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Green Corrosion Inhibitors for Mild Steel: Experimental and Predictive Modeling Studies

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Predicting the performance of corrosion inhibitors for a given corrosion problem is a serious and challenging hurdle in chemical process and allied sectors. In the present study, corrosion inhibition activity of ethanolic extract of *Mangifera indica* leaves (MIL) for mild steel under acidic environment was investigated. The inhibition effectiveness and corrosion rate at varied concentration of MIL was evaluated using weight loss method. Subsequently, Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy (SEM) was utilized for analysis of active constituents of MIL extract and surface morphology of samples. Additionally, predictive model utilizing Artificial Neural Network (ANN) was trained and developed to forecast the corrosion inhibition efficacy as a function of key variables namely inhibitor concentration, acid concentration, temperature and exposure duration based on the large dataset from published literatures and present study. According to experimental findings, inhibition efficacy increased as the immersion time and inhibitor concentration (200 – 1000 ppm) increased. The MIL extract exhibited good inhibition efficiency of 70.37% and 1.785 mm/yr corrosion rate against 1000 ppm acid concentration. Langmuir isotherm model very well fitted for the adsorption data with free energy value of −11.97 kJ/mol inferring physisorption process. SEM analysis confirmed the intact surface texture of MIL treated mild steel coupons. The developed ANN model prediction results revealed reasonably good accuracy with a correlation coefficient 0.8299 and 0.0102 mean-squared-error. The present findings will provide valuable insights on experimental and predictive modeling approach for corrosion inhibition activity study of environmentally friendly MIL extract for industrial corrosion treatment.

Keywords: Adsorption isotherm, Artificial neural network, Corrosion inhibitor, Inhibition efficiency, *Mangifera indica* leaf extract

Introduction

Corrosion-induced deterioration of metallic parts of process equipment is a critical problem encountered in chemical plants globally. Mild Steel (MS) is extensively utilized in chemical processing, automobile, petroleum, naval, pharmaceutical, and other industries owing to its excellent mechanical strength, toughness, and comparatively lower cost than other metals.[1] However, its exposure to aggressive acidic media, particularly hydrochloric acid (HCl), during industrial processes such as, chemical cleaning, descaling, acid pickling, chemical synthesis, oil well acidizing and waste water treatment etc. causes severe corrosion, resulting in environment and economic losses, reduced productivity and serious safety risks.[2–5] These concerns necessities efficient and sustainable corrosion mitigation strategies to improve the safety and operational efficiency in chemical process industry.

Industries typically employ cathodic protection, surface treatments, inhibitors, protective coatings and paints to mitigate metal corrosion.[6,7] The application of corrosion inhibitor provides simple and efficient approach for protecting the metallic surfaces against acidic corrosive media. Even though most of conventional corrosion inhibitors provide effective protection, they raise major concerns related to cost, toxicity, and high environmental persistence.[8] In contrast, green corrosion inhibitors synthesized using plant extract are nontoxic, inexpensive, biodegradable and easily available and their key organic contents are responsible for anticorrosive activity. These bioactive compounds can be readily extracted from distinct plant parts, encompassing leaves, flowers, roots, stems, seeds, fruits and fruit peels or processing waste, which are abundant, cost-effective and

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renewable resources with low environmental footprint. As a result, these plant-derived natural compounds have emerged as promising areas of investigations in recent years as sustainable alternatives to conventional synthetic chemicals.[9,10] Therefore, over the past few decades, variety of plant-derived extracts, including marigold flowers, neem, pomegranate and hibiscus leaves have been investigated as green corrosion inhibitors in acidic media.[11–14] Other studies have explored the *Cyperus rotundus, Opuntia ficus* and jackfruit pectin for corrosion inhibition. [4,8,10] Recent studies have demonstrated the effectiveness of rubber leaf extract (96.98% inhibition) for mild steel in 1 M HCl and *Andrographis paniculata* extract (95.14%) in concentrated H_2SO_4.[15,16] Other plant-based inhibitors, including hairy bamboo, *Murraya koenigii*, and chickpea extracts, have also shown promising corrosion protection under different corrosive conditions.[17–19] Overall, these previous research findings demonstrate that biodegradable, renewable, and non-toxic plant extracts are promising sustainable substitutes for protecting metal infrastructure in aggressive corrosive environment.

Mangifera Indica Leaves (MIL) are enriched with bioactive substances including mangiferin, tannins, quercetin, iriflophenone, gallic acid, containing oxygen rich functional groups along with aromatic π-electrons, that may promote adsorption onto metal surfaces and thus inhibits corrosion.[20] Previous studies have investigated mango leaf extracts for steel protection in different corrosive environments, including HCl.[7,20] Most importantly, pruned and fallen mango leaves are abundantly available biomass in India, unlike previously investigated seasonally restricted plant sources like fruit peels, flowers etc., offering potential for value addition through sustainable corrosion protection.[12,21] Additionally, most of corrosion inhibition research studies are limited to experimental evaluation with comparatively less emphasis on predictive modeling.[13–15]

However, further integration of experimental corrosion assessment with predictive modelling provides valuable insight for evaluating inhibitor performance and improving its estimation under different operating conditions. Such integrated approach not only distinguishes the present study from previous investigations but also provides the insight into the use of predictive modeling for improving corrosion protection strategies.

In agreement with this, experimental corrosion inhibition studies demonstrated that the corrosion-inhibition efficiency depends on several interacting parameters namely inhibitor concentration, concentration of acid, exposure time and temperature.[22–24] Evaluating the corrosion performance using experimental technique requires considerable time, chemicals, experimental runs, and high end sophisticated analysis instruments.[25] Hence, simple, fast, cheap and accurate alternative method/model is essential for the prediction of corrosion inhibition efficiency.

Nowadays, Artificial Neural Network (ANN) offers complementary approach to experimental investigations to estimate complex relationship between process variables and corrosion performance, in both cost and time effective manner.[26] In this sense, recent studies have used ANN based approaches to model corrosion inhibition of metals using plant-base extracts and other inhibitor systems.[24,26,27] For instance, Amodu *et al.*[24] developed ANN model to predict mild steel corrosion utilizing banana peel extract in HCl considering temperature and inhibitor concentration, but used a limited data set. Recently, Sanni *et al*.[28] used machine learning to predict copper corrosion inhibition by *Spinacia oleracea* leaf extract in HNO_3, demonstrating its ability to model nonlinear relationship and facilitate optimization. However, limited dataset and operating conditions restricted model generalizability, highlighting the need for broader datasets covering temperature, inhibitor concentration, and exposure time. Similarly, Abeng[29] investigated expired telithromycin as a mild-steel corrosion inhibitor in 0.5 M H_2SO_4 using experimental, machine-learning, and quantum chemical approaches to predict inhibition efficiency. The ANN and ANFIS models achieved a prediction error of 2.2%, demonstrating their effectiveness in predicting corrosion inhibition performance.

