are some of the examples.

Received: March 7, 2019
Accepted: May 29, 2019
Published: June 12, 2019
inhibition on commercial steel (CS) in a marine environment and its application in coatings.

In this work, the ethanolic extract of the MIL has been prepared and tested for anticorrosion efficiency at different concentrations. Further, the corrosion resistance and inhibition mechanism have been proved from electrochemical studies and X-ray photoelectron spectroscopy (XPS) analysis, respectively. The inhibition efficiency of the MIL extract encouraged its application in epoxy coatings, which was further achieved by developing an organic–inorganic hybrid. An excellent efficiency of 99% for the respective coating established the MIL extract as a worthy, environmentally benign, and anticorrosive material for steel in marine applications.

2. RESULTS AND DISCUSSION

2.1. Characterization of the MIL Extract. The Fourier transform infrared (FTIR) spectrum of the ethanolic MIL extract is shown in Figure 1a. The broad band present at 3334 cm\(^{-1}\) is attributed to typical –OH stretching vibrations of phenolic compounds and alcohols. Further, the peak at 1031 cm\(^{-1}\) was assigned to carboxylic acid carbonyl (C=O) groups in phenolic compounds. Hence, it can be inferred that the MIL extract must be a rich source of phenolic compounds. Moreover, aliphatic –CH stretching, C–C stretching vibrations, and –CH bending vibrations were also observed at 2936, 1612, and 1450–1317 cm\(^{-1}\), respectively.\(^{25}\)

In order to identify the major compound present in the MIL extract, high-performance liquid chromatography (HPLC) has been conducted, and the respective chromatogram is displayed in Figure 1b. A total of 16 peaks have been observed in the chromatogram, among which 8 major peaks have been identified by comparing the retention time of the 10 mg/mL—99% ethanolic MIL extract (Table S1, Supporting Information) with that of the standards shown in Figure S1 (Supporting Information). Chlorogenic acid (3), syringic acid (4), p-coumaric acid (5), ferulic acid (6), ellagic acid (7), and cinnamic acid (8) with retention times 23.8, 25.5, 28.17, 28.78, 31.7, and 32.66 min, respectively, were identified, though some of the peaks remained unknown because of a lack of standards. Apart from that, the literature reports speculate that peaks 1 and 2 correspond to gallic acid and epigalochatechin with retention times 4.4 and 14.89 min, respectively.\(^{18,26}\) In support of the FTIR results, the HPLC profile reveals that the MIL extract contains polyphenol as the affluent source.

2.2. Characterization of MIL–Precipitated Amorphous Silica Hybrid. Scanning electron microscopy (SEM) images of precipitated amorphous silica (PAS) and MIL–PAS hybrid are shown in Figure 2a,b. The micrograph displayed a...
groups as well as the removal of structural water molecules. The corrosion inhibition efficiency was represented as obtained by extrapolating the Tafel plot, where the anodic and cathodic slopes were compared to the corresponding to corrosion has a direct relation with current density ($I_{corr}$) given by the equation:

$$I_{corr} = \frac{Q_{corr}}{A}$$

where $Q_{corr}$ is the charge passed in the corrosion process, $A$ is the area of the electrode, and $t$ is the time. The corrosion rate is inversely proportional to the corrosion efficiency ($\eta$):$E_{corr}$.

The efficiency of the MIL extract on PAS was determined and is displayed in Figure S2 (Supporting Information). Carbon and nitrogen contents illustrated the presence of C, N, O, and Si in the MIL organic compounds present in the MIL extract in which higher concentration of C on Si ensured the complete covering of the MIL extract on PAS. Subsequently, energy-dispersive X-ray spectroscopy (EDS) analysis shown in Figure 2c conformed the successful formation of the MIL–PAS hybrid.

Two-step weight loss has been observed in the case of the MIL extract with total 72% decomposition. Evaporation of bound water between 50 and 150 °C followed the volatilization of phytochemicals in the plant extract at 160–800 °C. Two-step weight loss has been observed in the case of the MIL extract with total 72% decomposition. Therefore, it can be summarized that the optimum concentration of the MIL extract on CS was found to be 200 ppm for better corrosion prevention in the saline environment.

