

COMPREHENSIVE VIEW OF ISOLATION/DETECTION OF PHYTOCHEMICALS FROM PLANT EXTRACT: ECO-FRIENDLY CORROSION INHIBITOR IN VARIOUS CORROSIVE MEDIA

Monisha Ravi, Sanmugapriya Ravi, Arockia Selvi J

Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur-603 203, Tamil Nadu, India.

ABSTRACT

Plants are a source of chemicals that are now being explored in diverse applications in metal deterioration prevention in most systems as a possible substitute for harmful synthetic inhibitors. Over the previous few decades, natural extracts have been used to prevent metals from corroding. The plant extracts give corrosion inhibition efficiencies above 60%. Complex phytochemicals with electron-rich sites in plant extracts interact aggressively with the metallic surface. Numerous multiple bonds and polar functional groups are typically conjugated with these phytochemicals. The presence of π electron and heteroatoms cloud in conjugation significantly reduced the degradation of metals, according to the literature. Phytochemicals are good options for green and sustainable corrosion inhibitors due to their non-toxic nature. Corrosion inhibition efficiencies shown by isolated phytochemicals are more when they are compared to the extraction of plant parts. Important electrochemical experiments are commonly performed to evaluate the efficiency of these extracts as corrosion inhibitors and to determine weight loss. The majority of components in plant extracts are adsorbed on metals according to the Langmuir adsorption model, however, a few articles also include Frumkin's equation, Flory-Huggins, El-Awady, Freundlich, and Temkin adsorption isotherms. The current review paper summarizes a body of previously published research on the issue of "Phytochemicals (active components) are isolated or detected from plant extract as corrosion inhibitors for metals and alloys in several electrolytic media."

Keywords: Plant extract, Phytochemicals, Corrosion inhibitors, Metals, Corrosive media, Corrosion Studies.

1. INTRODUCTION:

Corrosion is a natural, iterative process that exists as an environmental interactive phenomenon. As a result, pure metals and their alloys decompose into sulphides, oxides, and hydroxides, among other stable forms [1]. Nowadays, metal deterioration in the form of corrosion is one of the main problems, as metals are widely used in businesses. Because of corrosion, the industrial loss is in trillion dollars, according to an estimate, and is a global problem in many industries such as gas and oil pipelines, water transport industry, automobiles, etc. Hence, inhibitors are needed to evade defects and damage to metal [2].

In a corrosive environment, the accompany of the protective layer is developed by adding a small amount of an inhibitor which is a chemical material plays a role in decreasing the corrosion rate. The inhibitors have a wide range of uses. They are effective corrosion inhibitors for steel structures in use, namely boilers, heat exchangers, oil, gas, and container tanks. Before being treated, metals are frequently exposed to acidic media (e.g., coating, welding, painting, or greasing). Corrosion products are also removed from damaged infrastructures such as pipelines, heat exchangers, petroleum wells, and tankers using acidification.

Inhibitors are effective in preventing corrosion reactions and related metal damage in some essential procedures. The choice of inhibitors is influenced by several important factors. The toxic effects of the inhibitor are one of the most critical considerations. Hazardous chemical inhibitors, including chromates, phosphates, and nitrates, for instance, are very volatile and produce noxious fumes that are detrimental to the environment [3].

Plant extraction is an option that can be employed in an environmentally beneficial manner. According to a literature review, several plant components such as bark, seeds, fruits, roots, roots, and flowers are commonly used as corrosion inhibitors. The leaf extract has the greatest overall protection effectiveness at low concentrations. Phytochemical compounds are primarily formed in the leaves assisted by the sun, H₂O, and carbon-di-oxide. Aqueous and organic extracts are the two types of extracts that are extensively utilized as metal deterioration reducers in a wide range of electrolytic systems for various metals and alloys [4].

Numerous studies have already documented that the several plant extracts as effective green corrosion inhibitors in various acidic conditions. The *Asparagus racemosus* leaves for MS specimens in 0.5M H₂SO₄ showed 93.25% inhibition efficiency at 100 mgL⁻¹ [5]. The *Allium sativa* showed 100% inhibition efficiency for mild steel in 0.5M HCl and 0.5M H₂SO₄ at 20% of its extract [6]. The *Robinia pseudoacacia* leaves for Mild Steel in 0.5M HCl showed 92%

inhibition efficiency at 2.00gL^{-1} at 25°C [7]. The *Robinia pseudoacacia*. L fruit for Bronze Alloy in 0.5M NaCl Showed 93.5% inhibition efficiency at 1800ppm [8]. *Magnolia grandiflora* for Q235 steel specimen in 1M HCl showed 85% inhibition efficiency at 500mgL^{-1} [9]. *Parthenium hysterophorus* for mild steel in 1M HCl showed 84% inhibition efficiency at 1100mgL^{-1} [10]. *Newboutlia laevis* for Aluminium alloy AA7075-T7351 in 1M HCl showed 86.1% inhibition efficiency at 0.6gL^{-1} [11]. *Acacia coninna* pod for Mild steel in $0.5\text{M H}_2\text{SO}_4$ showed 94% inhibition efficiency at 520mgL^{-1} [12]. *Sapindus mukorassi* fruit for Aluminium in 1M HCl showed 98% inhibition efficiency at 2000ppm [13]. *Myristica fragrans* fruit for Mild steel in $0.5\text{M H}_2\text{SO}_4$ showed 87.81% inhibition proficiency at 500mgL^{-1} [14].

The use of isolated active components (Phytochemicals) from the plant extract as a corrosion inhibitor is of interest, because of their more inhibitory efficiency than the direct usage of plant extract and their environmental acceptability and bio-degradable nature. Due to these benefits, isolated phytochemicals and extracts from several common plants have been tested as corrosion inhibitors for metals and alloys in various conditions. The major goal of this work is to give bibliophiles an overview of the extracted active constituents from plants that are used to prevent different metals from corroding. In addition, a brief description of the methodology employed in the corrosion inhibition study is summarized.

2. EXPERIMENTAL METHODS AND CONDITIONS OF CORROSION INHIBITION:

2.1 Methods Used for Phytochemicals Extraction, Isolation, and Detection:

Extraction is a critical step for segregating desirable natural products from raw components. The following processes are included: distillation, solvent extraction, pressing, Soxhlet extraction, and sublimation. Solvent extraction is the most common method. Modern extraction technologies are used for procuring optimal outcomes. Sublimation, expeller pressing, and enflourage are three extraction methods that are no longer routinely used for phytochemical analysis. The following steps are taken to remove the phytochemical: (i) Solvent entry into the solid matrix (ii) solute diffusion in the solvent (iii) Solute dispersion from the solid matrix and (iv) accumulation of retrieved solutes [15].

In the identification and characterization of bioactive constituents, separating active constituents with varying polarity from plant extracts remains a significant challenge. To produce pure constituents, different separation techniques are commonly used, such as Over Pressured Layer Chromatography (OPLC), High-Performance Thin Layer Chromatography

(HPTLC), Column Chromatography (CC), Thin Layer Chromatography (TLC), Paper Chromatography, Gas Chromatography-Mass Spectrometry (GC-MS), and High-Performance Liquid Chromatography (HPLC). Following that, pure and active chemicals are employed in corrosion applications [16].

2.1.1. Column Chromatography (CC):

In the separation process, the column is sometimes referred to as the "heart of chromatography.". In order to create repeatable and reliable operations, stable, high-performance stationary phases and columns are essential. Because of its constant strength and stiffness, relative inertness, and capacity to undergo chemical change, silica is the most often used column packing material. To improve the morphology and physicochemical properties of these silica materials, numerous adjustments have been made. Fully porous silicon microspheres [octadecyl-silica (ODS-silica)] are often used in HPLC columns because they provide numerous essential advantages such as high sample loading, durability, and widespread commercial availability [17].

For instance, a study on the extraction of *Neolamarckia cadamba* alkaloids using maceration techniques subsequently subjected to acid-base treatment was the most effective, with dichloromethane as a solvent. This crude alkaloid extract is again subjected to column chromatography to isolate the active phytochemical namely, 3 β -isodihydrocadambine which serves as an inhibitor in 1M HCl on mild steel [18]. *Artemisia pallens* extraction is done by maceration techniques using aqueous MeOH and their active constituents like Arbutin are isolated using column chromatography techniques. This active constituent is used as a corrosion inhibitor in 1 molL⁻¹ HCl on mild steel [19]. *Opuntia elatior* fruit extraction is done by the reflux method using ethanol and its main constituent opuntiol is isolated by CC which is utilized as a corrosion inhibitor in 1M H₂SO₄ & 1M HCl on mild steel [20]. *Alpinia galanga* extraction is done by the Soxhlet extraction using n-hexane and their active constituent 1'-acetachaviol acetate is isolated by CC. This phytochemical is used as a inhibitor in 1M Hydrochloric acid on mild steel [21]. The extraction of *Ochrosia oppositifolia* was done by the maceration method using hexane, 10% ammonia, and dichloromethane, and they are phytochemicals like isoreserpiline which is isolated using CC and utilized as a corrosion inhibitor in 1M HCl for Mild Steel [22].

2.1.2. Gas Chromatography-mass spectrometry (GC-MS):

Gas chromatography- mass spectrometry (GC-MS) is a method for recognizing each chemical compounds within a test sample that combines the features of gas chromatography and mass spectrometry. GC separates the volatile and thermally stable substitutes in a sample, while GC-MS fragments and identifies the mass of the analyte. An analytical method is suitable for measuring the concentration of an API in a specific compound concentration form. This enables the employment of simple procedures to validate the analysis procedure and produce a consistent measurement of an active ingredient in a chemical mixture [23,24].

