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An Eco-friendly *Mangifera indica* Leaves Extract Corrosion Inhibitor for Stainless Steel in Acidic Medium

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ABSTRACT

Corrosion of metals and alloys is one of the most frequent problems encountered in chemical and process industries. Inefficient corrosion control measures typically lead to an increased risk of unplanned downtime, huge economic loss, environmental damage, and health and safety hazards. Hence, it is essential to develop environment-friendly and cost-effective corrosion inhibitors over existing toxic anticorrosive agents. The main objective of this work is to examine the efficacy of eco-friendly ethanolic extract of *Mangifera indica* leaves (MIL) in different concentrations as a green corrosion inhibitor for stainless steel (SS-316L) under an acidic environment. The inhibition efficiency of *Mangifera indica* leaves extract in 1 M hydrochloric acid (HCl) was evaluated by conventional weight loss method along with adsorption isotherm analysis. Chemical compounds present in leaf extract and changes in surface morphology of SS-316L samples were assessed using Fourier Transform Infrared spectroscopy (FTIR) and Field Emission Scanning Electron Microscopy (FE-SEM) provided with elemental analysis. The results of the weight loss method revealed that the inhibition efficiency increases with increasing MIL extract concentration due to higher surface coverage. The highest inhibition efficiency of almost 63.43% in 14 days and minimum corrosion rate of 0.433 mm per year was obtained for SS-316 L in 1.0 M HCl with 1000 ppm concentration. The adsorption of MIL extract on SS-316L surface followed Freundlich adsorption isotherm, and the obtained value of free Energy of adsorption (ΔG°_{ads} = – 9.20 kJ.mol^{-1}) indicates the physical adsorption mechanism. The developed regression-based models can predict the corrosion rate as a function of inhibitor concentration and exposure time with good accuracy (>80%). Thus, the present findings demonstrate that *Mangifera indica* L. leaves extract can suitably be applied as an inexpensive, non-toxic, biodegradable, efficient green corrosion inhibitor for the protection of stainless steel in acidic media.

INTRODUCTION

Corrosion of metals and alloys is the primary concern in chemical and process industries, and mitigating it necessitates a tremendous amount of capital. The serious consequences of corrosion are irreparable damage to equipment, sudden failures leading to fire and explosion, and the release of toxic products that are harmful to the environment and also to human health. It can cause disruptions in operations, such as plant shutdowns and even loss of production, resulting in severe economic losses (Loto et al. 2020). According to the National Association of Corrosion Engineers (NACE International) IMPACT Report 2016, the global corrosion cost was estimated at $ 2.5 trillion (USD) per year, which is equivalent to 3.5% of the 2020 world Gross Domestic Product (GDP). In India, it costs 4.2% of the country's GDP and thus necessitates the appropriate measures for the prevention and control of corrosion (Impact Report 2016).

Stainless steel is one of the most widely used metal alloys in chemical process industries, oil and gas industries, construction industries, and many more due to their unique properties such as excellent corrosion resistance, high strength and toughness, durability, attractive appearance, recyclability and cost-effectiveness as compared to other metals (Aslam et al. 2022). SS-316L is among the most commonly used grades of the stainless-steel family of the 300 series. It is an iron-based alloy with 16 to 18% chromium content and other alloying elements. The addition of chromium imparts excellent corrosion resistance to SS-316 against many aggressive solutions via the formation of a thin passive film of chromium oxide covering the surface in the presence of an oxidizing environment. This film acts as a barrier that prevents the diffusion of corrosive ions into the metal surface, thus protecting it from corrosion attacks. However, stainless steel is unable to resist corrosion attack by an aggressive acid environment, namely hydrochloric acid, as

it breaks down the chromium oxide layer covering the surface, followed by localized corrosion (Simescu-Lazar et al. 2023). Hydrochloric acid (HCl) is widely used in various industrial processes such as acid pickling of steel and iron, chemical cleaning, descaling as well and oil well acidification and, thus, results in serious corrosion issues due to deterioration of passive film (Shamsheera et al. 2022, Oguike 2014).

Various methods such as cathodic protection, galvanizing, and the use of protective coatings and paints have been used in industries for corrosion control of metal surfaces for a long time (Veedu et al. 2019, Buchheit 2018). However, the usage of organic and inorganic inhibitors is considered one of the practical approaches to minimize corrosion (Aslam et al. 2022, Umoren et al. 2016). The corrosion inhibitor is a chemical substance which, in addition to even small amounts to the corrosive solution, decreases the rate of corrosion (Zhou et al. 2023). Some synthetic organic inhibitors are 1, 3-azole, pyridines, and fatty amides, whereas phosphates and chromates belong to inorganic inhibitors that have been used as efficient corrosion inhibitors (Salleh et al. 2021). These inhibitors resist the corrosion effectively because of the presence of heteroatoms such as C, N, O, or S (electronegative groups) and pi-electrons in their structures that facilitate their physical or chemical adsorption over the metal surface (having empty *d* orbitals), thereby isolating the surface from corrhibitor.

In past few years, various green inhibitors from plant origins, such as Pomegranate leaves, Marigold flowers, Neem leaves, Hibiscus leaves, Jackfruit pectin, etc. have been investigated by many researchers for metal and metal alloy corrosion against acidic medium (Shamsheera et al. 2022, Gaidhani et al. 2020, Abboud et al. 2016, Mourya et al. 2014, Sharma et al. 2009). Very recently, Pal & Das (2023) investigated the corrosion inhibition activity of extract from kitchen waste of onion peel against aggressive hydrochloric acid and sulfuric acid media for boiler-quality Stainless Steel. Their research revealed good inhibition efficiency of onion peel extract in both the acidic media (Pal & Das 2023). These literature reports demonstrated that plant extracts are rich sources of organic constituents with heteroatoms such as nitrogen, oxygen, and sulfur, which are responsible for their excellent corrosion-resistive activity. These compounds can be extracted from leaves, stems, or fruit peels using simple aqueous or ethanolic extraction processes, which are not only cost-effective but environmentally benign as well.

Limited literature is available on the evaluation of *Mangifera indica* leaf extract as a corrosion inhibitor on stainless steel (SS-316L) surface in HCl solution (Veedu et al. 2019, da Rocha et al. 2010). Veedu et al. (2019) have utilized extracts of mango leaf extract as corrosion inhibitors for commercial steel in marine environments. In contrast, another work used aqueous extracts of orange, mango, passion fruit, and cashew peel against corrosion of carbon steel in an HCl medium (da Rocha et al. 2010).