Electrochemical impedance spectroscopy is a nondestructive tool to study the anticorrosive performance of materials on a metallic surface. The measured impedance data were plotted as the Nyquist plot; Figure 3b exhibits the corrosion performance of the bare coupon was $R_{ct}$, as shown in the Figure 3b inset, in which $R_{ct}$ is the charge-transfer resistance existing between the working electrode–electrolyte interface, and $Q_{dl}$ represents the constant phase element results from the double-layer capacitance of the nonideal rough metal surface. Inhibition efficiency of each concentration of the MIL extract ($\eta$) was calculated using the equation:

$$\eta \% = \frac{I_{corr(CS)} - I_{corr(MIL)}}{I_{corr(CS)}}$$

where $I_{corr(CS)}$ and $I_{corr(MIL)}$ are the current densities in the absence and presence of an inhibitor, respectively. The impact of the MIL extract has significantly reflected in corrosion current density as well as in corrosion potential. The addition of very low concentration (100 ppm) extract itself brought a noticeable corrosion inhibition on CS, viz, decrease in $E_{corr}$ from 10.9 to 7.9 μA/cm² and increase in $E_{corr}$ from −1.04 to −0.96 V. Subsequently, the $R_{ct}$ value of the bare coupon was increased from 3481 to 4288 Ω cm². In order to study the effect of concentration on inhibition efficiency, further experiments were continued with 200 and 300 ppm extracts. Subsequently, a drastic increase in $E_{corr}$ and $R_{ct}$ to $-0.84$ V and $14,619$ Ω cm², respectively, and a decrease in $I_{corr}$ to 2.3 μA/cm² were observed for 200 ppm concentration with 78% inhibition efficiency. Surprisingly, the inhibition efficiency trend was dropped at 300 ppm concentration, further restricting the use of higher concentration of the MIL extract. Hence, it can be summarized that the optimum concentration of the MIL extract on CS was found to be 200 ppm for better corrosion prevention in the saline environment.

2.3. Anticorrosive Performance of the MIL Extract. Potentiodynamic polarization measurements were performed to calculate kinetic parameters of the corrosion inhibition process on CS specimens as a function of various concentrations of the MIL extract in 3.5 wt % NaCl. The Tafel plot of bare CS, 100, 200, and 300 ppm MIL extract is shown in Figure 3a. Weight loss of metal coupons corresponding to corrosion has a direct relation with current density ($I_{corr}$) and an inverse relation with corrosion potential ($E_{corr}$) given by the equation:

$$I_{corr} = \frac{Q_{corr}}{A}$$

where $Q_{corr}$ is the charge passed in the corrosion process, $A$ is the area of the electrode, and $t$ is the time. The corrosion inhibition efficiency ($\eta$) was calculated as follows:

$$\eta \% = \frac{I_{corr(CS)} - I_{corr(MIL)}}{I_{corr(CS)}}$$

The efficiency of the MIL extract on PAS was determined and is displayed in Figure S2 (Supporting Information). Carbon and nitrogen contents illustrated the presence of C, N, O, and Si in the MIL–PAS hybrid and corresponding wt % has been tabulated (Table S2, Supporting Information).

Table 1. Data from Electrochemical Analysis of the MIL Extract

| Sample       | $I_{corr}$ (μA cm⁻²) | $E_{corr}$ (V) | $b_1$ (V dec⁻¹) | $b_2$ (V dec⁻¹) | $R_p$ (Ω cm²) | η (%) | $R_{ct}$ (Ω cm²) | $Q_{dl}$ (μF cm⁻²) | η (%) |
|--------------|----------------------|----------------|-----------------|-----------------|---------------|------|-----------------|-------------------|------|
| Bare CS      | 9.10                 | −1.04          | 0.26            | 0.18            | 3481          | 640  | 1573            | 624               | 43   |
| +100 ppm     | 7.91                 | −0.96          | 0.46            | 0.09            | 4288          | 27   | 1573            | 624               | 43   |
| +200 ppm     | 2.38                 | −0.84          | 1.05            | 0.23            | 14,619        | 78   | 4280            | 640               | 79   |
| +300 ppm     | 7.38                 | −0.89          | 0.30            | 0.15            | 5783          | 32   | 2629            | 800               | 66   |