For instance, in the GC-MS of *Ficus hispida* leaves extract (Figure 2), 9 volatile organic compounds were identified. The notable compounds include 2,3-dihydro-3,5-dihydroxy-6-methyl-pyran-4-one (0.12%), neophytadiene (1.35%), palmitic acid (1.16%), phytol (1.43%), ethyl linoleate (0.34%), sitosterols (2.91%) 2-(benzyloxymethyl)-5-methyl furan (0.06%), and 5-(hydroxymethyl)-2-Furan carboxaldehyde (0.14%). The retention time (RT) of the Stigmasterol phytochemical (RT 32.94 having a maximum area of 82.38%) was revealed to be a major compound [25]. Furthermore, the chemically active components recognized using gas chromatography-mass spectroscopy analysis of ethanolic extract of *Kleinia grandiflora* leaves (Figure 3) revealed that the total compounds were higher. The quinic acid (32.18%) was detected to be the major component, followed by 6-deoxy D-galactose (2.75%), hexadecanoic acid (5.89%), linolenic acid (2.44%), 2-ethoxycarbonyl-5-oxopyrrolidine (1.98%), tetradecamethylcycloheptasiloxane (1.68%), [(2-fluorophenyl) methyl]-H-purin-6-amine (2.17%), and 9-octadecenyl ester-9-hexadecenoic acid (1.82%) [26]. The gas chromatography-mass spectroscopy study of the methanolic leaves extract of *Pongamia pinnata* (Figure 4) revealed the presence of 38 phytochemical components. The highest concentration of the compound found in the *Pongamia pinnata* leaves extract are: 3,7,11,15 – tetramethyl-2-hexadecane-1-ol; N,1-dimethyl-; (Z) 6, (Z) 9-pentadecadien-1-ol; hexadecanoic acid, methyl ester; 3-hexadecene, (Z); methyl ester, (Z, Z, Z)-; n-hexadecanoic acid; 4-piperidinamine, 9,12,15-octadecatrienoic acid, 3,7,11,15-tetramethyl-2-hexadecane-1-ol; octadecanoic acid; 2H-1-benzopyran, 6,7-dimethoxy- 2,2- dimethyl [27].

The presence of the major organic components in the extract is revealed to be the primary factor of the inhibitory efficiency, according to the GC-MS analysis.

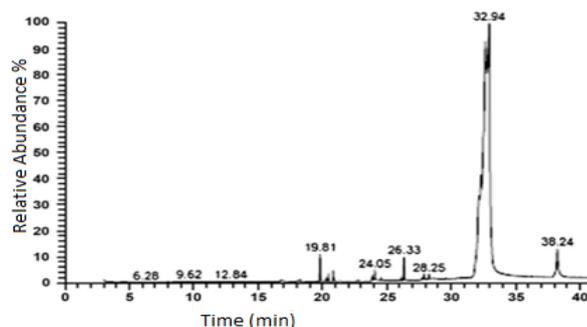


Figure 2. GC-MS spectrum of *Ficus hispida* Leaves Extract [25].

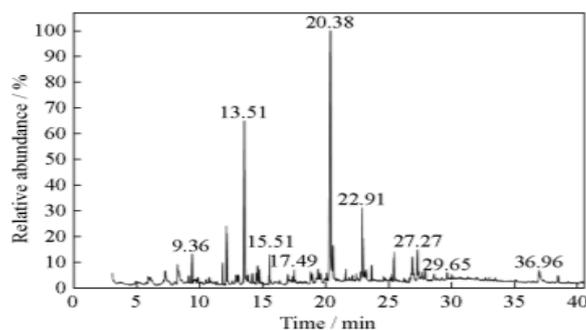


Figure 3. GC-MS spectrum of *Kleinia grandiflora* leaf extract [26].

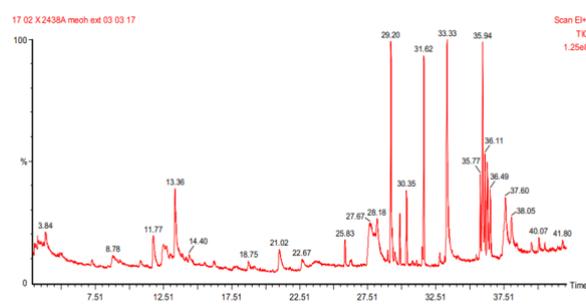


Figure 4. GC-MS of *Pongamia Pinnata* methanolic leaf extract [27].

2.2 Detection Methods:

2.2.1 Fourier-transform infrared spectroscopy (FT-IR):

Fourier-transform Infrared Spectroscopy is an advantageous method for identifying functional groups in plant extracts. It helps with molecular identification and structural characterization. FT-IR is a high-resolution analytical approach for detecting chemical components and determining structural compounds. Plant extracts or powders can be fingerprinted using FT-IR in a rapid and non-destructive manner [16].

For illustration, the *Neolamarckia cadamba* extract (Figure 5) as an eco-friendly corrosion inhibitor for mild steel in 1M HCl media described the FT-IR spectra of the uncontaminated alkaloid which revealed a phytochemical like 3 β -isodihydrocadambine and, a scraped shielding

layer was seen over the mild steel surface. The FT-IR spectra of 3 β -isodihydrocadambine showed peaks that may be assigned to O-H, N-H stretches, N-H bends, carbonyl of a methyl ester, and aromatic C=C stretches (indole moiety). Spectra of the protective film show a shift in the carbonyl peak combined with the N-H bending peak and with the aromatic C=C peak to produce a wide absorption group. These findings revealed that the aromatic indole moiety, as well as carbonyl bands of 3 β -isodihydrocadambine phytochemicals, might have a role in metal deterioration reduction [18]. Likewise, the FT-IR spectra of an *Opuntia elatior* fruit extract (Figure 6) reveal an environmentally friendly, mild steel corrosion inhibitor in an acid medium (1M HCl & H₂SO₄). The phytochemicals 6-hydroxymethyl-4-methoxy-2H-pyran-2-one (opuntiol) reveal a monomeric hydroxyl group around 3405 cm⁻¹, as well as a significant assimilation group of 1690 cm⁻¹, indicating the presence of a -C=O band in the isolated molecule. [20]. Furthermore, the green corrosion inhibition by alkaloid extracts of *Ochrosia oppositifolia* and its phytochemical-like isoreserpiline (Figure 7) against mild steel in a 1M HCl medium shows the FT-IR spectrum of isoreserpiline, as well as its scratched protective film formed over mild steel using the Potassium Bromide (KBr) pellet method. The FT-IR spectra of the phytochemical isoreserpiline and its protective layer demonstrated that the phytochemical isoreserpiline is adsorbed on the mild steel surface, protecting it from strong acid corrosion. This suggested that the lone pair electrons of the N-H group (pyrrole ring) and the π -electron clouds of the phenyl ring play a role in the isoreserpiline's coordination with the mild steel surface. As a result, the FT-IR studies have made it possible to detect the active coordination sites in multi-ring molecules [22].

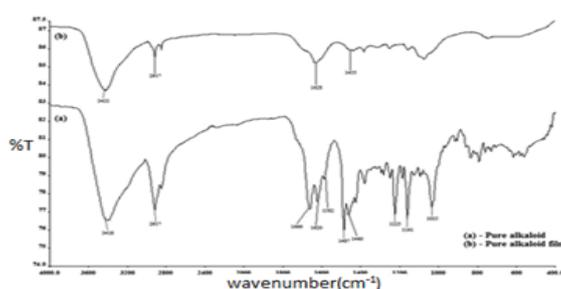


Figure 5. FT-IR absorption spectra for (a) 3 β -isodihydrocadambine, and (b) protective film formed by 3 β -isodihydrocadambine [18].

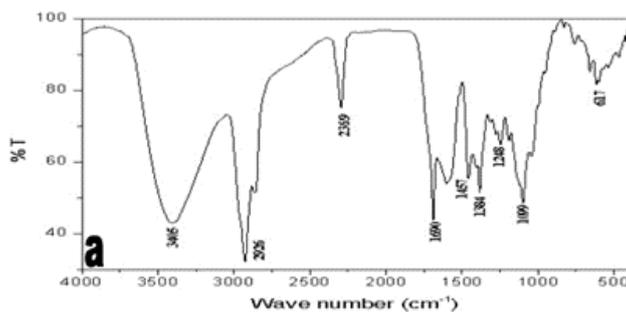


Figure 6. FT-IR absorption spectrum of opuntiol [20].

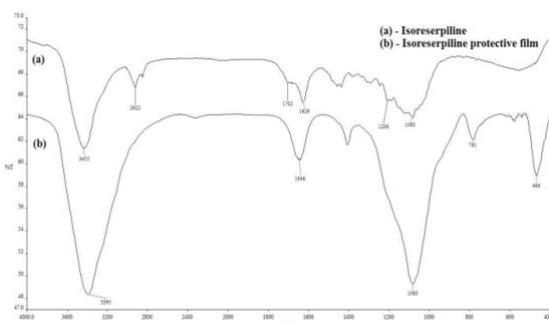


Figure 7. FT-IR absorption spectra for (a) Isoreserpiline and (b) protective film formed by Isoreserpiline [22].

2.2.2 Nuclear Magnetic Resonance (NMR):

Physical, chemical, and biological aspects of materials may all be determined via Nuclear-Magnetic Resonance spectroscopy. The use of a one-dimensional approach is common. However, two-dimensional NMR techniques might be utilized to produce the intricate structure of the molecules. NMR spectroscopy, which records the differences between the various magnetic nuclei offers a clear image of where these nuclei are in the molecule, allowing many researchers to investigate molecules. It will also display which atoms are present in neighbouring groupings. It will also be able to determine the number of atoms present in each of these conditions in the future. Individual phenols have been isolated using column chromatography, liquid chromatography, and preparative or semi-preparative thin-layer chromatography in the past, with the structures verified by NMR offline later [16].