Mangifera indica (also known as mango) is a tropical fruit crop that belongs to the Anacardiaceae family. India ranks first in area and production of mangoes in the world, and most importantly, it is abundantly available throughout the whole year in India. Extracts obtained from different parts of the mango tree are rich in phytochemicals such as mangiferin, phenolic acids, benzophenones, flavonoids, ascorbic acid, terpenoids, carotenoid, etc., and thus possess anti-cancer, anti-inflammatory, anti-diabetic, anti-oxidant and anti-microbial activity (Mirza et al. 2021). In spite of the great potential of mango leaves in the food and pharmaceutical industries, less importance was given to it in the corrosion protection research area. Additionally, all the above-mentioned corrosion inhibition studies in the literature are based on mild steel or carbon steel in an acid environment. However, till now, no research work has been reported on the investigation of *Mangifera indica* for SS-316L metal in an acid environment. Therefore, there is a need for systematic study and development of an effective green corrosion inhibitor from *Mangifera indica* for SS-316L metal in an HCl environment.

The main objective of the present work is to synthesize a green corrosion inhibitor using ethanolic extract of *Mangifera indica* leaves and evaluate its anti-corrosion activity on stainless steel (SS-316L) in an acidic medium (1 M hydrochloric acid solution). A direct quantitative weight loss method was employed to estimate corrosion rate and inhibition efficiency at different concentrations of MIL extract. Fitting adsorption isotherm models evaluated adsorption and thermodynamics parameters, and the mechanism of inhibitor adsorption on the SS-316L surface was studied. Additionally, Fourier Transform Infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FE-SEM), along Energy Dispersive spectroscopy (EDS) were utilized to provide additional insights into the corrosion inhibition mechanism of MIL extract. Later, multivariate regression-based models were developed to predict corrosion rate as a function of inhibitor concentration and exposure time. The novelty of this paper is the use of *Mangifera indica* leaves on SS-316 corrosion for the first time and the development of a mathematical model to predict the corrosion rate as a function of important process parameters. The findings of the present study demonstrated that MIL extract can be utilized as an efficient, non-toxic, cost-effective, and biodegradable anticorrosive material for stainless steel protection in reducing acid applications.

MATERIALS AND METHODS

Materials

Fresh *Mangifera indica* leaves (also known as mango leaves) were collected from a mango tree situated in local Pune, India, in November. Ethanol (C_2H_5OH, 98%), acetone (CH_3COCH_3, Merck company) & hydrochloric acid (HCl, 37%, Merck company) of AR grade were used for the synthesis of mango leaf extract and corrosive test solution for the study without any purification. Stainless steel (SS-316L) coupons of chemical composition (wt. %): C = 0.014%, Si = 0.75%, Mn = 1.26%, P = 0.041%, S = 0.006%, Cr = 17.34%, Mo = 2.10%, Ni = 10.12% and balance is Fe were sourced locally and tested following ASTM A 276/ 276 M method by Industrial metal test lab located at Mumbai. Coupons dimensions were in the range of 30 mm × 9 mm ×1.9 mm with a 5 mm drilled hole. Glass bottles were used to conduct the corrosion study.

Mangifera Indica Leaves (MIL) Extract Preparation

Mangifera indica leaves were washed with plenty of water to remove the extraneous material like dust particles and then dried in the hot air oven at 80°C for 3 h. To prepare the extract, dried mango leaves were ground to a fine powder (approx. 15 g) and extracted in 150 ml ethanol for 4 h in the agitated round bottom flask at ambient temperature. The obtained mixture was then filtered, and excess ethanol was removed by rotavapor at 85 °C to get the MIL extract.

Specimen Coupon's Preparation

Before the experiment, SS-316L coupons of rectangular shape were mechanically abraded with emery paper grade 200. After that, these coupons were washed with water to remove the dust and then rinsed with acetone. After washing, coupons were dried & kept in a desiccator to avoid contamination before corrosion studies.

Solution Preparation

1 M HCL solution, which acts as a corrosive environment, was prepared from 37% analytical grade HCL solution using distilled water. Prepared 1M HCL solution was kept in glass bottles with different concentrations of MIL extract of 0 ppm, 200 ppm, 400 ppm, 600 ppm, 800 ppm, and 1000 ppm. Anti-corrosive properties of each concentration of MIL extract have been tested on sample coupons using the weight loss method.

Weight Loss Measurement

Experiments were conducted to investigate the degree of metal corrosion in acidic solutions using standard weight loss methods reported in the literature (Bhardwaj et al. 2021). For weight loss measurement studies, the weight of each SS-316L coupon was recorded twice before the immersion test. The stainless-steel coupons were then immersed in 1M HCl as corrosive media without and with MIL extract of different concentrations ranging from 200 to 1000 ppm for 14 days. After specified periods, samples were removed from the acid solutions, followed by cleaning and drying. After that, the specimen samples were again weighed (recorded twice) to obtain the loss in weight upon exposure to test solutions (1M HCl) with and without MIL extract, and average values are reported here.

The rate of corrosion for both uninhibited and inhibited systems was calculated using the following equation (1),

$$C_R(\text{cm/h}) = \frac{\text{weight loss}}{\text{area} \times \text{time}} = \frac{(W_0 - W)}{(\rho \times A \times t)} \quad \ldots(1)$$

where, C_R is the corrosion rate in $cm.h^{-1}$. (which is later converted to $mm.yr^{-1}$.), W_0 and W denotes the weight of SS-316L coupons before and after immersion in acidic medium (g), ρ is the density of material in g/cm^3 (7.86 $g.cm^{-3}$ for steel), A represents the surface area of coupons in cm^2, t represents time of exposure in hrs.

The percentage inhibition efficiency (% IE) of the mango leaf extract as green corrosion inhibitor on SS-316L specimens in the presence of acidic (HCl) medium was computed using equation (2) as,

$$\text{IE \%} = \frac{\text{Corrosion rate without inhibitor} - \text{Corrosion rate with MIL inhibitor}}{\text{Corrosion rate of uninhibited system}} \times 100$$

$$\text{IE (\%)} = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \times 100 \quad \ldots(2)$$

where, C_{Ro} and C_{Ri} are the corrosion rates of immersed SS-316L coupons in acidic corrosive media and the corrosive solution containing varying concentrations of MIL extract as a green corrosion inhibitor, in ($mm.yr^{-1}$.), respectively.