Although machine learning models have shown potential for predicting corrosion inhibition, their applicability is often limited by small, inhibitor-specific datasets, increasing the risk of overfitting and reducing generalizability.[30,31] Therefore, this study integrates weight-loss measurements, surface characterization, and ANN modelling to evaluate *Mangifera indica* leaf extract corrosion inhibitor for MS in HCl. To enhance the predictive capability, ANN model was developed using 181 samples from published studies and present experiments, covering

diverse inhibitors and operating conditions. This integrated approach provides reliable inhibition-efficiency prediction while reducing dependence on time- and resource-intensive experiments.

In the viewpoint of industrial applications and great potential of plant extract for the corrosion inhibition, *Mangifera indica* leaves and mild steel material was chosen for this investigation. The present work focus is to synthesize corrosion inhibitor via green route utilizing an ethanolic extract of *Mangifera indica* leaves to mitigate the mild steel corrosion in hydrochloric acid environment. The corrosion control behaviour in terms of rate of corrosion and inhibition efficiency across a range of MIL extract concentrations was estimated using simple weight loss method. Inhibitor adsorption mechanism was evaluated based on adsorption and thermodynamics parameters obtained by fitting Freundlich, Langmuir, Flory-Huggins and Temkin adsorption isotherm models to experimental data. Fourier-transform infrared spectroscopy (FTIR), field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDS) were employed to investigate functional groups and changes in the steel surface. Additionally, an ANN model was developed using a dataset of 181 samples compiled from published studies and the present experimental data. Inhibitor concentration, acid concentration, exposure time, and temperature were used as input variables to predict inhibition efficiency. Later, the performance of developed ANN model was analyzed using correlation coefficient (R^2) and mean-squared-error (MSE). This combined experimental and predictive approach aims to evaluate the corrosion-protection efficacy of mango leaf extract while exploring data-driven prediction as a means of reducing dependence on extensive experimental trials.

Materials and Methods

Materials

Ethanol (C_2H_5OH, 98%), acetone (CH_3COCH_3) & hydrochloric acid (HCl, 37%) of AR grade was procured from Merck company and employed for MIL extract and corrosive media preparation. No additional purification of chemicals was carried out prior to their use. Freshly harvested green *Mangifera indica* (Mango tree) leaves were collected locally in Mumbai, India. MS coupons were fabricated with an 18.30 mm O. D. and 6.7 mm I. D. with 6.6 to 6.7 mm drilled concentric hole. Coupons were then immersed in glass bottles to perform the corrosion tests.

Preparation of *Mangifera indica* Leaves (MIL) Extract

The freshly collected green leaves of *Mangifera indica* were rinsed with distilled water to eradicate the accumulated impurities present on surface and subsequently placed in hot air oven maintained at 60 – 80°C for 3 – 4 h. After drying process, mango leaves were mechanically grounded to produce fine powder. Dried mango leaf powder (20 gm) was mixed with 200 ml ethanol and kept for 4 hours of agitation at room temperature using round bottom flask. Thereafter, filtration of obtained extract was carried out which is followed by evaporation of excess ethanol using rotary evaporator at 85°C. Lastly, the resultant concentrated MIL extract was utilized as green inhibitor in corrosion experiments. The digital photographs of eco-friendly synthesis of corrosion inhibitor using MIL ethanolic extract are illustrated in Fig. 1.

Preparation of Specimen Coupons'

Prior to every experimental run, disc shape MS samples were abraded using emery paper 200 grade. After polishing process, the disc coupons were thoroughly rinsed first with water, followed by acetone solvent and lastly allowed to dry. Later, these dried specimens were kept in desiccator to avoid any exposure or contamination.

Preparation of Corrosive Acid Solution

The aggressive corrosive 1 M acid solution from 37%, AR grade HCl solution was prepared by dilution

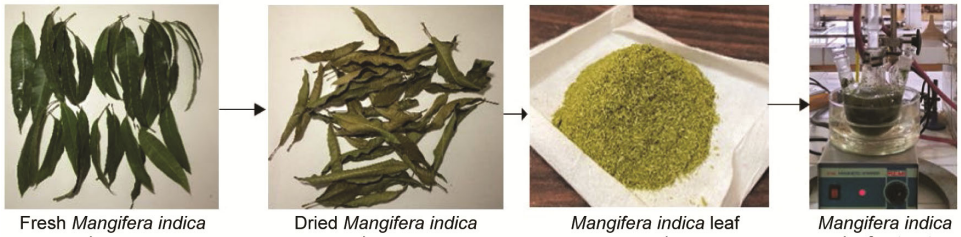


Fig. 1 — Digital photographs of synthesis of MIL extract

with distilled water. Experimental runs were carried out using MIL inhibitor concentrations of 0, 200, 400, 600, 800 and 1000 ppm. The prepared inhibitor solution was then evaluated in 1M HCl solution using glass bottles. Green synthesized mango leaves extract has been applied on MS coupons and then analyzed using weight loss method.

Weight Loss Measurement

In the weight loss experiments, initial weight of each MS sample was recorded twice and then immersed into 1M HCl corrosive solution in absence of inhibitor and in solutions containing varied MIL extract concentrations of 0–1000 ppm for the period of 13 days. The MS samples were then withdrawn from the solution, cleaned, dried and reweighed to record the loss in weight upon exposure to acid solution with and without MIL extract.

The rate of corrosion based on loss in weight at a given time was calculated using following expression (1) as,

$$C_R(\text{mm/yr.}) = \frac{87.6 \times (W_0 - W)}{(\rho \times A \times t)} \quad \ldots (1)$$

where, C_R indicates the corrosion rate in mm/yr., $W_0 \& W$ stands for loss in weight of each metal samples before and after corrosion test in corrosive acidic solution (mg), ρ represents the density of material in gm/cm^3, A denotes the specimen exposed surface area in cm^2, t is exposure time in h and the factor 87.6 is the standard conversion constant.