In the investigation of green corrosion inhibition by alkaloid extracts of *Ochrosia oppositifolia* and its phytochemical isoreserpiline against mild steel in a 1M HCl medium, the ^1H -NMR and the ^{13}C -NMR confirmed the structure of phytochemical isoreserpiline using CDCl_3 at 400 MHz and 100 MHz [22]. Furthermore, the essential phytochemical ingredients of *Valeriana willichii* extract were established by ^1H NMR that is used as long-lasting corrosion inhibitor for Mild steel in a corrosive environment (which contains Naphtholic acid, Iridoid, Analogue), = 6–7

respectively. The absorbance of the inhibitor solution before immersion of mild steel for about 24 hours is higher than that after immersion. The development of a complex between Fe^{2+} particles and inhibitor molecules can be illustrated by a change in the value of the absorption maximum or the absorbance point value. [28]. Similarly, UV-visible absorbance of *Catharanthus roseus* extract in 3.5% NaCl solution (Figure 10) shows the $\pi-\pi^*$ absorption due to flavonoid active species, with peaks at 380 and 350nm before immersion of Mild steel. But, the absorption wavelength of *Catharanthus roseus* extracts reduced from 350nm to 330nm after immersion of mild steel specimen for about 24 hrs. The reason might be attributable to bisindole chemisorption on the antithetical Mild Steel surface. The strong assimilation group of the stalk segregate at 380nm is linked to the electrical transition among the $\pi-\pi^*$ and $n-\pi^*$ levels. The synergy of polyphenolic blends on the Mild Steel surface causes the assimilation groups from each extract to differ significantly from those from isolated phytochemicals. The adsorption of extract molecules on the mild steel surface is supported by UV-vis absorption spectroscopy [31]. The absorption band at 200nm - 215nm was formed by the $n-\pi^*$ and $\pi-\pi^*$ transitions, which described the amine groups, ester, and carboxyl. Most conjugated molecules in aromatic and poly-aromatic compounds had $\pi-\pi^*$ electron transitions, which were associated with the other absorption band around 260nm–280nm. When they compared the UV-Vis spectrum of Radish Leaf Extract (which contains phytochemicals like O-Coumaric acid, Folic acid, Ascorbic acid, and Catechin) (Figure 11) to the UV-Vis spectrum of mild steel immersed solution containing radish leaf extract, they noticed a blue shift in absorbance peaks, indicating the formation of a complex between the extract molecules and Fe^{2+} ions [32].

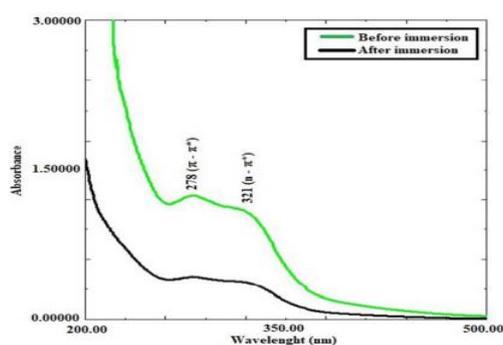


Figure 9. UV-vis absorption Spectra of *Valeriana willichii* extract (containing phytochemicals like Naphtholic acid, Iridoid, and Analogue) after and before immersion of Mild Steel in 0.5M sulphuric acid for 24 hrs at 298 K [28].

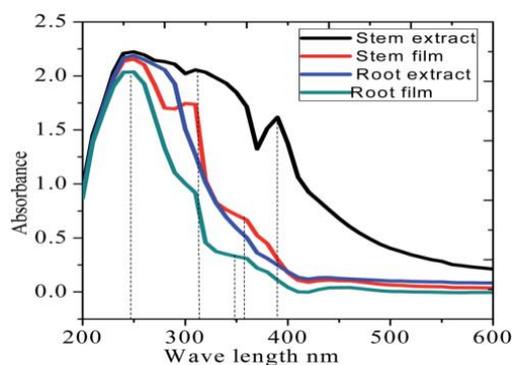


Figure 10. UV-vis absorption spectra of the *Catharanthus roseus* extract before and after Mild Steel immersion in 3.5% sodium chloride [31].

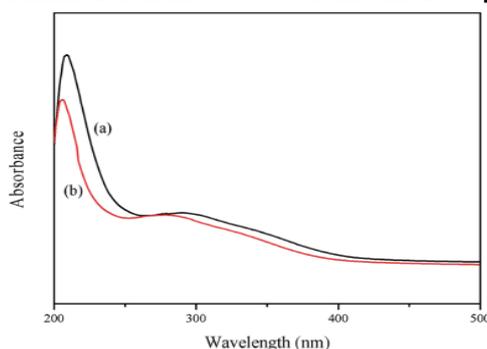


Figure 11. UV-vis spectra of Radish Leaf Extract (containing phytochemicals like O-Coumaric acid, Ascorbic acid, Folic acid, and Catechin,) (a) before and (b) after immersion of mild steel in 0.5M H₂SO₄ [32].

2.3 Corrosive Media:

2.3.1 Corrosion inhibition in hydrochloric acid (HCl):

The metallic surface frequently requires the elimination of rusts as well as flakes using powerful acids namely, sulphuric acid (H₂SO₄), hydrochloric acid (HCl), nitric acid (HNO₃), and phosphoric acid (H₃PO₄). This process of acid pickling is the name given to the process of acid cleaning. Industrialists often use concentrated HCl electrolytes to remove surface impurities through descaling and cleaning methods since HCl is less pricey and more spontaneous than H₂SO₄. Because of HCl is more reactive than H₂SO₄, pickling is usually done at a lower temperature in hydrochloric acid solution, whereas sulphuric acid pickling necessitates an elevated temperature. The remaining chloride (Fe²⁺ or Fe³⁺) generated by the HCl pickling procedure is easier to rinse off than residual sulfates (Fe²⁺ or Fe³⁺) created by the sulphuric acid pickling method. Nonetheless, all of these methods are highly corrosive and result in significant economic losses, particularly in industries. As a result, inhibitors are the most important source of corrosion protection [4,1].

Several phytochemicals from plant extracts have recently been employed as efficient HCl system inhibitors. *Cryptocarya nigra* extraction is done by cold percolation and maceration method using n-hexane & CH₂Cl₂ respectively, and their phytochemicals namely, N-methylisococlaurine **1**, N-methyl-laurotetanine **2**, & atherosperminine **3** is isolated by CC which is used as a metal deterioration inhibitor in 1M HCl on mild steel. *Cryptocarya nigra* dichloromethane extract (CNDE) and **2** inhibited corrosions strongly by a charge transfer mechanism, with an inhibition efficiency of 91.05 % and 88.05 %, respectively, at 500ppm, according to an electrochemical impedance investigation. Data from potentiodynamic polarisation revealed that CNDE worked as an anodic type inhibitor, whereas **2** was a mixed type inhibitor with anodic efficacy [33]. *Oxandra asbeckii* extraction is done by acid-base extraction using CHCl₃ and their phytochemicals like Liridenine, azafluorenones, alkaloids, triterpenoid are isolated by CC which is used as a corrosion inhibitor in 1M HCl on C-38 steel. *Oxandra asbeckii* plant extract (OAPE) is a mixed-type inhibitor, according to cathodic and anodic polarization curves. The effect of temperature on the corrosion behaviour of C38 steel in 1M HCl with and without the addition of plant extract was studied throughout a temperature range of 25-55oC. The adsorption of this plant extract on the C38 steel surface is governed by the Langmuir adsorption isotherm. By using surface analysis, the ability of this plant extract to prevent corrosion in HCl solution was also identified. An electrochemical impedance study showed that the *Oxandra asbeckii* plant extract reduced the corrosion significantly with an inhibition efficiency of 92% at 100mgL⁻¹[34]. *Dioscorea septembla* extraction is done by the reflux method using 75% ethanol and their phytochemicals like Dioscin, Dioscorone, β-sitosterol, and palmitic acid are identified by FT-IR, ¹H NMR, ¹³C-NMR which are used as a corrosion inhibitor in 1M HCl on Carbon Steel. The electrochemical Impedance study showed that Organic phase extract and water phase extract of *Dioscorea septembla* showed inhibition efficiency of 72.1% and 65.3%, respectively at 2.0gL⁻¹. Potentiodynamic Polarization data showed that the inhibition efficiency of Organic phase extract and water phase extract of *Dioscorea septembla* is 89.2 % and 82.8% respectively at 2.0gL⁻¹. Also, the polarization tests exposed that the anodic and cathodic parts of the potentiodynamic polarization curves for both extracts increased in more positive directions with an increase in temperature [35].

2.3.2 Corrosion rate in Sulphuric acid (H₂SO₄):

Electrolytes based on sulphuric acid (H₂SO₄), which are identical to HCl, are often used for basic corrosion inhibition techniques. High concentrations of H₂SO₄ are utilised in industrial applications such as acid pickling, acid descaling, and cleaning. Pickling with sulphuric acid

demands a higher temperature than pickling with hydrochloric acid. H₂SO₄-oriented electrolytes are extremely hazardous, specifically in manufacturing sectors; as a result, corrosion inhibitors, which are external additions, are required [4]. Several phytochemicals obtained from plant residues are found as excellent metal deterioration inhibitors in H₂SO₄-oriented electrolytes with the help of various spectroscopic methods.

For Specimen, *Oryza sativa* is extracted by maceration and distillation with ethyl alcohol, and its phytochemicals, such as β -Sitosterol (β -sitosterol-3-O- β -D-glucoside), are utilized as a metal deterioration reducer in 1M H₂SO₄ on Mild Steel. Isolated β -sitosterol was identified to be a good corrosion inhibitor in electrochemical experiments. The optimal inhibition efficiency of β -sitosterol was 95% at 500ppm. According to polarisation studies, β -sitosterol is a mixed-type inhibitor that regulates mutually the anodic as well as cathodic procedures [29]. Radish leaf extracts are made using ethyl alcohol and their phytochemicals, such as ascorbic acid, folic acid, catechin, and O-coumaric acid, are utilized as corrosion inhibitors in 0.5M H₂SO₄ on mild steel. The inhibitory performance increased with the concentration of Radish Leaf Extract but decreased as the temperature increased. The inhibition performance with 300 mgL⁻¹ at 298 K was 93 %. Radish Leaf Extract was found to be a mixed-type inhibitor. The bioactive constituents in Radish Leaf Extract adsorb on the surface of mild steel to prevent corrosion, which was the inhibitory mechanism. Physical and chemical adsorption happened when the Langmuir adsorption isotherm was followed. Folic acid and catechin had a stronger influence on the corrosion inhibition of Radish Leaf extract, according to theoretical simulations. After 28 days, radish leaf extract deteriorated at an 82% rate [32]. *Aloe* plant extract, extraction is done by maceration & distillation process using ethyl alcohol and their phytochemicals like Aloesin, Aloin, Aloe & Aloe Resin is used as a corrosion inhibitor in 1M Sulphuric acid on stainless steel. Direct Current polarization proved that the Aloe extract could be classified as a mixed-type corrosion inhibitor with predominantly anodic action. The Langmuir isotherm shows the adsorption of Aloe extract on the surface of stainless steel was based on physical interaction. Electrochemical Impedance study, Polarization study, and Electrochemical Noise revealed that 98%, 96%, and 96% corrosion inhibition efficiency of this plant extract at 30% v/v respectively [36]. *Coptis chinensis* extraction is done by maceration & distillation process using ethyl alcohol and their phytochemicals like Berberine are implemented as a corrosion inhibitor in 1M H₂SO₄ on mild steel. For berberine concentrations greater than 5.0x10⁻³M, inhibition efficiency measured by the weight loss test can reach approximately 98 %. Potentiodynamic results showed that for berberine concentrations more than 1.0x10⁻⁴M, both

anodic and cathodic processes are reduced, while smaller values primarily inhibit cathodic reaction. [37].