The concentration of green corrosion inhibitor used and surface coverage with green corrosion inhibitor provided to SS-316L were the main components of this study. Surface coverage (θ) of MIL extract was calculated using the following equation (3)

$$\theta = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \quad \ldots(3)$$

Characterization of MIL Extract and Metal Specimens

Fourier transform infrared spectroscopy was utilized to identify the functional groups present in mango leaf extract, which are responsible for the anti-corrosive effect. The FTIR analysis was performed using Bruker ALPHA II Model

(available at Central Instrumentation Facility, Savitribai Phule Pune University, Pune) in the range of 500-4000 cm^{-1}.

The Field Emission Scanning Electron Microscopy (of Carl Zeiss make, (model ULTRA 55) available at the Indian Institute of Technology (IIT) Bombay was used to obtain the changes in surface morphology of corroded SS-316L samples. The samples were cut into 5.0 × 5.0 × 3.0 mm for SEM analysis. In addition, energy dispersion spectroscopy (EDS) analysis was performed for the same samples to get the elemental concentration. Two-dimensional images of different resolutions were taken for detailed analysis. For SEM and EDS analysis, SS-316L coupons immersed in the absence of MIL extract and with 600 ppm and 1000 ppm MIL extract were selected for the study.

Adsorption Isotherm Study

Adsorption isotherms are generally used to predict the adsorption behavior of green corrosion inhibitor (MIL extract) on the SS-316L surface. Different isotherms, such as Freundlich, Langmuir, Temkin, and Flory Huggins adsorption isotherms, etc., are widely used in previous studies to characterize the corrosion inhibition study (Ogunleye et al. 2020). In this study, Langmuir and Freundlich's isotherms were utilized for the adsorption study because of their simplicity, and their model parameters give complete information related to the corrosion inhibition study.

Langmuir isotherm model is described by Eqn. (4) as

$$C\left(\frac{1-\theta}{\theta}\right) = \frac{1}{K_{ads}} \quad \ldots(4)$$

In general, Eqn. (4) is linearized to obtain Eqns. (5 or 6) as follows

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

$$\log\left[\frac{\theta}{(1-\theta)}\right] = \log K_{ads} + \log C \quad \ldots(6)$$

where C is the concentration of MIL inhibitor in g/L θ represents the fraction of the metal surface covered with the inhibitor calculated using Eqn. (3), and K_{ads} is the equilibrium adsorption constant in $L.g^{-1}$.

The plot of (C/θ) versus C or log [θ/(1-θ)] versus log C gives a straight line with a unit slope, which obeys Langmuir isotherm**.** The correlation coefficient (R^2) close to 1 indicates best-fit isotherm model. The value of K_{ads} is estimated from the reciprocal of the intercept of the linear fit of the plot (C/θ) versus C.

In addition, data obtained from the weight loss study was used to fit the Freundlich adsorption isotherm model is expressed as

$$\theta = K_{ads}\, C^n \quad \ldots(7)$$

It is expressed in linear form as

$$\log\theta = \log K_{ads} + n \log C \quad \ldots(8)$$

where n denotes the slope of the straight-line fit of the graph log θ vs. log C (Freundlich isotherm) The intercept yields the value of the equilibrium constant of adsorption, K_{ads}.

The standard adsorption free energy ΔG^0_{ads} is related to the obtained equilibrium constant (K_{ads}) from isotherm models as presented in Eqn. (9). It is used to represent the feasibility and nature of adsorption, such as physisorption or chemisorption.

$$\Delta G^0_{ads} = -2.303\, RT \log\,(55.5 \times K_{ads}) \quad \ldots(9)$$

where, ΔG^0_{ads} is a change in standard Gibb's free Energy ($kJ.mol^{-1}$), K_{ads} represents the adsorption equilibrium constant obtained from the isotherm plot, *55.5* denotes molar heat of adsorption of water in solution (Akinbulumo et al. 2020), R denotes universal gas constant, and T is the absolute temperature (K). The value of $\Delta G^0_{ads} \leq -20$ kJ mol^{-1} is associated with the physisorption mechanism and $\Delta G^0_{ads} \geq -40$ $kJ.mol^{-1}$ indicates chemical adsorption (Bhardwaj et al. 2021, Akinbulumo et al. 2020).

RESULTS AND DISCUSSION

Weight Loss Analysis

The weight loss method is widely used for quantitative

Table 1: Results of weight loss method of SS-316L coupons immersed in 1 M HCl solution without and with MIL extract after 14 days of immersion.

Concentration of MIL extract [ppm]	Weight Loss after 14 days [g]	Corrosion rate C_R [$mm.yr^{-1}$]	% Inhibition efficiency	Surface coverage [θ]
Blank (or 0 ppm)	0.259	1.184	-	-
200	0.250	1.145	3.33	0.0333
400	0.219	1.094	7.61	0.0761
600	0.173	0.702	40.68	0.4068
800	0.121	0.585	50.59	0.5059
1000	0.105	0.433	63.42	0.6342

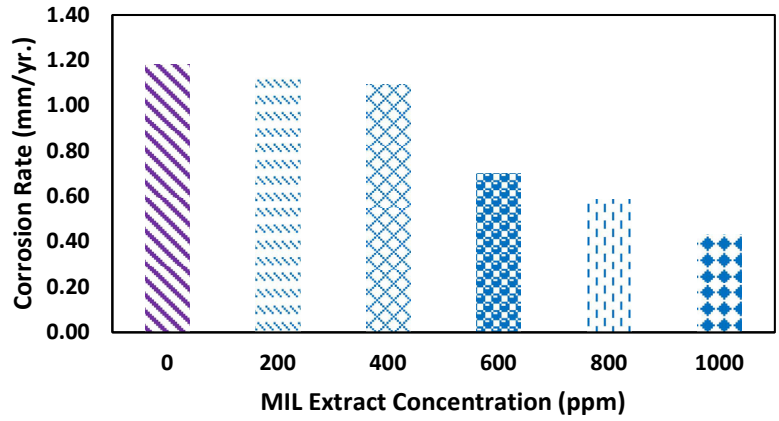

Fig. 1: Bar diagram of Corrosion rate (mm/yr.) of SS-316L after immersion in 1M HCl medium without and with MIL extract at different concentrations for 14 days.