The inhibition efficiency expressed in % IE was evaluated from Eq. (2) as,

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

In above expression, C_{Rwo} and C_{Rwi} represents the rates of corrosion (mm/yr.) of MS coupons when exposed to corrosive acidic solution without and with MIL extract of different dosage respectively.

The degree of surface coverage (θ) was computed according to following relationship as

$$\theta = \frac{C_{Rwo} - C_{Rwi}}{C_{Rwo}} \quad \ldots (3)$$

Characterization of MIL Extract and MS Specimens

The synthesized MIL extract was characterized using a Bruker ALPHA II FTIR spectrometer (500 – 4000 cm^{-1}) at Savitribai Phule Pune University, to gain the vital insight on existence of functional groups in MIL. The FE-SEM with EDS was employed to analyze the surface morphology and determine elemental constituents of mild steel samples before and after the corrosion tests at different resolutions. The MS samples were treated with MIL extract (1000 ppm) as well as in absence of extract were utilized for analysis.

Adsorption Isotherm models

Adsorption isotherms are typically utilized to evaluate adsorption mechanism of synthesized MIL extract over the metal surface. Therefore, different adsorption isotherm models namely Freundlich, Langmuir, Flory-Huggins and Temkin were applied to the obtained corrosion inhibition experimental results.

Langmuir isotherm model can be expressed mathematically by Eq. (4) as follows[9]

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

wherein, C corresponds to concentration of MIL inhibitor used for study in g/L, K_{ads} refers to adsorption equilibrium constant in L/g.

The linear plot of Langmuir isotherm model i.e. [C/θ versus C] yields straight line with slope is near unity and R^2 close to 1. The isotherm parameter K_{ads} is estimated from the plot intercept.

The second isotherm model given by Freundlich is expressed as[9]

$$\log \theta = \log K_{ads} + n \log C \quad \ldots (5)$$

In this equation, n corresponds to slope of the plot whereas the intercept value is used to determine K_{ads}. Flory-Huggins isotherms is represented as[32]

$$\log \theta / C = \log K_{ads} + b \log(1 - \theta) \quad \ldots (6)$$

Here, the value of b is calculated from slope of $\log {}^{\theta}/_{C}$ and $\log\ (1 - \theta)$ plot while the intercept provides the value of K_{ads}.

Temkin adsorption isotherm model is expressed as[9]

$$\theta = K_{ads} + \ln C \quad \ldots (7)$$

For this model, intercept of linear plot of θ vs. $\ln C$ gives the adsorption constant K_{ads} value.

The obtained K_{ads} was used to determine the change in Gibbs free energy (ΔG°_{ads} in kJ/mol) of adsorption as follows

$$\Delta G^{\circ}_{ads} = -2.303\ RT \log\ (55.5 \times K_{ads}) \quad \ldots (8)$$

where, ΔG°_{ads} = standard Gibb's free energy change of adsorption (kJ/mol). The 55.5 constant value states molar heat of adsorption of water in solution[9], R equals gas-law constant (8.314 J.mol^{-1}K^{-1}) and T absolute temperature in K. It is noted that the negative

value of ΔG°_{ads} indicates the spontaneous adsorption process, whereas value ≤ −20 kJ mol^{-1} is associated predominantly with physical adsorption and chemical if ≥−40 kJ mol^{-1}.[32]

Predictive Model using Artificial Neural Network

Multilayer perceptron (MLP) is typically feedforward artificial neural network model comprises of multiple layers inclusive of one input layer, one output layer along with one or more hidden layers. Each neuron present in the input as well as output layer corresponds to neural network model's input and output variables respectively. Neurons in every neighbouring layer are interconnected with weighted links. The activation function takes the weighted sum of neurons inputs which introduces non-linearity to the neural network.[33] There are various algorithms reported in published literature to train the neural network such as Levenberg–Marquardt (LM), Quasi-Newton (BFG), Gradient Descent (GD), Scaled Conjugate Gradient (CG) in which model coefficients namely weights and bias values are adjusted until the sum of squared errors between predicted output and actual output is minimized.[34] In practice, optimal number of hidden neurons is usually decided via trial and error method and best fit model is selected using least mean squared error (MSE) value of the validation dataset and high value of correlation coefficient (R^2 or R-square) of training, testing and validation datasets.[24]

The relationship of targeted output of ANN model with inputs, associated weights, biases and activation function is represented as in following mathematical expression:

$$Y_m = f\ (b_m + \sum_{i=1}^{n} w_i\ x_i) \quad \ldots (9)$$

where, $x_1, x_2, \ldots, x_n$ represents input variables, $w_1, w_2, \ldots, w_n$ denotes associated weights with the input variables, b_m describes added bias term of mth hidden neuron, f represents nonlinear activation function and Y_m stands for targeted output i.e. inhibition efficiency.

It is essential to normalize the actual input and output data set before presenting it to the neural network in order to train the network more efficiently and then denormalized after the predictions from the network.[35] Later normalize dataset is randomly partitioned into three subsets namely training, testing and validation dataset respectively. In the present study, Mathworks R2024a's neural network toolbox was employed for ANN model development with one input layer comprises of four neurons based on four input variables, one output layer with one neuron for one output variable and one hidden layer. The MLP network was trained using Levenberg–Marquardt (LM) algorithm with hyperbolic tangent functions (TANSIG) in the hidden and output layer with linear function (PURELIN). Here, four operating parameters namely corrosive acid concentration, inhibitor (synthesized via green route) concentration, exposure time and temperature were utilized as the network inputs and output of network was inhibition efficiency (%). Total data sets of 181 samples after normalization were divided into three classes of training, testing and validation in a ratio of 70:15:15 randomly that is widely used in machine learning.

Subsequently, hidden-layer neurons were changed from 2 to 6 using trial and error and the optimal model with 6 neurons was selected based on minimum MSE and higher correlation coefficient. This 70:15:15 data split was implemented to ensure comprise between effective model training, parameter tuning and unbiased final evaluation of model performance, as widely employed in machine learning studies.[36]

The schematic diagram of ANN architecture utilized in present study with four input variables, hidden layer which comprises 6 neurons and one output is depicted in Fig. 2.