2.4. Effect of temperature:

Corrosion on metal surfaces is greatly influenced by temperature. Phytochemicals from plant extracts mixed with inhibitors can modify the interaction between hostile media and the metal and alloy surface. Some phytochemicals have a propensity to lose inhibitory efficacy as temperature rises. Other extracts, on the other hand, demonstrate a variety of behaviors [38]. Most of the time, the inhibition efficacy dropped as temperature increased, demonstrating that the procedure is most effective at room temperature or below. When using mild steel in high-temperature applications, the fact that inhibitory efficiency was often high at high temperatures can be advantageous [39]. As a result, determining the inhibitory efficacy since a function of temperature is significant, as each extract may operate differently.

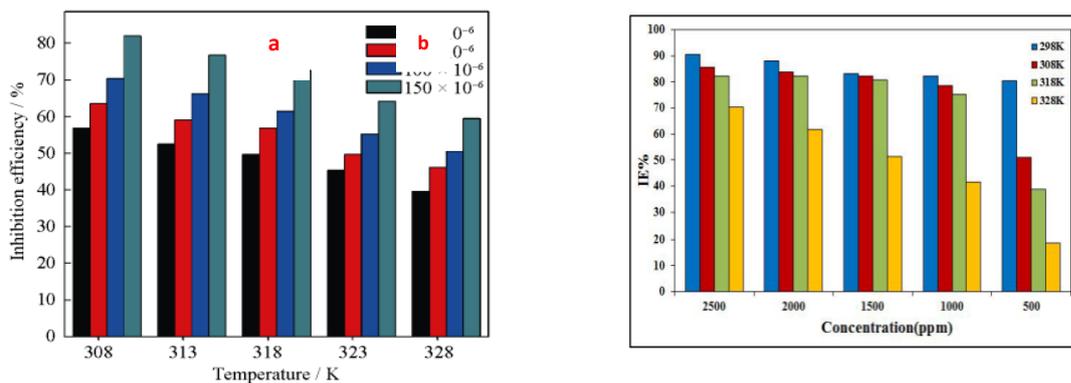


Figure 12. (a)Inhibition effectiveness of *Kleinia grandiflora* leaf extract varies with temperature (containing phytochemicals like 6-deoxy D-galactose, hexadecanoic acid, linolenic acid, etc.,) [26]. (b)Dissimilarity of inhibition efficiency with varying concentrations of *Ficus racemosa*(Hexadecanal, Octadecanal, Squalene, Vitamin, Stigmasterol, etc.,) stem extract at different temperatures [40].

For illustration, *Pimentadioica* contains phytochemicals like Eugenol as a corrosion inhibitor for Mild Steel dipped in 1M HCl. At a 0.13 (v/v percent) concentration and 303K temperature, this extract had a maximal inhibitory efficiency of around 99.35 %. With increasing concentrations of *Pimentadioica* extracts and its phytochemical eugenol, electrochemical impedance studies reveal an increase in charge transfer resistance and a decrease in double-layer capacitance. Polarization data suggest that *Pimetadioica* extracts show mixed-type behavior of corrosion inhibition. The same is the observation for eugenol. Adsorption investigations demonstrated that the Langmuir adsorption isotherm absorbed both *Pimentadioica* extracts and eugenol on the mild steel surface. [41]. *Magnolia grandiflora* also

includes phytochemicals that act as corrosion inhibitors on Q235 steel submerged in 1M HCl. At a 500mg/L concentration and 298K temperature, this extract had maximal inhibitory effectiveness of around 85 percent. The G_{ads}° is 27.7 kJ/mol, indicating that the *Magnolia grandiflora* Leaf Extract exhibits both physical as well as chemical adsorption on the surface of Q235 steel. *Magnolia grandiflora* extract adheres to the Langmuir single-layer adsorption model at the Q235 steel/solution interface [42]. The presence of phytochemicals such as n-hexadecanoic acid in *Tephrosia purpurea* leaf extracts as a possible mild steel corrosion inhibitor in 1N HCl media has been established by GC-MS. *T. purpurea* leaves extracts efficiently prevent metallic separation response, with optimal inhibitory efficiency of 95.4 % in 1N hydrochloric acid at 300 ppm, according to gravimetric and electrochemical experiments. *T. purpurea* has mixed-type behavior, according to Tafel polarization measurements. The Langmuir isotherm is observed to govern the adsorption of the *T. purpurea* leaves extract [43].

Table 1: Evaluation of plant extracts as corrosion inhibitors for several metals and alloys in different corrosive mediums: Plant name, Phytochemicals, Extraction solvent, and the Metals or alloys used for corrosion inhibition performance tests, concentration, corrosion inhibition efficiency, and Isotherm model:

S. No.	Plant Names	Phytochemicals	Extraction Solvents	Corrosive medium	Metal or alloy	Corrosion Inhibition Efficiency	Concentration	Isotherm Model	Reference
1.	<i>Neolamarckia cadamba</i>	3 β -isodihydrocadambine	Hexane, dichloromethane	1M HCl	Mild Steel	80%	5mgL ⁻¹	Langmuir	[18]
2.	<i>Artemisia pallens</i>	Arbutin	Aq. methanol	0.1 Mol L ⁻¹ HCl	Mild steel	93%	400mgL ⁻¹	Langmuir	[19]
3.	<i>Opuntia elatior</i>	Opuntiol	Ethanol	1M H ₂ SO ₄ & 1M HCl	Mild Steel	73%	50ppm	Temkin	[20]
4.	<i>Alpinia galanga</i>	1'-acetochavicol acetate	n-hexane	1M HCl	Mild Steel	84.6%	1000ppm	Langmuir	[21]
5.	<i>Ochrosia oppositifolia</i>	Isoroserpiline	Hexane, dichloromethane	1M HCl	Mild steel	>85%	20-25mgL ⁻¹	Langmuir	[22]
6.	<i>Ficus hispida L.</i>	Stigmasterol	Ethanol	1M HCl	Mild Steel	90%	250ppm	Langmuir	[25]

7.	<i>Kleinia grandiflora</i>	6-deoxy D-galactose, hexadecanoic acid, linolenic acid, etc.,	Ethanol	1M H ₂ SO ₄	Mild steel	85.09% at 18 hr	150 × 10 ⁻⁶ M	Langmuir	[26]
8.	<i>Pongamia Pinnata</i>	4-piperidinamine, hexadecanoic acid, N,1-dimethyl-; (Z)6, (Z)9-pentadecadien-1-ol; etc.,	Methanol	1N H ₂ SO ₄	Mild steel	94.6%	100ppm	Temkin's	[27]
9.	<i>Valeriana willichii. R</i>	Naphtolic acid, Iridoid, Analogue	Ethanol	0.5M H ₂ SO ₄	Mild Steel	93.47%	500mgL ⁻¹	Langmuir	[28]
10.	<i>Oryza sativa L.</i>	β – sitosterol	Methanol	1M H ₂ SO ₄	Mild Steel	95%	500ppm	Langmuir	[29]
11.	Apple pomace	C ₂₆ H ₅₀ NO ₇ P, C ₃₁ H ₄₃ N ₅ O	Liquid Extract	3.5% NaCl brine.	C1010 Mild Steel	98.8%	3% v/v	Langmuir	[30]
12.	<i>Catharanthus roseus</i>	Polyphenolic	Ethanol	3.5% NaCl	Mild Steel	70%	3.5 wt%	-	[31]
13.	<i>Radish Leaf Extract</i>	Folic acid, Catechin, O-Coumaric acid, Ascorbic acid	Water, methanol	0.5M H ₂ SO ₄	Mild Steel	93%	300mgL ⁻¹	Langmuir	[32]
14.	<i>Cryptocarya nigra</i>	N-methylisococlaaurine, N-	Hexane, Methanol, Dichloromethane	1M HCl	Mild Steel	91.05%	500ppm	Langmuir	[33]

		methyllaurotetanine, Atherosperminie.							
15.	<i>Oxandra asbeckii</i>	Liriodenine, azafluorenones alkaloids, triterpenoid	Chloroform	1M HCl	C38 Steel	92% (EIS)	100mgL ⁻¹	Langmuir	[34]
16.	<i>Dioscorea septemloba</i>	Diosin, Dioscorone A, β-sitosterol, Palmitic acid	Ethanol	1M HCl	Carbon Steel	89.2% (PDS)	2.0gL ⁻¹	-	[35]
17.	<i>Aloe Plant extract. L</i>	Aloesin, Aloin, Aloe, & Aloe Resin	Water	1M H ₂ SO ₄	Stainless Steel	98% (PDS) 96% (EIS) 96% (EN)	30% v/v	Langmuir	[36]
18.	<i>Cotis chinensis</i>	Berberine	-	1M H ₂ SO ₄	Mild Steel	98%	5.0 x 10 ⁻³ M	Langmuir	[37]
19.	<i>Ficus racemosa</i>	Hexadecanal, Octadecanal, Squalene, Vitamin, Stigmasterol, etc.,	Methanol	1N H ₂ SO ₄	Mild steel	90.5%	2500ppm	Langmuir	[40]
20.	<i>Pimenta dioica</i>	Eugenol	Ethanol	0.5M & 1M HCl	Mild Steel	99.35% (PDS)	520mgL ⁻¹	Langmuir	[41]