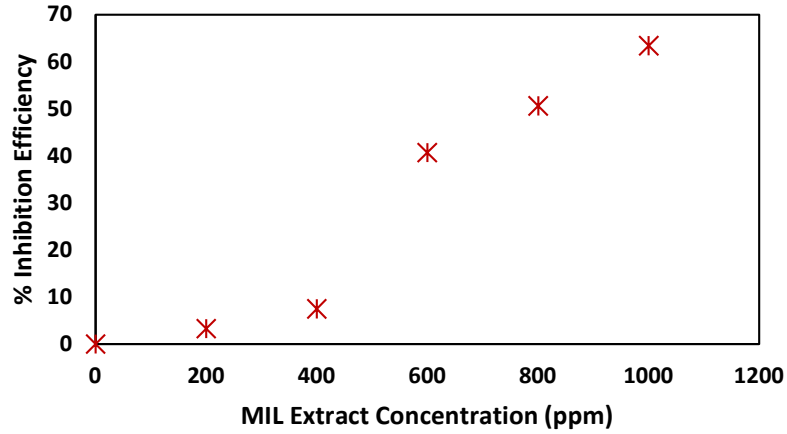

Fig. 2: Percentage inhibition efficiency of SS-316L after immersion in 1M HCl medium without and with MIL extract at different concentrations for 14 days.

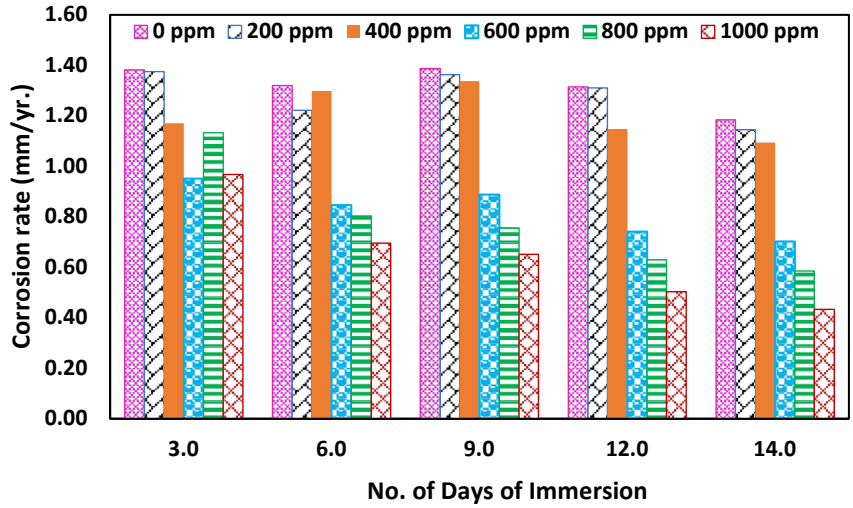

Fig. 3: Variation of Corrosion rate (mm/yr.) of SS-316L with time and variation of MIL extract concentrations.

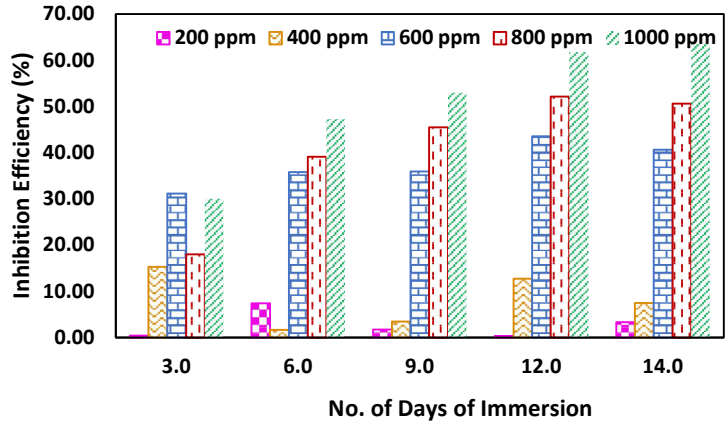

Fig. 4: Variation of Inhibition efficiency of SS-316L with time and different concentrations of MIL extract in 1 M HCl.

evaluation of metal corrosion inhibition as it utilizes simple and easy-to-measure parameters, i.e., loss in weight of the metal after exposure to a corrosive medium. The corrosion rate and percentage inhibition efficiency of SS-316L coupons obtained from the systematic weight loss experimental runs for various concentrations of MIL extract ranging from 200 to 1000 ppm after 14 days of immersion in acidic corrosive media are exhibited in Table 1 and Figs. 1 and 2, respectively. The presented data in Table 1 indicated that weight loss after 14 days of immersion in 1M HCl with 1000 ppm of MIL extract is 0.105 g as compared to a greater weight loss of 0.259 g in the absence of an inhibitor. Figs. 1 and 2 depict that the value of the corrosion rate of SS-316L decreases with an increase in the concentration of MIL extract, resulting in an increase in inhibition efficiency after immersion in 14 days. It is seen from the plots that inhibition efficiency is less than 50% up to 600 ppm MIL extract, and after that, it increases significantly with an increase in inhibitor concentration. The maximum % corrosion inhibition efficiency of 63.42% and minimum corrosion rate (0.433 $mm.yr^{-1}$.) were obtained using 1000 ppm of MIL extract.

Similarly, detailed result analysis of variation of corrosion rate ($mm.yr^{-1}$.) and inhibition efficiency (%) with time (3, 6, 9, 12, and 14 days) and MIL extract concentrations (0, 200, 400, 600, 800 and 1000 ppm) are shown in Figs. 3 and 4, respectively. Analysis of figures reveals the impact of the MIL extract on corrosion rate as well as in inhibition efficiency with time. This finding implies that mango leaf extract forms a protective film on the SS-316L surface and thus gives a significant reduction in corrosion rate and