The performance of developed ANN model for predicting inhibition efficiency was assessed using two performance parameters namely mean squared error (called as MSE) and correlation coefficient (R^2) and are presented in Eqs 10 and 11 as

$$MSE = \frac{1}{n}\sqrt{\sum_{i=1}^{n}\left(IE_{expt.i} - IE_{pred.i}\right)^2} \quad \ldots (10)$$

Correlation coefficient is expressed as follows

$$R^2 = \frac{1}{n}\sqrt{1 - \frac{\sum_{i=1}^{n}\left(IE_{expt.i} - IE_{pred.i}\right)^2}{\sum_{i=1}^{n}\left(IE_{expt.i} - \overline{IE_{expt.i}}\right)^2}} \quad \ldots (11)$$

where, $IE_{expt.i}$, $IE_{pred.i}$ and $\overline{IE_{expt.i}}$ denotes actual/experimental inhibition efficiency, ANN model predicted inhibition efficiency of i^{th} sample and average value of experimental or actual inhibition efficiency, and here, n represents the sample size used for model development. A model with smaller values of MSE and higher value of R^2 exhibits the better performance of the model.

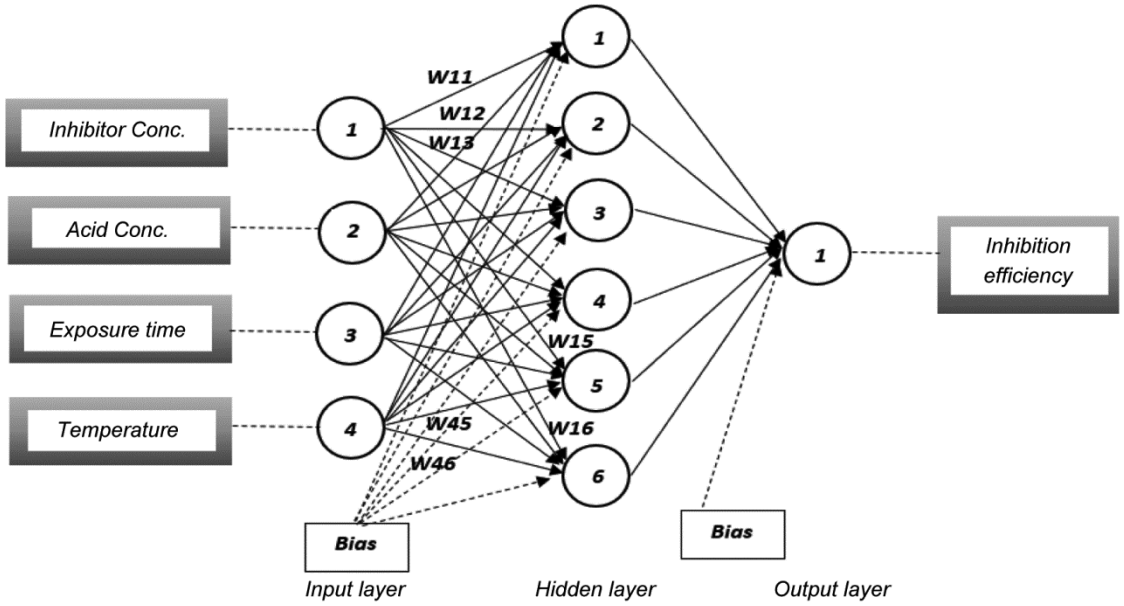


Fig. 2 — Schematic diagram of ANN model developed in this study

Table 1 — Statistical parameters of experimental data utilized for developing ANN model

Operating variable	Parameter	Minimum	Maximum	Mean	Standard deviation
Concentration of GCI (ppm)	Input	30.00	8540	856.74	1405.74
HCl Concentration (M)		0.50	2.00	0.9790	0.3380
Temperature (°C)		25.00	60.00	30.511	8.7429
Exposure time (h)		0.50	72.00	10.090	14.240
Inhibition Efficiency (%)	Output	35.00	97.00	79.144	13.486

Dataset Gathering for Model Development

In this research study, dataset of 181 samples were taken for development of prediction model of inhibition efficiency utilizing green corrosion inhibitors over the surface of mild steel using ANN. The data sets were collected from previous research studies[9,10,23,24,37–44] in which they have reported experimental data of different green corrosion inhibitors utilized for mild steel in acidic media, along with present experimental data. The authors have used different green corrosion inhibitors derived from *Arbutus unedo* leaves, Banana peel, Lemon balm, Mustard seed, Pomegranate peel, waste of lychee fruit, *Luffa cylindrica* leaves, *Hibiscus sabdariffa* leaves, *Murraya koenigii* leaves, *f Rosa canina* fruit, Jackfruit pectin, *Holoptelea integrifolia* leaves.

In present corrosion study, four key experimental factors comprise inhibitor dosage, exposure duration, acid concentration, and operating temperature affecting inhibition efficiency were taken from published literature for the network model development. The statistical parameters of present study and collected experimental data are provided in Table 1.

Results and Discussion

Weight Loss Analysis

The results of corrosion rate and percentage inhibition efficiency at 200 to 1000 ppm MIL extract after 13 days exposure in 1 M HCl are presented in Fig. 3 and Table 2. As presented in Table 2, the corresponding weight loss of MS disk treated with 1000 ppm inhibitor concentration is 0.113 gm compared to 0.383 gm for the uninhibited sample. From Fig. 3, it is observed that as the concentration of MIL extract increases from 200 to 1000 ppm in the corrosive media, the corrosion rate of MS specimens in HCl decreases and inhibition efficiency increases markedly with increase in MIL inhibitor dosage from 200 to 1000 ppm in the corrosive media. This result shows that the maximum 70.37% corrosion inhibition efficiency and minimum (1.785 mm/yr.) corrosion rate was achieved at MIL extract of 1000 ppm. Similarly, analysis of change in corrosion rate (mm/yr.) versus exposure duration of 3, 6, 10 and

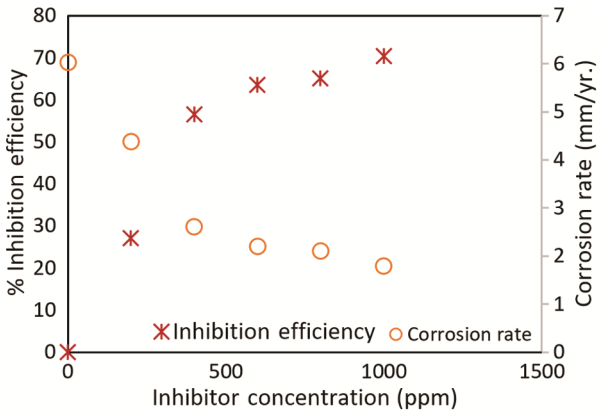


Fig. 3 — Effect of MIL Inhibitor concentrations on mild steel inhibition efficiency and corrosion rate after 13 days immersion