21.	<i>Magnolia grandiflora</i>	3,7- Diemthyl-2,6-octadien-1-ol, Santamarine, Lanuginasine, Anonaine	Water	1M HCl	Q235 steel	85%	500mgL ⁻¹	Langmuir-single layer	[42]
22.	<i>Tephrosia purpurea</i>	n-hexadecanoic acid	Methanol	1N HCl	Mild Steel	95.4%	300ppm	Langmuir	[43]
23.	<i>Matricaria aurea F.</i>	Apigetrin	n-hexane, methanol, water	1.0M HCl	Mild Steel	94% (PDS)	0.464mM	Langmuir	[44]
24.	<i>Pistacia terebinthus</i>	α - pinene, Limonene, α -Terpineol	-	3% NaCl	Iron	86.4%	3000ppm	-	[45]
25.	<i>Oryza sativa L.</i>	Momilactone	Methanol, ethyl acetate, hexane	1M HCl	Mild Steel	88%	1000ppm	-	[46]
26.	<i>Green Eucalyptus L.</i>	Ellagic Acid, Eucalyptone, Macrocarpal A, Macrocarpal E	Water	1M HCl	Mild Steel	88%	800ppm	Langmuir	[47]
27.	<i>i. Senna cana, ii. Byrsonima sericea DC,</i>	4-(methylamino)benzoic acid	Aqueous ethanol	0.1M HCl	Carbon Steel	81.9%	2700ppm	Langmuir, Temkim	[54]

iii.
Dimorphandra
gardneriana
Tull.

iv. *Mangifera*
indica L. and

v. Branches of
Zanthoxylum
syncarpum Tull

28.	<i>Rauvolfia</i> <i>macrophylla</i>	Tetrahydroalstonine and Perakine	CH ₂ Cl ₂ : MeOH (1:1)	0.5M H ₂ SO ₄ & 1M HCl	C38 Steel	97% by 1M HCl	200mgL ⁻¹	Langmuir	[55]
29.	<i>Mansoa alliacea</i>	Apigenin, luteolin, scutellarein-7- glucuronide	Ethanol	3% NaCl	Zinc	90%	300mg/L	Langmuir	[56]
30.	<i>Phyllanthus</i> <i>amarus</i>	Phyllantin	Ethanol	1M HCl	Mild Steel	95%	4 (v/v%)	Langmuir	[57]
31.	<i>Guatteria</i> <i>ouregou</i> L. & <i>Simira tinctoria</i> B.	Harmane	NH ₄ OH, CH ₂ Cl ₂	0.1 M HCl	Low carbon Steel	92%	520mgL ⁻¹	Langmuir	[58]
32.	<i>Olive Leaf</i> <i>Extract</i>	Oleuropein, Hydroxytyrosol	Water	2M HCl	Carbon Steel	91%	900ppm	Langmuir	[59]
33.	<i>Cymbopogon</i> <i>citratus</i> (Lemongrass)	Neral, Geranial, β-myrcene, Nerol	-	Produced oilfield Water	Carbon Steel	58.19%	400ppm	-	[60]

34.	<i>Henna Extract</i>	Lawsone, Gallic acid, α -D-Glucose & Tannic acid	Water	1M HCl	Mild Steel	92.06%	1.2gL ⁻¹	Langmuir	[61]
35.	<i>Turbinaria ornata</i>	10-Octadecenoic acid	Diethyl ether, Chloroform, Methanol	1L HCl	Mild Steel	100%	25gL ⁻¹	-	[62]
36.	<i>Bagassa guianensis</i>	Steppogenin, Katuranin, Dihydromorin	Ethanol	3% NaCl	zinc	97%	100mg/L	Langmuir	[63]
37.	Peach pomace extract	Thymol, Hexanal, Cinnamaldehyde and α -Terpineol	2-propanol/ethanol/ water (v:v:v=50/20/30)	0.5 M NaCl	Mild Steel	88%	800ppm	-	[64]
38.	<i>Gentiana olivieri</i>	Gentiopicroside, isoorientin, sucrose	Methanol, Ethyl acetate, n-butanol	0.5M HCl	Mild steel	93.7%	800 mgL ⁻¹	Langmuir	[65]

3. CORROSION STUDIES:

3.1 Weight-Loss method or Gravimetric Method:

This technique considers exposing a metal specimen to a specific atmosphere within a set time, then removing the sample from the situation and calculating the difference in weight before and after exposure. This approach for calculating metal corrosion rates is simple, precise, and accurate. The metal sample is ground with emery paper before being washed with double distilled water, degreased with acetone, and dried before the test. A balance is used to weigh the specimen that will be used for measurement. The metal is then dipped in various test media at a specified temperature for a specific period without and with various inhibitor concentrations, according to the technique. The sample was cleaned, dried, and weighed when the experiment was done. The inhibitor concentration for weight loss was measured [2]. Corrosion rate (CR), surface coverage (Θ) and inhibition efficiency (IE%), were calculated from the following equation:

$$\text{Surface coverage } (\theta) = \frac{W_o - W_i}{W_o} \text{ ----- (1)}$$

$$\text{Inhibition efficiency (IE \%)} = \frac{w_o - w_i}{w_o} \times 100 \text{-----(2)}$$

Where,

w_o - a weight loss of the metal when an inhibitor is not present,

w_i - a weight loss of the metal when an inhibitor is present.

$$\text{Corrosion rate (CR) (mm/y)} = \frac{w}{A D t} \times 87.6 \text{ -----(3)}$$

Where,

w - a weight loss of mild steel (mg)

A - area of the coupon in cm^2

t - exposure time in hr

D - density of mild steel (gmL^{-1})

87.6 is a constant

For illustration, Weight loss measurements at 298 K were used to study the inhibitory effect of different doses of Radish Leaf Extract (which contains phytochemicals such as O-Coumaric acid, Catechin, Folic acid, and Ascorbic acid) on mild steel corrosion in the 0.5M Sulphuric acid solution. Corrosion inhibition efficiency improved as Radish Leaf Extract content increased, whereas corrosion rate decreased. The corrosion rate was only $2.65 \text{ gm}^{-2}\text{h}^{-1}$ when the concentration of Radish Leaf Extract was 300 mgL^{-1} (Figure 13), and the corrosion IE was 93%. The inclusion of numerous organic components in Radish leaf extract is likely

responsible for its outstanding corrosion prevention activity against mild steel. Protective coatings can be applied to the mild steel surface as a consequence of the adsorption process, increasing the surface area covered and minimizing the rate of mild steel corrosion in the Sulphuric acid medium [32]. In addition, Figure 14 shows the weight loss data of Mild Steel in 1N hydrochloric acid having different concentrations of *Tephrosia purpurea* leaves extract (which includes n-hexadecanoic acid phytochemical) (50–400 ppm) at 303K for a 1hr immersion period. The corrosion rate of mild steel in 1N HCl solution with *Tephrosia purpurea* leaves extract decreased with an increase in inhibitor concentration, while the IE (%) increased. At 300ppm of *Tephrosia purpurea* leaves extract for a 1hr immersion period at room temperature, the maximum inhibitory efficiency of 92.4% was achieved. There is little change in inhibitory efficiency above 300ppm, indicating that the limiting point has been reached. The rise in inhibition efficiency as the concentration of leaves extract increases is attributable to the adsorption of inhibitor constituents on the Mild Steel strips surface. Figure 14b shows that as immersion duration increases, inhibition efficiency decreases; the IE percent drops from 92.4 % (for 60 minutes) to 81.6 % (for 24 hrs). This observation implies that the adsorbed inhibitor molecules desorb from the mild steel surface as the immersion time increases. Though the inhibition efficiency decreases as the immersion period increases, *Tephrosia purpurea* demonstrates reasonable inhibition behavior, with an IE of 81.6% over 24 hours [43]. Likewise, the assessment of *Matricaria aurea* extract as an efficient corrosion inhibitor for Mild Steel in 1.0M hydrochloric acid is gravimetrically analyzed. The concentration of inhibitors is demonstrated to enhance Inhibition Efficiency. This is due to inhibitor molecules adsorbing on a mild steel surface. As a result, the inhibitor molecules surround the active site region of mild steel and protect it from corrosion. The maximum IE was reported to be attained at 0.464 mM concentration in this study, and further increasing the concentration of *Matricaria aurea* Extracts (Apigetrin) had no appreciable impact on the green inhibitor protective action (Figure 15). The effective concentration of *Matricaria aurea* Extracts (Apigetrin), a green inhibitor, was therefore determined to be 0.464 mM [44].

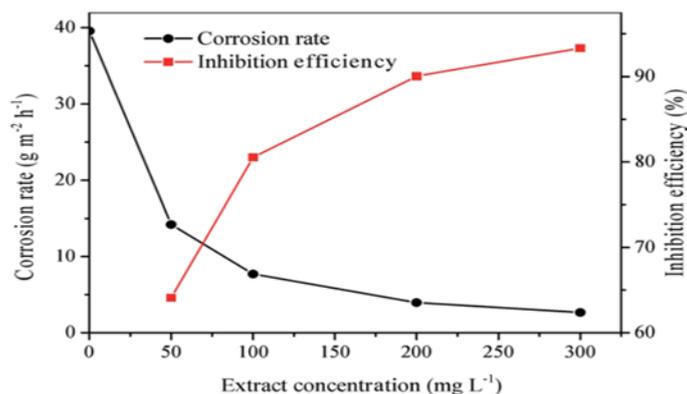


Figure 13. Corrosion rate and inhibition efficiency of Radish Leaf Extract at different concentrations (Which Contains phytochemicals like O-Coumaric acid, Catechin, Folic acid, and Ascorbic acid) in 0.5M H₂SO₄ solution [32].

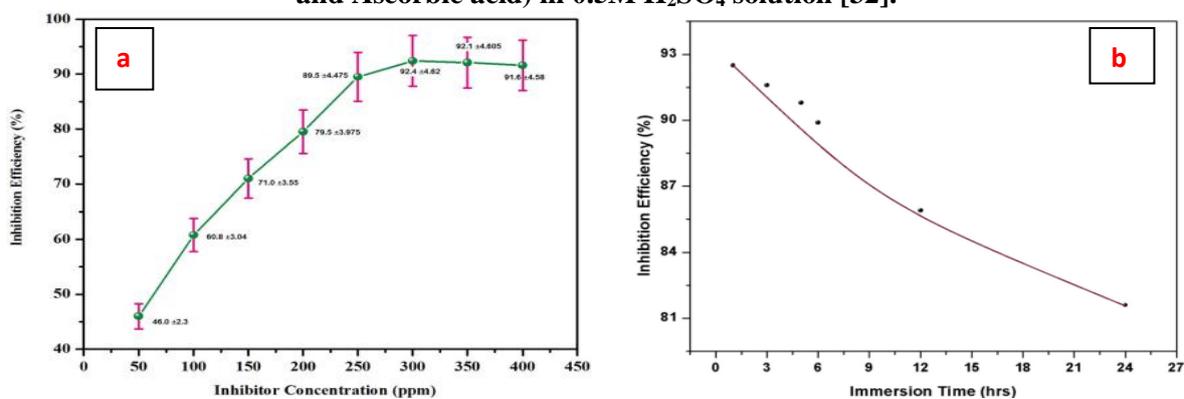


Figure 14. (a) The inhibition efficiency of *Tephrosia purpurea* leaves extract (Which contain n-hexadecenoic acid phytochemical) at different concentrations (b) Consequence of immersion time on corrosion of mild steel in 1N HCl in the presence and absence of *Tephrosia purpurea* leaf extract (Which contain n-hexadecenoic acid phytochemical) at 303K [43].