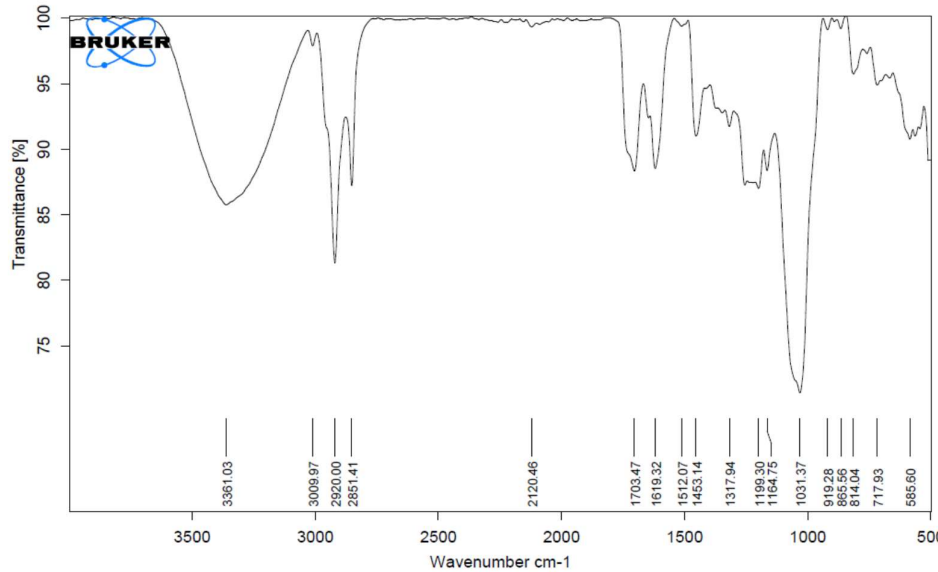

Fig. 5: FTIR spectrum of *Mangifera indica* Leaf extract.

increment in inhibition efficiency in an acid environment. This corrosion inhibition film of MIL extract on SS-316L can be attributed to the presence of many active functional groups in organic components of MIL extract, such as gallic acid, mangiferin iriflophenone, etc., and thus, may act as inhibitors to protect the metal surface. Results presented in Table 1 also show that maximum surface coverage was obtained at 1000 ppm of MIL extract. Previous investigations showed a similar trend of corrosion rate and inhibition efficiency of green inhibitors for mild steel corrosion in an acidic (HCl) environment (Shamsheera et al. 2022, Akinbulumo et al. 2020). Overall, it can be concluded that this MIL extract acts as an efficient green corrosion inhibitor for stainless steel grade SS-316L in a hydrochloric acid medium.

FTIR Analysis

The FTIR spectrum of the mango leaf extract was conducted, and the results are reported in Fig. 5. The spectra of mango leaf extract depict a broad peak at wavenumber 3361.03 cm^{-1} exhibits O-H bond stretching vibration of phenolic compounds and alcohols. Three peaks of aromatic ring C-H bond stretching were observed at 3009.97 cm^{-1}, 2920 $cm^{-1,}$ and 2851.41 cm^{-1}. Further, the peak of O-H/C-H bending of the phenol group appeared at 1317.94 $cm^{-1,}$ and C=C bond stretching in the aromatic ring was confirmed at 1453.14 and 1512.07 cm^{-1}. Three peaks at 1619.32, 1703.47 $cm^{-1,}$ and 1031.37 cm^{-1} with medium to strong intensity were attributed to the presence of stretching vibration of carbonyl groups (C=O and C-O). These peaks are identical to the FTIR spectrum of mango leaf extract reported by Veddu et al., 2019 and Ramezanzadeh et al., 2019. Hence, previous findings and present results revealed the presence of various functional groups in MIL extracts such as gallic acid (3,4,5-Trihydroxybenzoic acid), mangiferin (C 2-β-d-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone) and iriflophenone (4-hydroxyphenyl) -(2,4,6-tri hydroxyphenyl) methanone) etc. (Ramezanzadeh et al. 2019, Veedu et al. 2019). This FTIR analysis confirms the corrosion inhibition activity is mainly due to the presence of heteroatoms in the synthesized MIL extract that can easily adsorb on metal surfaces and thus act as a protective film to inhibit stainless steel corrosion. Further investigation using SEM and EDS analysis along with adsorption isotherm analysis was conducted to infer more information about the protective layer formation of synthesized green corrosion inhibitor on the SS-316L surface.

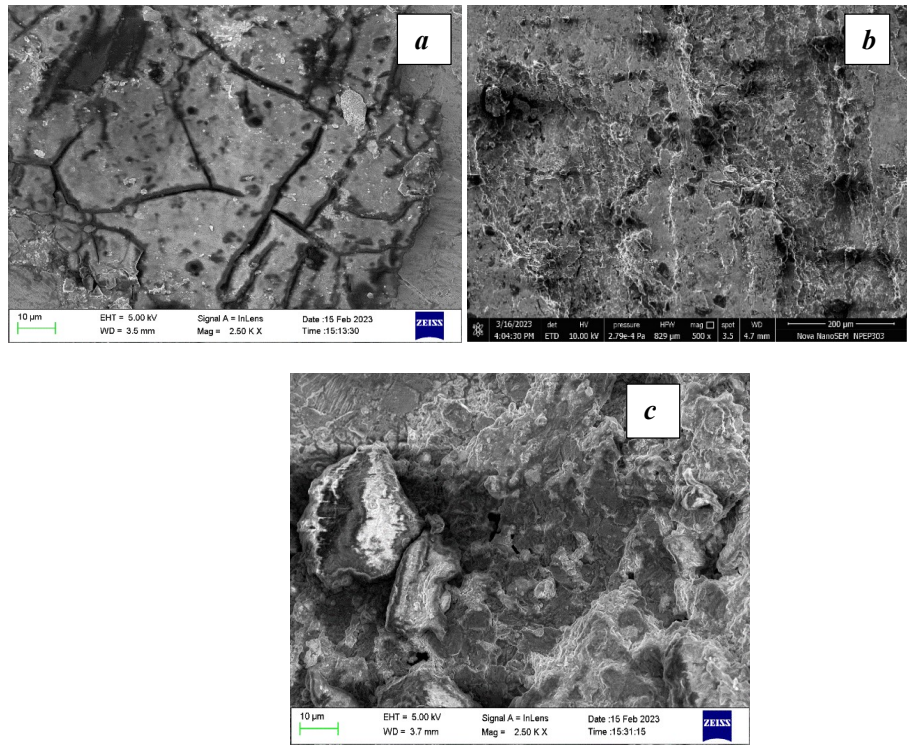

Fig. 6: FE-SEM image of SS-316L coupons immersed in 1 M HCl solutions (*a*) without MIL extract, (*b*) with 600 ppm MIL extract, (*c*) with 1000 ppm MIL extract.