Table 2 — Results of weight loss experiments utilizing MS coupons in 1 M HCl after immersion for 13 days

MIL inhibitor Concentration (ppm)	Weight Loss (gm)	Corrosion Rate C_R (mm/yr.)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank (0 ppm)	0.383	6.025	—	—
200	0.276	4.394	27.07	0.2707
400	0.166	2.617	56.57	0.5657
600	0.141	2.203	63.43	0.6343
800	0.134	2.104	65.08	0.6508
1000	0.113	1.785	70.37	0.7037

13 days and varying MIL dosage (200–1000 ppm) is exhibited in Fig. 4 which clearly demonstrating the effect of the MIL inhibitor dosage on corrosion rate with time. Moreover, surface coverage (θ) values presented in Table 2 represents fraction of metal interface occupied by adsorbed inhibitor species which provides the additional insight into adsorption behaviour as it is directly related to inhibition efficiency. In addition, findings indicate that as over the MIL concentration range of 200 to 1000 ppm, the surface coverage improved from 0.2707 to 0.7037, signifying the greater extent of adsorption of several phytochemical constituents on steel substrate. This increased surface coverage reduces the active sites accessible for the favourable corrosion reactions, which lowers the corrosion rate while maximizing the inhibition efficiency.

The reduced corrosion rate alongside increased inhibition efficiency in HCl is primarily due to efficient adsorption of MIL extract onto the MS specimens' surface. The organic components including gallic acid, mangiferin and iriflophenone etc. contribute significantly for metal surface protection as demonstrated by weight loss analysis.

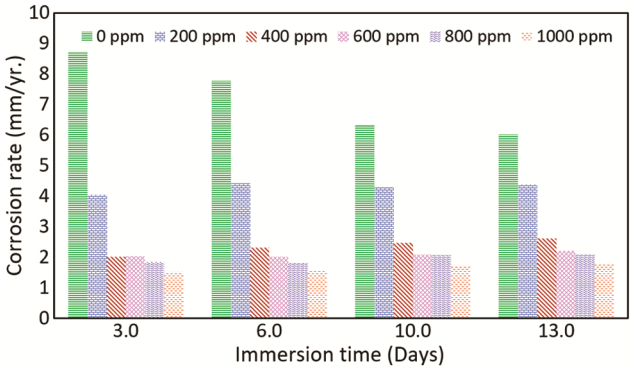


Fig. 4 — Trend in corrosion rate of mild steel with variation in immersion time at varied inhibitor concentrations

Similar decreasing trends have been reported in previous research studies.[9,10] These results reveal that role of MIL extract adsorption in suppressing the corrosion.

FTIR Analysis

The FTIR spectrum was analyzed to determine the active organic functional groups exist in MIL extract attributed to corrosion inhibition performance and results are displayed in Fig. 5. The first broad peak appeared at 3361.03 cm^{-1} implies presence of hydroxyl group which is mainly associated with phenolic and alcoholic constituents present in MIL extract. The C-H bond stretching peaks of aromatic ring appeared between 2800 to 3000 cm^{-1} along with C=C, out of plane C-H bending of phenol group were appeared 1453.14 and 1512.07 $cm^{-1}$and 1317.94 cm^{-1}. The carbonyl groups C=O in phenolic compounds alongside C-O or C-N stretching vibration were observed at 1619.32, 1703.47 cm^{-1} and 1031.37 cm^{-1} respectively. With reference to these functional groups alongside aromatic π-electron systems present in MIL extract provide active adsorption sites which actively participate in coordination bonding with the vacant *d*-orbitals of iron (Fe) atoms via lone-pair electron donation and π-*d* interactions, thus enhancing effective adsorption on the mild steel surface.[45]

Consequently, these observed functionalities of MIL extract are attributed to key phytoconstituents such as polyphenols, phenolic acids (e.g. ellagic acid and gallic acid), flavonoids (e.g. iriflophenone, mangiferin and quercetin) along with tannins and alkaloids, whose hydroxyl and carbonyl groups facilitate the deposition of interfacial protective film on the MS surface.[9]

Moreover, this is further supported through negative free energy of adsorption (ΔG°_{ads}) estimated

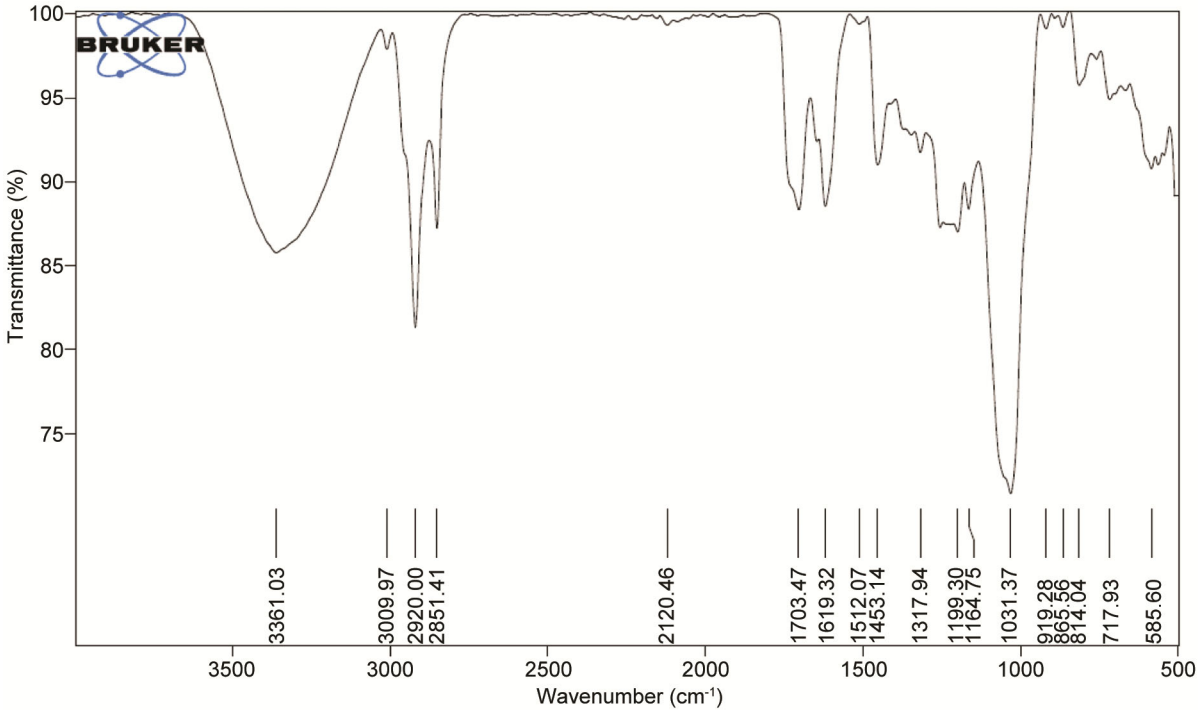


Fig. 5 — Fourier transform infrared spectral analysis of synthesized *Mangifera indica* Leaf extract