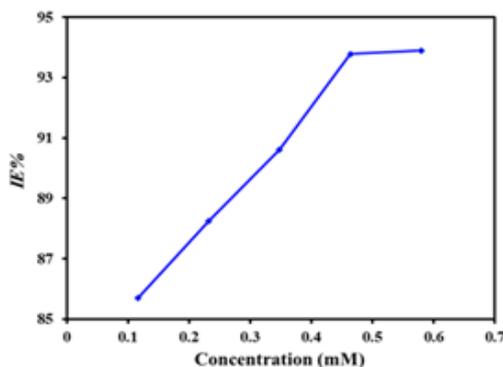


Figure 15. The inhibition efficiency of Mild Steel immersed in 1.0M HCl in addition to various concentrations of *Matricaria aurea* extract (Which contain phytochemicals like Apigetrin) [44].

3.2 Electrochemical Measurements

3.2.1 Electrochemical Impedance Spectroscopy (EIS):

Electrochemical impedance spectroscopy is a useful tool for determining the properties and kinetics of electrochemical reactions at metal/aggressive media contacts. On top of a Direct

Current potential, a low amplitude alternating potential (or current) wave is imposed, with the input voltage and the output current providing the impedance. The amplitude and phase angle of the variation in impedance is used to analyze the data. The frequency response analyzer examines the out-of-phase relationship between the input voltage and output current. The capacitor, resistor, and inductor are ubiquitous circuit elements. However, the impedance data for a solid electrode/electrolyte interface frequently reveal a frequency dispersion that these simple elements cannot explain. And this frequency dispersion is attributed to a “capacitance dispersion,” which is described in terms of a dispersed electrical element known as the constant-phase element (CPE). The capacitance of the adherent film was computed from the EIS data using an RRC circuit and the standard deviation was obtained using equation (4).

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \text{ -----(4)}$$

where C_{dl} double layer capacitor, where f_{max} is the frequency at the apex of the Nyquist plot, and R_{ct} is defined as charge transfer resistance.

$$IE\% = \frac{R_{ct} - R_{ct}^{\circ}}{R_{ct}} \times 100 \text{ -----(5)}$$

Where R_{ct}° and R_{ct} are Charge Transfer Resistance when an inhibitor exists in the environment and the nonexistence of an inhibitor in the environment correspondingly. To provide an additional understanding of the corrosion inhibition process, we create two types of graphical presentations using data obtained from equipment. These are the Nyquist and Bode plots [2].

For instance, the Nyquist plot representations for various concentrations of n-hexane crude extract of *Alpinia galanga* and its phytochemical 1'-acetochavicol acetate are shown in Figure 16. The evaluated EIS parameters for the inhibitors described that the corresponding increase in R_{ct} values with increasing concentrations of n-hexane crude extract of *Alpinia galanga* and 1'-acetochavicol acetate is documented and they show the contrary trend in the C_{dl} values with the rise in R_{ct} values. This is due to a decline in the local dielectric constant as a result of an increase in the thickness of the electrical double layer and their percentage inhibition efficiencies were calculated from R_{ct} values. The higher the R_{ct} values, the lower the C_{dl} with an attendant surge in surface coverage by the inhibitors for mild steel thereby increasing the inhibition efficiency [21]. Also, Nyquist plots of mild steel in 1N H_2SO_4 with and without various concentrations of *Pongamia pinnata* leaf extract were analyzed (Figure 17). The Nyquist plot reveals that in the presence of *Pongamia pinnata* leaf extract, the impedance behavior of mild steel in the 1N sulfuric acid medium has altered dramatically. The arc curvatures demonstrate that the inhibition is because of a Charge transfer mechanism with a

maximum inhibition efficiency of 70%, as the R_{ct} values increased with increasing inhibitor molecule concentrations. The addition of an inhibitor has a slight influence on the solution resistance but does not affect the open circuit potential (OCP). The existence of a single semicircle indicates that inhibitor molecules have an impact on more than one charge transfer mechanism. The semicircle's depressing nature is typical of a solid electrode, and it is primarily owing to the mild steel electrode's micro-roughness and "inhomogeneities". The R_{ct} value is inversely proportional to the corrosion rate and measures electron transport across the electrode-solution interface. The Bode curve displays a single peak of about 125 Hz to 158 Hz, with little variation as the inhibitor concentration is improved. The presence of an inhibitor is accompanied by an increase in R_{ct} and a decrease in C_{dl} , indicating that the charge transfer process is primarily responsible for the mild steel breakdown. This is due to an intensification in the inhibitor molecules' surface coverage (θ), which increases the inhibition efficiency [27]. Likewise, the releasing of adsorbed intermediate products from the mild steel surface causes inductive loops in the EIS curves of a blank solution of *Valeriana willichii* Roots Extract (which contains phytochemicals like Naphthoic acid, Iridoid, and Analogue). They show that the inductive loop is removed at different concentrations, which is generally taken into account. In the Bode modulus curves, the semicircle width in the Nyquist plot corresponds to the changing drift of impedance values with the *Valeriana willichii* concentration level (Figure 18). The Nyquist plot's onetime constant is confirmed by all phase angle-frequency curvatures that reveal a single wave. According to the literature, the electrochemical behavior of the steel solution contact is capacitive or resistive depending on whether the phase angle is 90° or 0° . Naphthoic acid, Iridoid, and Analogue phytochemicals were identified in abundance in *Valeriana willichii* extracts. As a result, these molecules can be adsorbed onto the mild steel surface by providing π -electrons out of aromatic rings or lone-pair electrons out of heteroatoms to the empty orbital of Fe. These substances can create a preventive layer on the Mild Steel surface, blocking the flow of charges and ions and protecting it from corrosive media. The findings show that the *Valeriana willichii* inhibitor inhibits Mild Steel corrosion at any concentration used and that the inhibitor's efficiency increases as the concentration is increased [28].

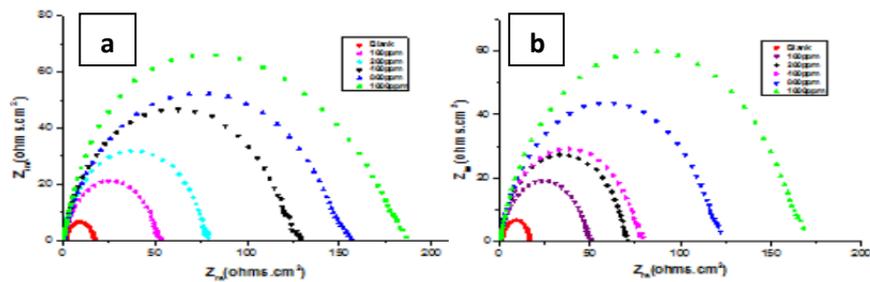


Figure 16. Nyquist plots for corrosion of mild steel in the absence and presence of different concentrations of (a) n-hexane crude extract of *Alpinia galanga* and its phytochemical (b) 1'-acetochoavicol acetate [21].

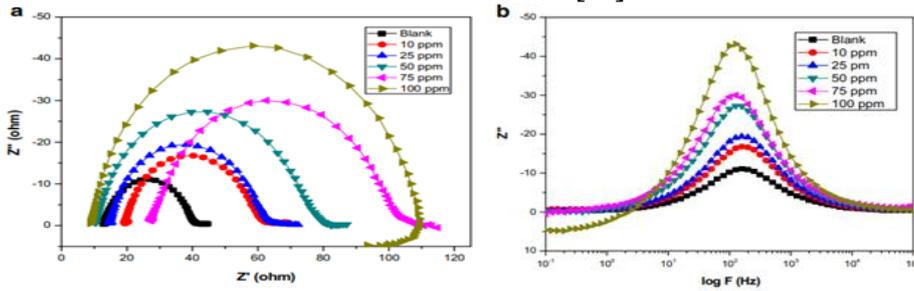


Figure 17. (a) Nyquist plot for mild steel in 1N H₂SO₄ in the presence and absence of different concentrations of *Pongamia pinnata* leaf extract (contain 4-piperidinamine, N,1-dimethyl-; (Z) 6, (Z) 9-pentadecadien-1-ol; hexadecanoic acid, methyl ester; 9,12,15-octadecatrienoic acid, etc.,) (b) Bode plot for mild steel in 1N H₂SO₄ in presence and absence of different concentrations of *Pongamia pinnata* leaf extract [27].

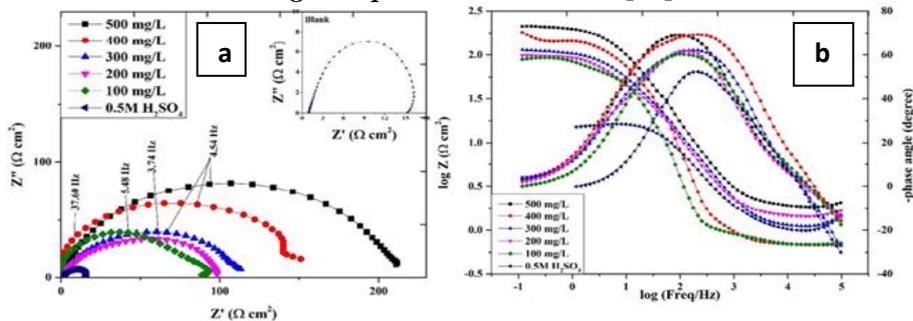


Figure 18. (a) Nyquist plots for mild steel in 0.5M H₂SO₄ from 0 to 500 mg/L concentrations of *Valeriana willichii* extract (Naphtholic acid, Iridoid, Analogue) (b) Bode-Z and Bode-phase plots for mild steel in 0.5M H₂SO₄ with 0 to 500 mgL⁻¹ concentration of *Valeriana willichii* extract at OCP and 298K [28].