Scanning Electron Microscopic Analysis

The surface morphology of SS-316L coupons exposed to 1 M HCl solution without and with MIL extract (1000 and 600 ppm concentration) was evaluated using FE-SEM images. FE-SEM image for SS-316L coupon immersed in 1 M HCl solution without inhibitor is displayed in Fig. 6 a, and with 600 and 1000 ppm MIL extract are presented in Figs. 6 b and c, respectively. It is seen from the FE-SEM image that the SS-316L sample immersed in 1M HCl solution without MIL extract inhibitor has a rough and corroded texture on the surface (Fig. 6 a), indicating the severe corrosion of the specimen. Figs. 6 b and c exhibited the formation of the protective layer of MIL extract (white film observed) but with some localized pitting corrosion (black spots). This deposition of inhibitor film on the surface indicated the covering of the ML extract on the metal specimen surface, which prevents contact of corrosive media with the surface. Therefore, the damage to the SS-316L surface is noticeably less in the presence of an inhibitor (Figs. 6 b and c). Many

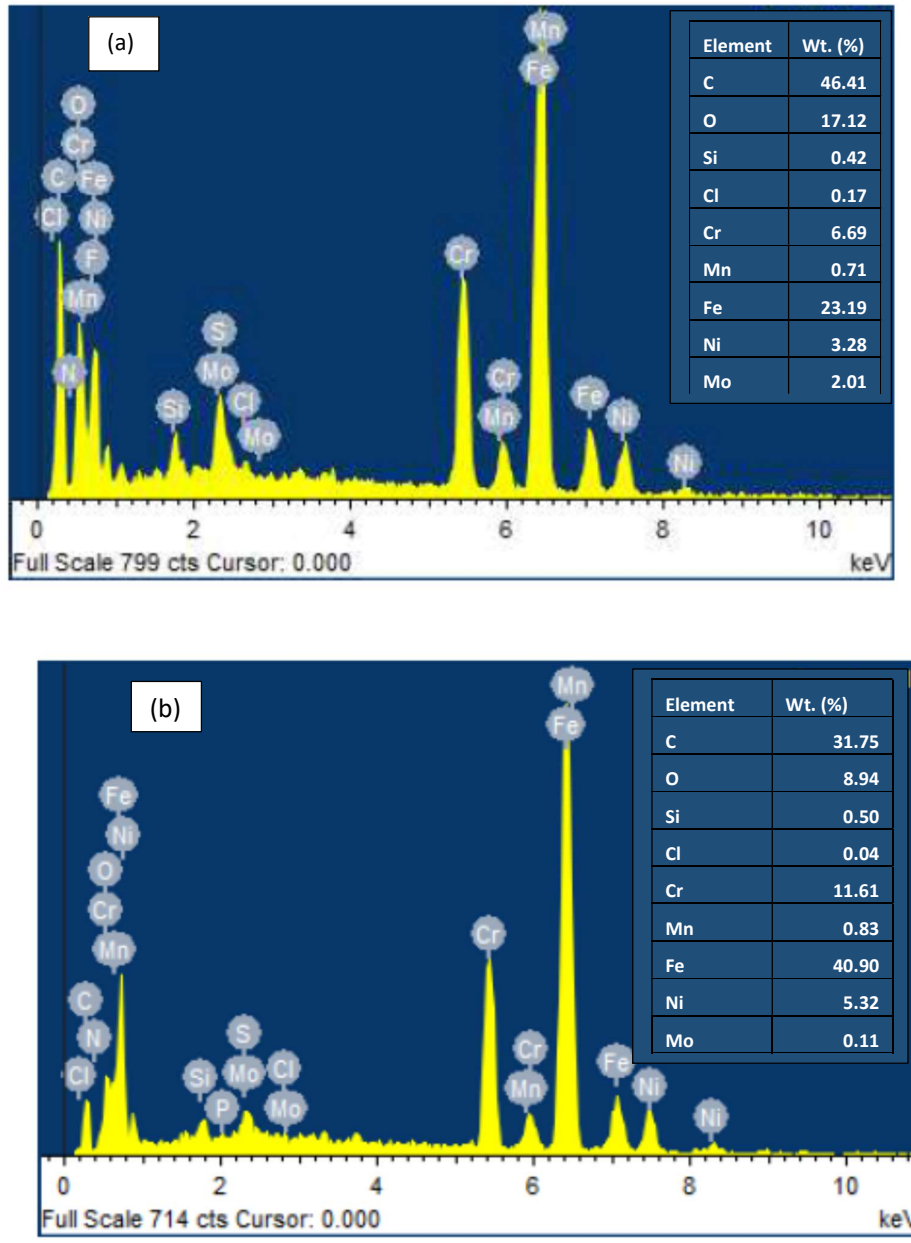

Fig. 7: EDS spectrum of SS-316L coupons after 14 days of immersion in 1M HCl (*a*) without MIL inhibitor (*b*) with 1000 ppm MIL inhibitor.

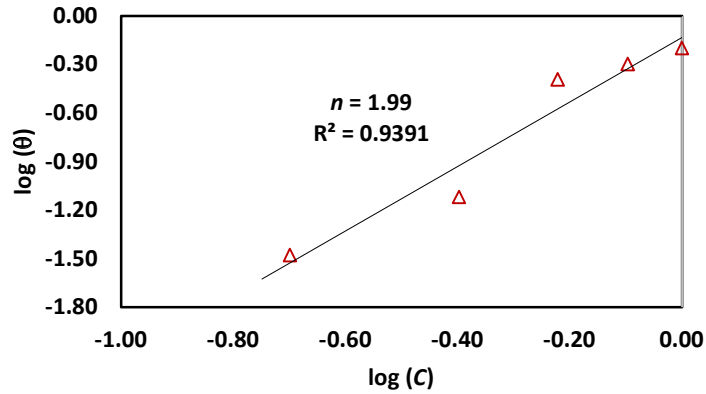

Fig. 8: Freundlich Adsorption Isotherm of MIL inhibitor.

cracks and pits were observed on the surface of the sample due to corrosion in the absence of an inhibitor, and localized pitting was observed at a low concentration of 600 ppm of inhibitor, as exhibited in Fig. 6 b. Compared to a specimen immersed in 1000 ppm, the metal coupon immersed in 600 ppm is more corroded but less than the bare specimen. Thus, it can be concluded that bare stainless steel is hard to resist the corrosion of acid. In contrast, the protected surface, due to the layering of the inhibitor (Figs. 6 b and c), provides more corrosion resistance. The present results are confirmed with similar results of corrosion inhibition reported by Ramezanzadeh et al. (2019) with *Mangifera indica* leaf extract on the mild steel surface.