using experimental adsorption isotherm data, indicating spontaneous and energetically favourable adsorption that enhances surface coverage of the inhibitor, thereby mitigating corrosion.

Surface Analysis

The surface analysis of MS coupons immersed in 1 M HCl, untreated and treated with MIL for 13 days was analyzed using FE-SEM (Fig. 6). FE-SEM images of samples with no inhibitor are shown in Fig. 6 (a, c), whereas Fig. 6 (b ,d) exhibit samples with 1000 ppm MIL, at 30 and 10 µm resolution respectively. The morphology of MS sample displayed in Fig. 6 (a and c) clearly shows heavily corroded surface in absence of MIL inhibitor. Many black spots were clearly observed on the specimen surface due to localized pitting as exhibited in Figs 6 (a & c). However, the sample treated with 1000 ppm MIL extract exhibits smooth surface with less damage (less localized pitting corrosion spots) [Figs 6 (b & d)], due to formation of protecting MIL extract layer (white film observed). Overall, SEM result analysis clearly indicates development of protective covering from MIL constituents on the MS specimen surface significantly inhibits the extent of metallic corrosion exposure to hydrochloric acid. This observed trend of corrosion damage of mild steel specimens without and with MIL extract is in close agreement with findings of weight loss measurements. On the other hand, EDS characterization of MS specimens was also performed under uninhibited and inhibited conditions using 1000 ppm of MIL extract concentration and spectrum is presented in Figs 6 (e & f). In absence of MIL extract, the spectra mostly consist of distinctive peaks of Fe, C, O, Si and Cl with their weight percentage of C:23.81%, O: 32.02%, Si: 0.66%, Cl: 0.41%, Fe: 43.10%. In contrast, in presence of inhibitor (1000 ppm), weight percentage of O and Cl decreases to 19.73% and 0.35% whereas higher Fe concentration of 49.60% was observed. These results clearly reveal that inhibitor effectively suppresses the process of development of corrosion products namely metal oxides and chlorides onto metal substrate. Alternatively, the increase in weight percent of C from 23.81 to 28.84% further validates the enhanced interaction of MIL inhibitor with the mild steel substrate which form a protective adsorbed film on the surface.[30] Hence, it is clearly evident that adsorbed MIL extracts enhances corrosion resistance and thus suppresses the formation of corrosion products.

Adsorption Study

The adsorption mechanism of MIL on MS surface was evaluated using Langmuir, Freundlich, Flory-Huggins and Temkin adsorption isotherm plots at 298 K temperature, as shown in Fig. 7 (a–d). As clearly