3.2.2 Potentiodynamic Polarization technique:

Polarization analysis is an excellent and practical tool for investigating corrosion mechanisms. Polarization curves make it simple to understand the kinetics of anodic and cathodic reactions. Readings are taken over a predetermined range of potentials and at a predetermined scan rate. The kinetics of corrosion reactions can be measured using polarization techniques. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (c), anodic Tafel slope (a), and percentage inhibition efficiency (I.E %) as

an indicator of inhibitor concentration level are computed with the help of the graphs using the polarisation technique. The methodology of the procedure will define the nature of the retardation as cathodic, anodic, or both. The E_{corr} values will establish the type of inhibitor utilized. When the graph's curve approaches a low current density, it indicates that the corrosion rate is reducing [2].

For instance, the Tafel graphs for varied inhibitor concentrations of the *Valeriana willichii* extract (which contains phytochemicals such as Naphtholic acid, Iridoid, and Analogue) on the polarization behavior of mild steel in 0.5M H_2SO_4 were examined. The Tafel plots reveal a reduction in the current densities of the anodic as well as cathodic prolongations in the presence of inhibitors. The effects of covering mild steel surfaces with adsorbed inhibitor molecules on decreasing steel surface zone dissolution have also been investigated. At 100-500 mg/L, the increased concentration resulted in a reduced current density (i_{corr}). As the inhibitor concentration rises, so does the amount of surface covering. Once inhibitors were introduced to the corrosive medium, all anodic metal disintegration and cathodic hydrogen evolution reactions were stopped. The inhibition of these activities is maintained as inhibitor concentrations increase. Charge transfer still governs both the anodic and cathodic reaction processes, as seen by the almost unchanged anodic and cathodic Tafel slopes before and after adding *Valeriana willichii* extract (Figure 19). Thus, *Valeriana willichii* extract active components were effectively adsorbed into the steel surface and inhibited mild steel corrosion without changing the response mechanism. *Valeriana willichii* extract contains natural chemicals that are well-adsorbed on Mild Steel surfaces due to electrostatic contact and induce effective coordination bonds with Fe through heteroatoms. As a result of the combination of physisorption and chemisorption, the inhibitor's functional constituents are systematically adsorbed on the Mild Steel surface shielding the metal from degradation as seen by decreased corrosion current density values [28]. The potentiodynamic polarization behavior of mild steel immersed in 1M H_2SO_4 in the absence and presence of the β -Sitosterol inhibitor from rice hulls (at various concentrations) was also investigated, with the corresponding potentiodynamic curves given in Figure 20. The corrosion current (I_{corr}) values in the presence of the inhibitor were found to be lower than in the absence of the inhibitor. The fact that the I_{corr} values gradually dropped suggests that the corrosion reaction was retarded by the inhibitor-containing phytochemicals. The corrosion potential (E_{corr}) values shifted little in one way or the other. E_{corr} 's maximum displacement is 0.0188 mV. The addition of an inhibitor influenced both the cathodic and anodic Tafel slopes, signifying that β -sitosterol efficiently controls the Mild Steel dissolving procedure as well as the cathodic H_2 evolution response. According to the findings,

β -sitosterol is a mixed-type inhibitor [29]. Also, the graph of the Potentiodynamic polarisation curves of Q235 MS specimens immersed in 1M hydrochloric acid having and not having various levels of *Magnolia grandiflora* leaves concentrations that contain phytochemicals such as 3,7-Dimethyl-2,6-octadien-1-ol, Santamarine, Lanuginasine, and Anonaine is shown in Figure 21. As the concentration level increases, the i_{corr} of the mentioned specimens in the hydrochloric acid metal deterioration environment reduces. This suggests that a phytochemical-rich extract extracted from *Magnolia grandiflora* leaves effectively inhibits Q235 steel corrosion in 1M hydrochloric acid. Furthermore, as the concentration of inhibitor increases, the cathodic branch's polarisation curve tends to drop faster than the anodic branch. This shows that the inhibitor's adsorption influence on the cathodic hydrogen suppression specimen surface is significantly stronger than that of anodic iron ion precipitation. It's worth noticing that the cathodic branch polarisation curves follow a similar pattern. The adsorption of *Magnolia grandiflora* leaves extract onto the specimen exterior did not affect the cathodic response procedure, indicating that it is unaffected. In comparison to the blank solution, the change values after including the *MG* leafage concentrate are significantly less than 85 mV, indicating that *Magnolia grandiflora* leaves extract is a mixed-type corrosion inhibitor. Furthermore, the corrosion inhibition efficiency of *Magnolia grandiflora* leaves extract is 88.2 % when the inhibitor concentration reaches 500 mg/L. As a result, they have demonstrated that the *Magnolia grandiflora* leaves extracts, which contain phytochemicals such as 3,7-Dimethyl-2,6-octadien-1-ol, Santamarine, Lanuginasine, and Anonaine, have retardant opposing properties for the given specimens in 1M hydrochloric acid [42].

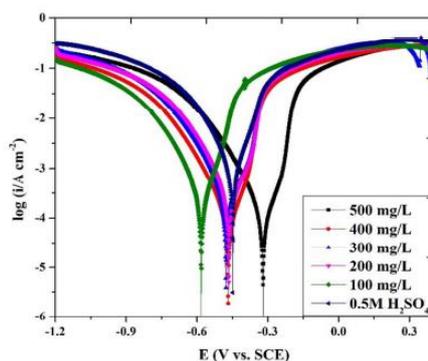


Figure 19. Potentiodynamic polarization curves for mild steel in 0.5M H₂SO₄ with 0 to 500 mg/L concentrations of *Valeriana willichii* extract (Which contains phytochemicals like Naphtholic acid, Iridoid, and Analogue) [28].

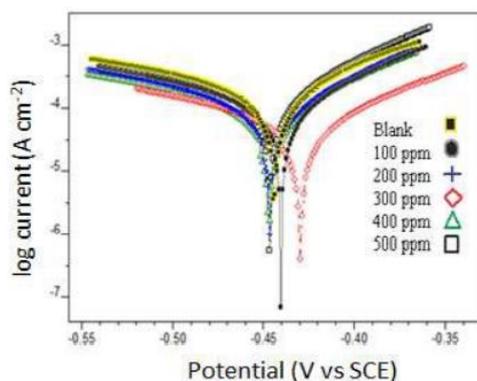


Figure 20. Polarization curves for mild steel in 1M H₂SO₄ with β -sitosterol from rice hulls [29].

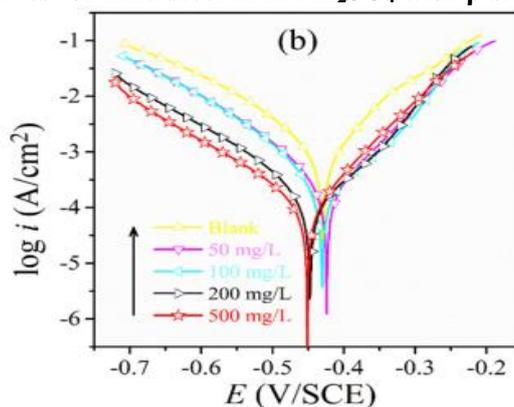


Figure 21. Polarization curve of Q235 steel immersed in 1M HCl with and without different concentrations of *Magnolia grandiflora* leaves (contain phytochemicals like lanuginosine, 3,7-dimethyl-2,6-octadien-1-ol, santamarine, and anonaine) extract [42].

3.3 Surface Morphology:

3.3.1 Scanning Electron Microscopy (SEM):

Scanning Electron Microscopy (SEM) can be used to determine the surface morphology of metals with and without the presence of phytochemicals as an inhibitor extracted from plant extracts. The formation of a protective inhibitor layer on the metal surface can be approved using SEM. Due to rapid corrosion and uncontrolled dissolving without inhibitors, the metal surface becomes rough. In the presence of an inhibitor, the metal roughness is reduced, resulting in a smoother surface [2]. Energy Dispersive X-ray Analysis (EDX) was commonly used to determine the elemental composition present on the metal surface in the absence and presence of the phytochemicals as an inhibitor which is isolated from the plant extracts. It provides information about the element compositions present on the surface of the metals like hetero atoms. In the presence of inhibitor molecules, heteroatoms such as O, C, and Fe can give an unshared pair of electrons, resulting in the complicated formation of metal atoms during the adsorption process and preventing further metal dissolution [31].

For example, the surface morphology of Mild steel using *Ficus hispida* leaf extract which has phytochemical namely, Stigmasterol in 1M HCl was studied by using SEM, and elemental composition was analyzed by EDX spectra (Figure 22). In comparison to corroded rough and uneven mild steel surfaces submerged in 1M HCl alone, SEM images of this compound showed that the metal submerged in the inhibitor contains Stigmasterol solutions and has a favorable environment with smooth surfaces. The EDX profile confirms that *FicusHispida* Leaves Extract, which contains the phytochemical Stigmasterol, adsorbed on the mild steel surface and prevented metal corrosion by blocking weak damages through its adsorption on the surface [25]. Likewise, after 24 hrs of immersion in a 3% NaCl solution, scanning electron microscope/energy dispersive x-ray methods were used to examine the interactivity of Essential Oils inhibitor with the metal surface. Figure 23 (a₁) depicts a front perspective of a scanning electron image of the blank specimen, which is rusted and depicted by an extremely coarse surface having metal deterioration indications on it. The iron surface damage was greatly decreased in the vicinity of the inhibitor as seen in Figure 23 (b₁, c₁, and d₁), and the coupons seemed smooth. After 24hrs of exposition to a corrosive solution having 3000 ppm of Terebinth Essential Oils, this inspection validated the establishment of a protecting boundary overlay on the Fe surface. The elements present on the iron surface were shown using EDX without and with Terebinth Essential Oils. In the absence of Essential Oils inhibitors, the assortments largely featured the distinctive peaks of Iron, Carbon, Oxygen, Chlorine, and Sodium, as shown in Figure 23 (a₂). On the iron surface, this validated the production of metal oxides/hydroxides as well as chlorides as metal deterioration outcomes. The reduction in peak intensity also causes the chlorine and sodium to vanish in the presence of the Essential Oils inhibitors Figure 23 (b₂, c₂, and d₂). As a result, Terebinth Essential Oils molecules adsorb to the Fe surface, inhibiting the production of oxides/hydroxides as well as chlorides. Furthermore, the % of Carbon reduces as a result of the synthetic constitution of the inhibitors, demonstrating that Essential Oils inhibitors adsorb on the iron surface, forming a protective coating [45]. Also, the surface morphology of Mild steel using Rice Hull's extracts which contain phytochemicals, and momilactone A in 1M HCl were studied using SEM (Figure 24), and elemental composition was analyzed by EDX spectrum. The momilactone A inhibitor could efficiently defend the Mild steel from an aggressive condition. In the presence of a phytochemical inhibitor, mild steel has an even surface with less corrosion, signifying that the metal surface has a strong protective coating. The EDX spectra of the Mild steel surface film in the absence as well as the presence of the inhibitor are discussed. They compared these composition values of mild steel before and after and concluded that the formation of iron oxide

is the reason for corrosion in the case of the steel sample in 1 M HCl solution where the oxygen, as well as sulphur essential configurations, are minimized [46].