Figure 3. (a) Potentiodynamic polarization curves and (b) Nyquist diagrams of bare CS, 100, 200, and 300 ppm MIL extract in 3.5 wt % NaCl.
where \( R_{ct(MIL)} \) represents the charge-transfer resistance of various concentrations of the MIL extract and \( R_{ct(CS)} \) denotes the charge-transfer resistance of the bare metal.

Fitted electrochemical data are summarized in Table 1. All the curves obtained from the complex plot show the same behavior evident from its similar semicircular plot, but different in area, which was evaluated as the variation in charge-transfer resistance from a higher to a lower frequency. CS specimens were efficiently protected from corrosion in the NaCl environment by the addition of the MIL extract, in which 200 ppm concentration exhibited a maximum efficiency of 79% with a higher \( R_{ct} \) 4280 \( \Omega \) cm\(^2\) and lower \( Q_{dl} \) 640 \( \mu F \) cm\(^{-2}\). The high efficiency of the particular concentration was proposed to be the formation of a barrier between the metallic surface and corrosive media. Consequently, this should provide a better corrosion resistance at higher concentration; unfortunately, the expected trend was found to reverse in experiments. Impedance data were in good agreement with potentiodynamic polarization measurements and their unusual behavior was further investigated by means of XPS surface analysis.

### 2.4. XPS Surface Analysis of the CS Specimen

XPS was used to identify the surface chemical composition of the CS specimen and investigate the corrosion inhibition mechanism involved during the addition of the MIL extract. According to the results obtained from electrochemical tests, bare CS coupon, 200 ppm MIL extract-adsorbed coupon having maximum inhibition capacity, and 300 ppm MIL extract-adsorbed coupon were selected. The same experimental setup as that of electrochemical tests was adopted, and coupons were vacuum-dried overnight before the analysis.

Constituent elements having various chemical environments and oxidation states were examined via XPS curve fitting employing CasaXPS software. The survey spectrum (Figure S3, Supporting Information) shows that Fe, O, and C are the major components present in all samples. It is interesting to note that the peak intensity corresponding to Fe and O varies in the order CS < 300 ppm < 200 ppm, which indicates the reduction of the corrosion product in tandem.

Similarly, because of organic molecules present in the MIL extract, a sharp peak was observed for C in the extract-adsorbed coupons compared to bare coupons. Carbon correction was performed for each high-resolution spectrum. Impedance data were in good agreement with potentiodynamic polarization measurements and their unusual behavior was further investigated by means of XPS surface analysis.
The curve fitting of O 1s spectra of three investigated samples are shown in Figure 4a,c,e. Three major peaks were deconvoluted at binding energies 529.8 ± 0.3 eV (blue), 531.4 ± 0.2 (red), and 532.3 ± 0.3 eV (green) attributed to Fe₂O₃/Fe₃O₄, Fe(OH)₂/Fe(OH)₃/FeO(OH), and adsorbed water in the oxide layer (Fe₂O₃·nH₂O) related to nonuniform porosity, respectively. Figure 4b,d,f displays Fe 2p spectra in which two major peaks have been identified in all samples at binding energies 710−711(blue) and 713 ± 0.3 eV (green) which represent Fe₂O₃/Fe₃O₄ and peak asymmetry arising from the Fe-oxide band envelope, respectively. Moreover, in spectrum shown in Figure 4d, an additional intense peak was detected at 711.3 ± 0.3 eV (red) corresponding to FeO(OH) species. The spectral peak area data are tabulated in Table 2 (total peak area = 100%).