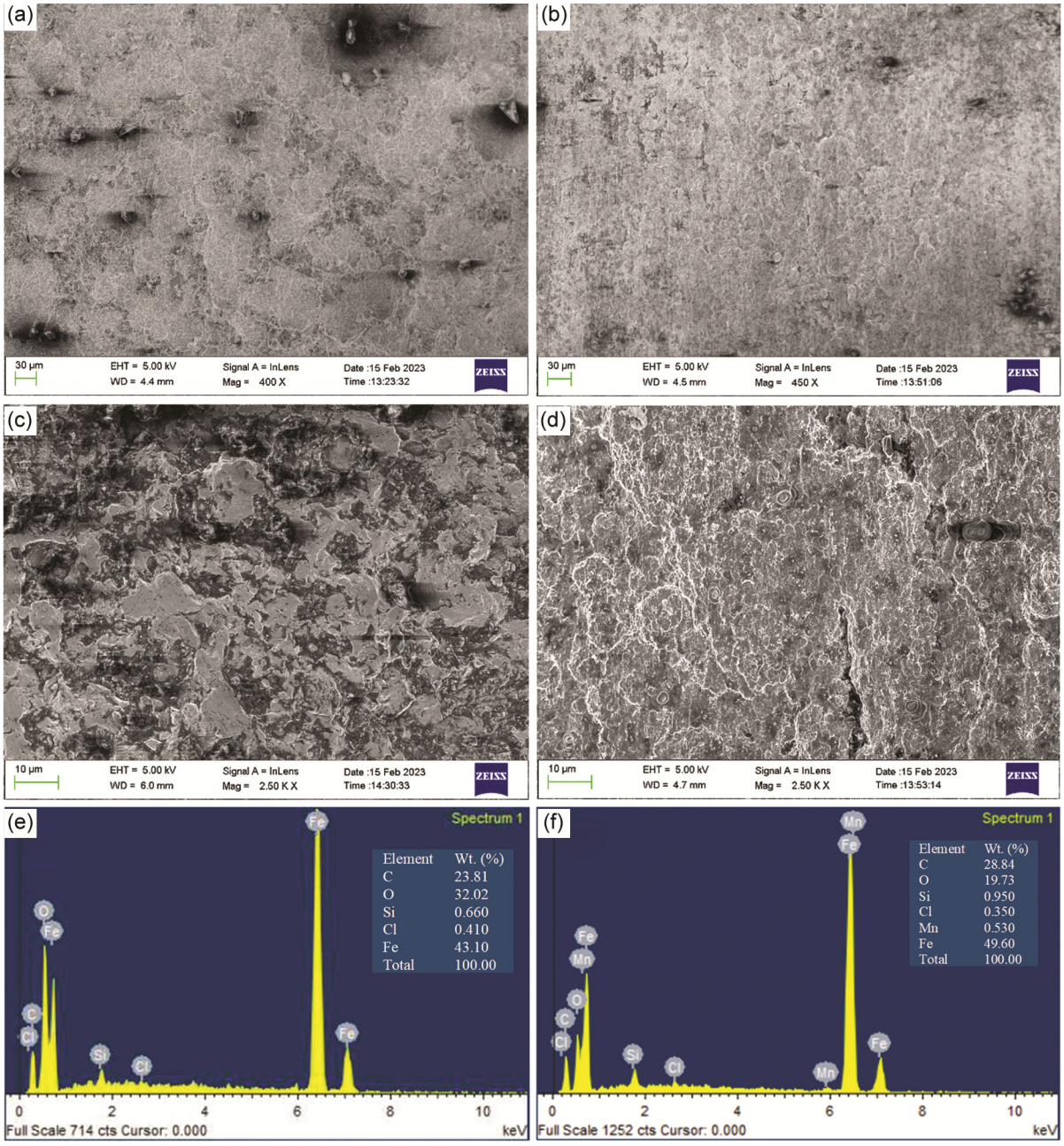


Fig. 6 — FE-SEM surface images of MS specimens exposed to 1 M HCl in (*a* and *c*) absence of MIL extract at 30 and 10 µm resolution (*b* and *d*) presence of 1000 ppm MIL extract at 30 and 10 µm, (*e* and *f*) EDS for MS coupons without and with 1000 ppm MIL extract

seen, Langmuir adsorption isotherm model provides better conformity to the experimental data with coefficient of regression value $R^2 = 0.921$ (refer Fig. 7 a). The obtained slope of the Langmuir isotherm plotis 0.943 and the value of K_{ads} is 2.26 L/g. Subsequently, Fig. 7(b) depicts R^2 value of 0.867 for the fitting of Freundlich adsorption isotherm model to experimental data and the corresponding K_{ads} is 0.779 L/g. Similarly, obtained K_{ads} from the intercept of the Flory-Huggins and Temkin isotherm plots are 1.90 L/g and 0.734 L/g with corresponding R^2 of 0.62 and 0.92 respectively. Comparison of all four adsorption isotherm models revealed that good fitting of Langmuir adsorption model for the present experimental data which confirms strong adsorption of MIL extract over the MS surface.

Moreover, computed values of Gibbs free energy of adsorption(ΔG°_{ads}) using Eq. (8) for Langmuir,

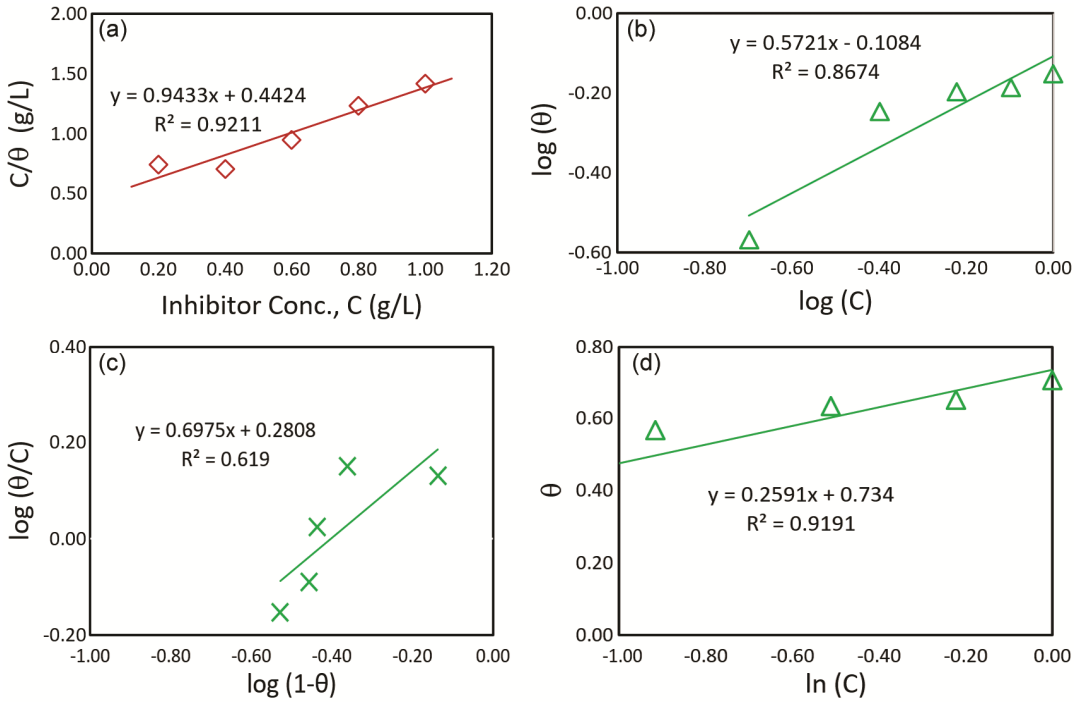


Fig. 7 — Adsorption Isotherm of MIL inhibitor (a) Langmuir (b) Freundlich (c) Flory-Huggins and (d) Temkin

Freundlich, Flory-Huggins and Temkin adsorption plots are–11.97 kJ/mol, – 9.33kJ/mol, –11.55 kJ/mol and –9.18 kJ/mol at 298 K. This negative values of ΔG°_{ads} of present findings indicates MIL adsorption is spontaneous and feasible. These results of present study are comparable with findings of earlier reported research on the corrosion inhibition performance and adsorption behaviour using *Luffa cylindrica* extract inhibitor with ΔG°_{ads}= –10.81 kJ/mol at 303 K, while the corresponding value of K_{ads}=1.36 L/g.[9] These results further confirm that adsorbed MIL constituents form protective covering on MS, enhancing corrosion resistance in acidic media.