Subsequently, EDS analysis was performed to determine the elemental analysis of metal specimens in the absence and presence of an inhibitor. EDS spectrum of SS-316L coupons after 14 days of immersion in 1M HCl without MIL inhibitor and with 1000 ppm MIL inhibitor are presented in Fig. 7 a and b, respectively. It is important to note that the addition of an inhibitor forms a protective film on the metal surface to protect it from an HCl attack. This resulted in a higher content of Fe, Cr, Ni, and Mn and less carbon, chlorine, and oxygen content in the presence of 1000 ppm MIL inhibitor than blank solution, as exhibited in Fig. 7 b. Conversely, as evident from Fig. 7 a, higher amounts of C, O, and Cl species and less percentage of Fe were obtained with uninhibited samples, indicating the formation of corrosion products on the surface. This reveals that in the absence of an inhibitor, the inherent protective film of chromium oxide is unable to resist the attack by HCl, resulting in increased pitting and even crack formation (Fig. 6 a). These findings illustrated that the organic compounds with heteroatoms present in the MIL extract help to evade the contact of stainless-steel surface with corrosive media and, hence, increased inhibition efficiency (Table 1).

In contrast, without MIL extract, the corrosion rate of stainless steel in an acidic solution was significantly enhanced. These results are consistent with the observed trend from the weight loss method, FTIR, and SEM analysis. Hence, the morphological characterization confirmed the formation of the anticorrosive film of MIL extract on the SS-316L surface and thus resisted the acid corrosion efficiently.

Adsorption Study

The result obtained from the fitting of various isotherms provides detailed insight into the adsorption mechanism and inhibition activity of the MIL extract at the interface between the corrosive medium and SS-316L surface. Firstly, the Langmuir isotherm plot was plotted between C/θ versus C based on Eqn. (5), but the fitting of the experimental data results in a poor fit with a low R^2 value, and hence, results are not reported here.

Later, Freundlich isotherm was plotted with obtained experimental data of log (θ) versus log (C) for MIL extract after 14 days and displayed in Fig 8. Freundlich isotherm parameters n and equilibrium adsorption constant K_{ads} were evaluated from the slope and intercept of the same plot. Fig. 8 depicts the best fit of the Freundlich adsorption isotherm model to experimental data with an R^2 value of 0.94 and an obtained value of n from the slope of the graph close to 2. This fitting of Freundlich adsorption isotherm confirmed the development of multilayer adsorption (i.e., physisorption) of MIL extract at heterogenous sites on the SS-316L surface, which is the main assumption of the Freundlich equation. In contrast, Langmuir isotherm assumes monolayer adsorption on homogeneous sites and, thus, results in poor fitting for the present data.

Furthermore, the obtained K_{ads} value from the intercept of the best-fit line at 298 K is 0.7389 $L.g^{-1}$, showing effective adsorption of MIL extract on the SS-316L surface, which indicates better protection of metal specimen and hence efficient anti-corrosion nature of synthesized green corrosion inhibitor. The obtained value of free Energy

of adsorption (ΔG°_{ads}) from Eqn. (9) is – 9.20 kJ.mol^{-1} at 298 K (< – 20 kJ.mol^{-1}), indicating adsorption of MIL extract on SS-316L surface is spontaneous, feasible, and via physisorption mechanism as a result of electrostatic interaction between the charged metal and the inhibitor molecule. The obtained results showed good agreement with the previous investigation of corrosion inhibition study using leaves and stem extracts of Sida Acuta with values of free Energy of adsorption at 303 K (ΔG°_{ads} = – 10.6 kJ.mol^{-1}) and K_{ads} value of 1.22 L.g^{-1} by Umoren et al. (2016). So, it can be concluded from the obtained ΔG°_{ads} values that the MIL adsorbed physically on the SS-316L surface for the development of protective layers against corrosion.

Mathematical Model Development for Prediction of Corrosion Rate

In this study, two mathematical models (linear and quadratic) based on multivariate regression analysis were developed for the estimation of the corrosion rate for SS-316L against 1 M HCl. The experimental data of the corrosion study obtained in this work were utilized to develop the models, which comprise inhibitor concentration and exposure time as the input parameters and corrosion rate as the out parameter. The effect of individual variables and the interaction between them was considered in both models.

Multivariate regression is a standard statistical method used to estimate the relationship between the one dependent variable of interest (also known as a response variable, i.e., the targeted output) and multiple independent variables (called predictor variables).

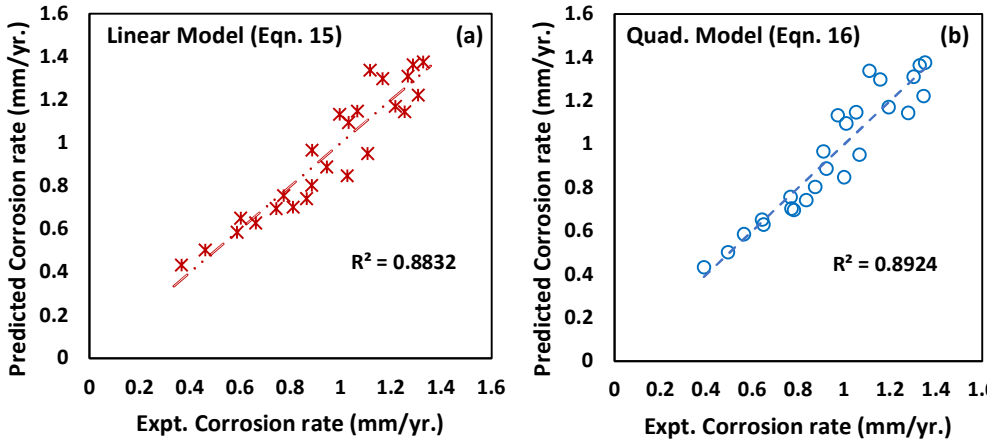

Fig. 9: Predicted corrosion rate using (a) linear model eqn. 15 (b) quadratic model eqn. 16 versus experimental corrosion rate.