Curve fitting of O 1s and Fe 2p spectra of bare CS coupons in 3.5 wt % NaCl reveals the presence of typical corrosion products such as unstable magnetite (Fe₃O₄) and stable hematite (Fe₂O₃), which suggest the conventional corrosion process. Because of the presence of the MIL extract, a decrease in iron oxide concentration has been noticed along with the formation of hydroxides and oxy-hydroxides. The Fe 2p spectra of the 200 ppm adsorbed metal establish the formation of a specific stable oxy-hydroxide species FeO(OH) which contribute toward the corrosion resistance. The results show that there must be a protective mechanism that occurred at an optimum concentration of the MIL extract involving FeO-(OH) between electrolytes and metal; later, its absence collapses the anticorrosive mechanism and leads to a fall in resistance.

3. CORROSION INHIBITION MECHANISM

The major component of the MIL extract was found out from the FTIR and HPLC techniques to be polyphenols, which possess hydroxyl and carbonyl functional groups, having antioxidant property. Interaction of such structurally complex molecules on the metal surface was difficult to trace out; however, with the aid of XPS surface analysis, a possible inhibition mechanism was suggested.

The traditional corrosion process in the marine environment is shown in Figure 5a and the mechanism was described as follows (eqs 3a−3d)³

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+/3+} + 2e^-/3e^- \text{ (anode)} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \text{ (cathode)} \\
\text{Fe}^{2+/3+} + 2\text{Cl}^-/3\text{Cl}^- & \rightarrow \text{FeCl}_2/\text{FeCl}_3 \\
\text{FeCl}_2/\text{FeCl}_3 + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2/\text{Fe(OH)}_3 + 2\text{HCl}/3\text{HCl} \text{ (unstable)}
\end{align*}
\]

The soluble byproduct HCl in the media initiates pitting corrosion, and at the same time, unstable iron hydroxides begin to form an amorphous oxy-hydroxide (FeO(OH)) layer. Initially, this layer separates the electrolyte and metal surface, behaving as a diffusion barrier, even though the chloride attack further ruptures this layer by replacing hydroxyl/water molecules from FeO(OH) and form a soluble Fe−Cl intermediate. It will restart metal dissolution and end up accumulating rust (eq 3e). The high peak area concentration in XPS for Fe₃O₄ and Fe₂O₃ in bare CS strongly supports this mechanism (Figure 4a,b).

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+/3+} + 2e^-/3e^- \text{ (anode)} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \text{ (cathode)} \\
\text{Fe}^{2+/3+} + 2\text{Cl}^-/3\text{Cl}^- & \rightarrow \text{FeCl}_2/\text{FeCl}_3 \\
\text{FeCl}_2/\text{FeCl}_3 + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2/\text{Fe(OH)}_3 + 2\text{HCl}/3\text{HCl} \text{ (unstable)}
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\text{FeCl}_2/\text{FeCl}_3 + 2\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_2/\text{Fe(OH)}_3 + 2\text{HCl}/3\text{HCl} \text{ (unstable)}
\end{align*}
\]

The incorporation of the 200 ppm MIL extract reflected from XPS as reduced peak area percentage for iron oxides and appearance of the oxy-hydroxide peak are shown in Figure 4c,d. It points out that unlike bare CS, the iron oxy-hydroxide species somehow remains stable and protects the metal surface. It leads to the belief that the FeO(OH) passive layer interaction with Cl⁻ and formation of the soluble compound
has been restricted while the addition of the MIL extract. It could be because the functional groups −OH and C=O present in the polyphenols of the MIL extract overtake Cl−, forming an insoluble stable organometallic complex (eq 3),14,38−41 as shown in Figure Sb.