Artificial Neural Network Results

In the present work, four input parameters were utilized to predict the inhibition efficiency using ANN approach using dataset of 181 samples. The correlation plot of ANN predicted and experimental inhibition efficiency for training, testing, validation as well as overall data set of the model is depicted in Fig. 8 which indicates that ANN model gives close predictions with good fits for all the data sets. Thus, it signifies the better predictive capability of the ANN model developed in the present study as experimental as well as predicted data points lies close to diagonal line. Moreover, R^2 value obtained from the correlation plots (refer Fig. 8) for the training, testing, validation and full dataset are 0.8269, 0.8280, 0.8798 and 0.8299 respectively, indicating reasonably good prediction accuracy. Lastly, Fig. 9 displays the variation of MSE values with the number of epochs for the trained neural network model. The figure indicates that best validation performance was obtained at the epoch twenty-two in terms of MSE i.e. 0.01021. Overall, the lower value of MSE (0.01021) and of relatively high R^2 value (0.82 – 0.87), confirm that ANN model provides better predictive performance of inhibition efficiency. Moreover, the present predictive performance findings of the developed ANN model were then compared with the machine learning models reported by Sanni *et al.*[27] for inhibition efficiency prediction utilizing egg shell extract inhibitor. In their study, the ANFIS model exhibited slightly better predictive capability than the LMBP-ANN model and obtained R^2 of 0.8523 (for both the models) for prediction of inhibition efficiency for training and 0.8345 (R^2ANFIS) and 0.8129 (R^2 LMBP-ANN) for testing dataset. This comparison results clearly revealed that the developed ANN model in this study provides reliable prediction of inhibition efficiency even though it was trained on a more diverse dataset comprising both published literature and present experimental results. Present finding clearly indicates the advantage of the inclusion of literature-derived data, as it enhances the

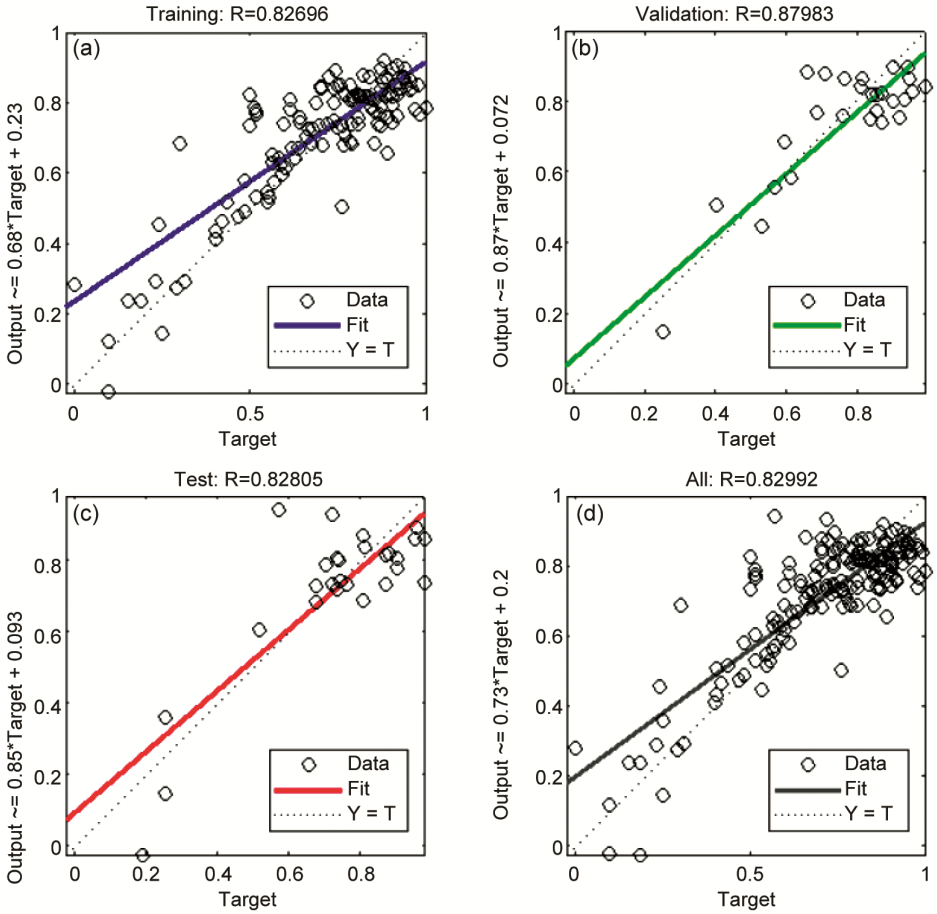


Fig. 8 — Correlation plots (R plots) between ANN predicted and experimental inhibition efficiencies for datasets of (*a*) training, (*b*) validation, (*c*) testing, and (*d*) overall

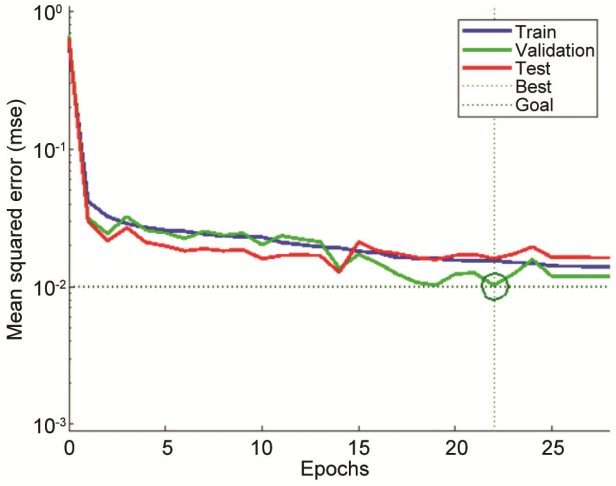


Fig. 9 — Mean squared error of the developed ANN model against no. of epochs for training validation and testing data sets

robustness and generalization of the model, enabling it to capture a wide range of experimental conditions than models developed only based on specific experimental datasets.

Conclusions

The present investigation through integration of experimental, characterization and predictive modelling approach demonstrates the corrosion potential of *Mangifera indica* leaf extract as a sustainable inhibitor for mitigating the corrosion of mild steel exposed to HCl medium, achieving the maximum inhibition efficiency of 70.37% at 1000 ppm MIL concentration. FTIR analysis, FE-SEM and EDS study and the four parameter predictive model involving artificial neural network (ANN) approach successfully predicted inhibition efficiency with high correlation coefficient. Such systematic and integrated experimental-ANN approach provides a valuable framework for predicting corrosion inhibition efficiency and thus demonstrating the potential of data-driven predictive modeling for the development of efficient corrosion protection strategies with reduced time, cost and resources. In present work, short-term immersion study integrated with ANN modeling was employed

for the evaluation of corrosion inhibition performance of MIL extract on to mild steel–HCl system. Future work may extend the modelling framework to other metal–corrosive medium and plant-derived inhibitor. This will help to develop sustainable corrosion protection strategies for applications involving acid cleaning, pickling and oilfield acidizing.

Conflict of Interest

The authors confirmed that they have no conflicts of interest associated with present work.

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