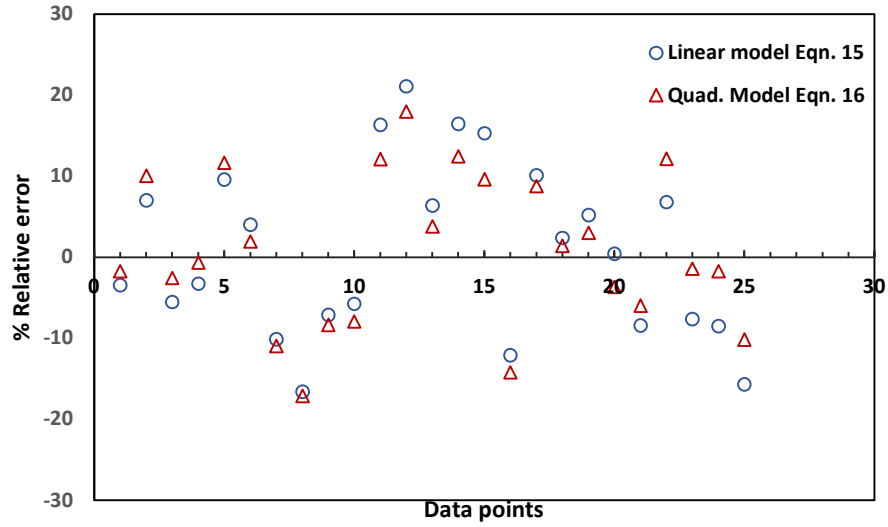

Fig. 10: % Relative error for the relevant data points using (o) linear and (Δ) quadratic model.

Multivariable linear model was developed in the form mentioned below:

$$C_R = a_0 + a_1 \times C + a_2 \times t + a_3 \times C \times t + \varepsilon \quad \ldots(10)$$

Similarly, the developed multivariable quadratic model can be expressed by the following equation:

$$C_R = a_0 + a_1 \times C + a_2 \times t + a_3 \times C^2 + a_4 \times t^2 + a_5 \times C \times t + \varepsilon \quad \ldots(11)$$

where C_R represents corrosion rate, C denotes inhibitor concentration, and t is exposure time, a_0, a_1, a_2, a_3, a_4 and a_5 are model parameters, and ε is residuals between predicted and experimental values.

The optimal parameters a_0, a_1, a_2, a_3, a_4 and a_5 of proposed models (Eqns. 10 and 11) that best fit the data points were estimated using a least square method that minimizes the square of residuals (SSR).

$$SSR = \sum_{i=1}^{n} \varepsilon_i^2 = \sum_{i=1}^{n} \left(Y_i - \sum_{j=1}^{k} a_j X_{ij}\right)^2 \quad \ldots(12)$$

In this equation, n is the number of experiments, Y represents the experimental output (C_R) and X denotes the experimental inputs (C and t).

To evaluate the efficiency and accuracy of the developed regression-based models, two statistical parameters, namely percentage relative error and coefficient of determination, were utilized.

Performance of the Developed Models Using Statistical Error Analysis

To measure the efficiency and accuracy of the developed model, two statistical metrics, namely percentage relative error and coefficient of determination, were used. Percentage relative error or percentage error that represents the relative deviation of predicted corrosion rate from the experimental value.

$$E_i = \left(\frac{(C_R)_{Pred.} - (C_R)_{expt.}}{(C_R)_{expt.}}\right) \times 100, i = 1, 2, \ldots, n \quad \ldots(13)$$

The coefficient of determination indicates how close the model's predicted value is to the actual experimental value.

$$R^2 = 1 - \frac{\sum_{i=1}^{n}\left[(C_R)_{Pred.} - (C_R)_{expt.}\right]^2}{\sum_{i=1}^{n}\left[(C_R)_{Pred.} - \overline{(C_R)}_{expt.}\right]^2} \quad \ldots(14)$$

If the value of R^2 is close to unity means the model is best fitted to experimental values.

The optimal parameters were computed using multivariate regression using EXCEL, and overall linear and quadratic models are represented by Eqns. 15 and 16 as follows:

$$C_R = 1.43 - 0.0004 \times C + 0.00343 \times t - 5.1 \times 10^{-5} \times C \times t \quad \ldots(15)$$

$$C_R = 1.507 - 0.00088 \times C + 0.01302 \times t + 3.98 \times 10^{-7} \times C^2 - 0.00056 \times t^2 \quad 5.1 \times 10^{-5} \times C \times t \quad \ldots(16)$$

Fig. 9 a and b depict the linear and quadratic model predicted results of corrosion rate (using Eqns. 15 and 16) versus experimental corrosion rate data. As depicted in Fig. 9 a and b, the predicted corrosion rate using multivariate regression linear and quadratic models exhibits good agreement with experimental data. However, as evident in Fig. 9 b, the quadratic model exhibits slightly better performance than the linear model by achieving higher coefficient of determination values of 0.89 as compared to the linear model (R^2 = 0.88). Finally, the percentage relative deviation from the multivariate linear and quadratic regression models versus the relative data index is illustrated in Fig. 10. As can be seen in this figure, the maximum percentage relative error is higher in the linear model (21%) as compared to the quadratic model (17%). These results reveal that the quadratic model predicts corrosion rate with a higher accuracy of 82% as compared to the linear regression model with an accuracy of 79%.

CONCLUSIONS

The corrosion resistivity of eco-friendly *Mangifera indica* leaves extract on the surface of stainless steel (SS-316L) in hydrochloric acid solution was evaluated using weight loss, adsorption isotherm, FTIR spectroscopy, Scanning electron microscopic and Energy dispersive spectroscopic techniques. Weight loss analysis reveals that *Mangifera indica* leaf extract efficiently inhibits corrosion of stainless steel (SS-316L) in 1 M HCl media with inhibition efficiency of 63.42% at 1000 ppm MIL concentration. The enhancement in inhibition efficiency and detraction in the corrosion rate of SS-316L was obtained with an increase in MIL extract concentration and immersion time. Furthermore, FTIR analysis confirmed the presence of functional groups with heteroatoms (electron donating) in the MIL extract, which exhibited the corrosion-resistant effect against the hydrochloric acid solution. Detailed analysis using SEM and EDS further confirmed the severely corroded metal surface in the absence of MIL extract. The results of the corrosion behavior of MIL extract at different concentrations obtained using weight loss measurements are in good agreement with those obtained from FTIR, SEM, and EDS analysis. The Freundlich adsorption isotherm fits well with the data, clearly indicates the multilayer adsorption of organic constituents

present in MIL extract, which implies physisorption on the surface of stainless steel. The obtained negative value of ΔG^{o}_{ads} indicates corrosion reaction is spontaneous in an acidic solution. Lastly, the developed multivariate regression-based models can predict corrosion rate with a relative percentage error of less than 21%. Hence, it can be concluded that *Mangifera indica* leaf extract can be utilized as an eco-friendly, low-cost, and efficient green corrosion inhibitor in the hydrochloric acid environment for stainless steel (SS-316L) as a substitute for existing toxic and costly corrosion inhibitors.

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