Fe−OHads → FeO(OH)ads → Fe−MILads + H2O (3)

It will stabilize the passive layer by further restricting the chloride attack, eventually resisting corrosion observed in the electrochemical analysis. Later, the declining trend in anticorrosion efficiency observed in electrochemical measurements at higher concentration questioned the stability of the Fe−organometallic complex. Consequent extenuation of the FeO(OH) peak in the Fe 2p spectrum established the possibility of the formation of the soluble organometallic complex rather than insoluble complex.14 Hence, the mechanism substantiated that the MIL extract performed as an efficient green corrosion inhibitor for CS at an optimum concentration of 200 ppm.

4. APPLICATION STUDIES

Anticorrosive performance of the MIL extract in epoxy coatings has been studied. In order to overcome the MIL-extract epoxy compatibility issue, PAS has been utilized as a supportive substrate and an organic—inorganic MIL−PAS hybrid has been prepared. Further, coatings were developed by incorporating the MIL−PAS hybrid in the epoxy-polyamide system. Thickness of the coat was measured using a profilometer to be 14.9 μm, as shown in Figure S4 (Supporting Information). The electrochemical experiment was conducted in 3.5 wt % NaCl via potentiodynamic polarization and EIS measurements by maintaining the same conditions used above as shown in Figure 6, and the corresponding equivalent circuit is given in Figure SS (Supporting Information).

PAS is a well-recognized anticorrosive inorganic material, which shows very high corrosion resistance when compared to bare epoxy.42−44 Incorporation of the MIL extract raised the anticorrosion performance of PAS coating, where at 5 wt % MIL, the epoxy coat showed a 1 order increase in Rct with a drastic positive shift in Ecorr and 99.15% inhibition efficiency. The subsequent increment in MIL concentration was found to bring down the efficiency (Figure S6, Supporting Information), possibly because of coat saturation,23 even though it exhibited better resistance than bare PAS demonstrating the capability of the particular extract. Experimental results are summarized in Table 3 to evaluate that very low concentration of the natural organic extract has exquisitely modified the corrosion performance of chemically synthesized inorganic PAS. Comparing recent studies on Zn−CILL hybrid coat and silane-treated Mentha longifolia, the MIL−PAS hybrid coat shows an exceptional enhancement (1000 times) in corrosion resistance.21,23 It substantiates that metal coating based on the environmentally benign MIL extract is an excellent candidate for the protection of steel in the marine environment.

5. CONCLUSIONS

The MIL ethanolic extract was prepared in which the major organic constituent was identified to be polyphenols. The corrosion resistivity of the material has been established from the potentiodynamic polarization and electrochemical impedance spectroscopy. The maximum efficiency of 78−79% was obtained at 200 ppm concentration. XPS surface analysis confirmed the formation of iron oxy-hydroxy (FeO(OH)) species, which developed the hypothesis on an Fe−polyphenol insoluble organometallic compound responsible for the anticorrosive property. Further dip in inhibition efficiency at 300 ppm determined the existence of a soluble organometallic complex. Application of the extract in epoxy coatings has been achieved through the MIL−PAS hybrid, where a maximum efficiency of 99% was observed for 5 wt % extract loading. The MIL−PAS hybrid simultaneously increased the anticorrosive performance of PAS and synergistically developed an exceptional environmentally benign epoxy-based anticorrosive coating over steel in the marine environment. Moreover, the present hybrid coat exhibited a superior anticorrosive performance than that of the existing natural organic−inorganic hybrid coatings.
6. EXPERIMENTAL SECTION

6.1. Materials and Sample Preparation. MIL was washed, dried in an air oven at 100 °C, and ground to a powder form. About 20 g of the powdered sample was soaked in 99% ethanol in a 200 mL volumetric flask and left to stand for 48 h at room temperature. A soaked sample was filtered and excess solvent was removed by the rotary evaporator. The dried residue was stored in a vacuum desiccator. Experiments were performed using CS specimens having chemical composition (wt %) C = 0.24; Mn = 0.92; Al = 0.03; Si = 0.14; Cr = 0.04; V = 0.10; P = 0.08; Cu = 0.06; and remaining Fe. Coupins were cut into a rectangular shape with 4 × 3 × 0.2 cm dimension and mechanically abraded with emery paper grade 220–1000. Before each experiment, metal specimens were degreased with acetone, dried, and kept in a vacuum desiccator. NaCl (3.5 wt %, analytical grade) was prepared using distilled water (pH = 6.8) to mimic the corrosive attack in the marine environment. MIL extract was characterized by XPS analysis. The author K.K.V. also acknowledges CSIR, Financial support from Science and Engineering Research Board (SERB), DST, Government of India, through Physical chemistry (EEQ/2016/000342). We thank Dr. P. Nisha and Dr. Saaju Pillai (CSIR-NIIST, Thiruvananthapuram) for HPLC and XPS analysis. The author K.K.V. also acknowledges CSIR, New Delhi for the award of Junior Research Fellowship.

6.2. Characterization. The MIL extract was characterized by HPLC on a prominence UFLC system containing an LC-20AD system controller and Bruker Alfa-E FTIR. Surface analyses of the MIL extract-adsorbed mild steel specimens were carried out using XPS. Data analysis and curve fitting were performed with CasaXPS software. The photoelectron peak identification was achieved from literature data. Morphological analysis of PAS and MIL−PAS hybrid was performed using the SEM JEOL JSM-5600 model. EDS was conducted to detect the elements present in the hybrid sample using a silicon drift detector X-MaxN attached with a Carl Zeiss EVO SEM apparatus. Epoxy coating thickness was measured with a Profilometer. Variation in weight loss of MIL extract powder, PAS, and MIL−PAS hybrid was confirmed from the thermogravimetry which was carried out in the temperature range 30−1000 °C using the Hitachi STA7300 TG-DTA instrument in the nitrogen atmosphere at a heating rate of 5 °C/min.

6.3. Electrochemical Measurements. Electrochemical experiments were performed in a PC-controlled multichannel potentiostat/galvanostat (Autolab) having a three-electrode cell using saturated calomel, graphite, and CS coupon as reference, counter, and the working electrodes, respectively. A working electrode with a surface area of 1.2 cm² was immersed in electrolyte 3.5 wt % NaCl solution. Open-circuit potential was stabilized for 20 min. Electrochemical impedance spectroscopy was conducted in the frequency range of 10² to 0.01 Hz and with an ac signal of 5 mV amplitude. Potentiodynamic polarization curves were obtained at a scan rate of 0.001 mV/S in the polarization range of ±250 mV with respect to the open circuit potential. EIS spectra and potentiodynamic polarization curves were analyzed by Nova 2.1 software. Experiments have been performed with bare CS specimen in the presence of different ppm concentrations of the MIL extract and with various concentrations of MIL−PAS hybrid-coated specimens in the electrolyte. The experiments were repeated thrice for each concentration.

ASSOCIATED CONTENT

6 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00632.

HPLC chromatogram of standards, thermal analysis of PAS, MIL, and MIL−PAS hybrid, XPS survey spectrum of bare CS specimen, 200 and 300 ppm MIL-adsorbed CS in 3.5 wt % NaCl, profilometry thickness measurement, electrochemical equivalent circuit for MIL−PAS hybrid epoxy coat, electrochemical graphs of MIL−PAS-7.5, and tables of HPLC chromatogram—peak identification and EDS data of the MIL−PAS hybrid (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: nishanthkg@niist.res.in. Phone: +91471 2515508. Fax: +91471 2491712.

ORCID

Krishnapriya Karattu Veedu: 0000-0002-7417-1502
Nithyaa Jayakumar: 0000-0002-6161-196X
Nishanth Karimbintherikkal Gopalan: 0000-0001-7293-5946

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from Science and Engineering Research Board (SERB), DST, Government of India, through Physical chemistry (EEQ/2016/000342). We thank Dr. P. Nisha and Dr. Saaju Pillai (CSIR-NIIST, Thiruvananthapuram) for HPLC and XPS analysis. The author K.K.V. also acknowledges CSIR, New Delhi for the award of Junior Research Fellowship.

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