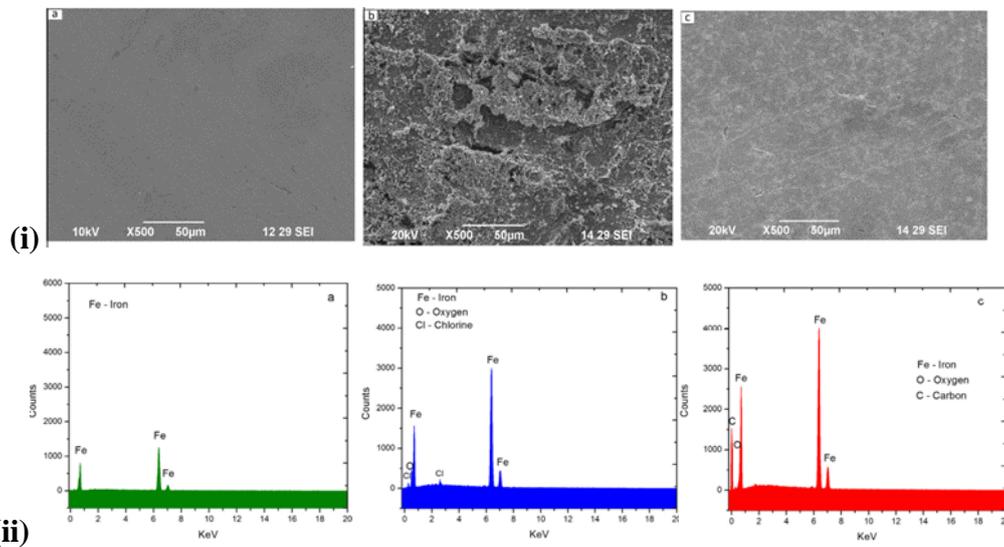


Figure 22. (i) SEM images of (a) Polished mild steel surface, (b) after 2hrs of immersion at 308 K in 1M HCl and (c) after 2hrs of dipped at 308 K in 1M HCl + *Ficushispida* Leaf extract (Which contain phytochemicals like stigmasterol). (ii) EDX graphs of (a) Polished mild steel surface, (b) mild steel specimens exposed in 1M HCl and (c) mild steel exposed in 1M HCl + *Ficushispida* Leaf [25].

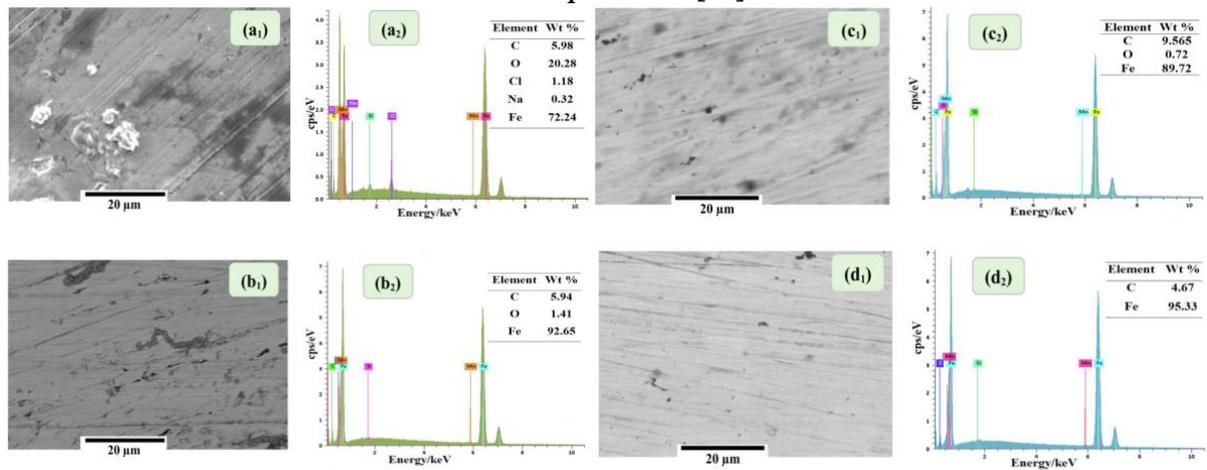


Figure 23. SEM&EDX analysis of the iron dipped in the 3% NaCl solution without ((a₁, a₂) blank) and with 3000 ppm of essential oils from (b₁, b₂) leaves, (c₁, c₂) twigs, and (d₁, d₂) fruits of Terebinth [45].

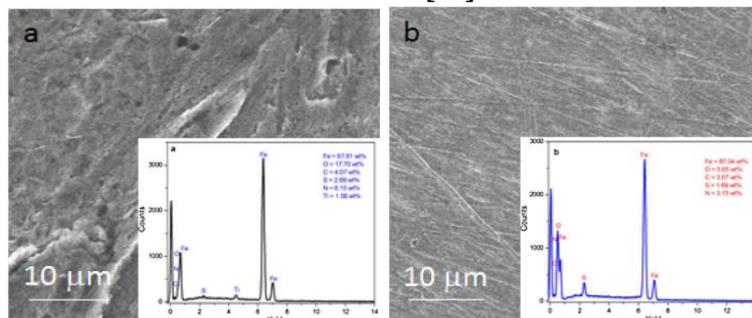


Figure 24. SEM-EDX spectra of mild steel in (a) 1M HCl and (b) 1M HCl + Rice hulls extract (containing momilactone A) inhibitor [46].

3.3.2 Atomic Force Microscopy (AFM):

Atomic Force Microscopy (AFM) is a valuable instrument for surface research because it may reveal the microstructure and determine whether a corrosion inhibitor has thin-film adsorption on the metal surface. AFM provides quantitative data and 3-D topography of the metal sample. Surface changes with and without phytochemicals as an inhibitor can be analyzed with this technique clarifying how adding an inhibitor to a sample reduces the average roughness of the metal specimen. Both protected and unprotected samples have their root mean square (RMS) and average roughness values computed in Nanometres (nm) and these data are then compared [2].

For instance, *Magnolia grandiflora* Leaves extract (Figure 25) was used to examine the AFM of Q235 steel, which contains the regular phytochemicals. In the form of a protective film layer, they operate as corrosion inhibitors. When phytochemicals from *Magnolia grandiflora* leaf extract are adsorbed, the culmination of the Q235 steel surface is approximately 250 nm, while the peak valley value is around 120 nm. When compared to the average roughness of Q234 steel before immersion of phytochemicals as a corrosion inhibitor, the complete Q235 steel surface was consistent as well as even, and the average roughness values (Ra) became reduced. The whole Q235 steel surface's peaks and valleys are greatly decreased. Therefore, they concluded that the surface of the Q235 steel is protected by using the leaf extracts which contain phytochemicals and reduce further corrosion [42]. Also, the surface morphology of mild steel metal was examined using an Atomic Force Microscope to see how it changed during the corrosion process without as well as with *Tephrosia purpurea* leaves extract (Figure 26), which contains phytochemicals such as n-hexadecanoic acid. They discovered that polished mild steel has a lower average surface roughness than mild steel that has been acid-treated which is attributable to strong metal disintegration. However, when mild steel was treated with *Tephrosia purpurea* extract and 1N HCl, the phytochemical rapidly decreased. The reason is primarily due to the Mild steel producing a protective coating, which also prevents further corrosion [43]. Likewise, the AFM of the mild steel surface was analyzed with and without *Green Eucalyptus* leaf extract (Figure 27) which contains phytochemicals like Ellagic acid, Eucalyptone, Macrocarpal A, and Macrocarpal E. They reveal that the Mild Steel surface roughness after exposure to HCl solution without inhibitor is much higher than the metal exposed to leaf extract where the phytochemicals are adsorbed to the metal. The arithmetic means deviation (S_a) for the metal with an acid solution was about 97 nm. However, after adding an Extract of the *Green Eucalyptus* leaves the S_a decreased to 3 nm. So, this change of

S_a shows that the surface of the Mild Steel protected by *Green Eucalyptus* leaves Extract is much smoother than the unprotected metal where the phytochemicals of this extract are absorbed in the metal surface. This means that the Phytochemicals of the extract could effectively reduce the metal surface dissolution rate [47].

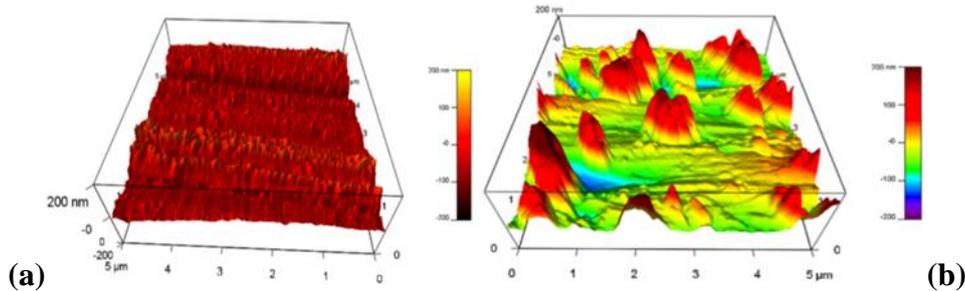


Figure 25. AFM images of Q235 steel after immersion in 1M HCl (a) with and (b) without *Magnolia grandiflora* leaves extract, which contains phytochemicals like Santamarine, 3,7-Dimethyl-2,6 Octadien-1-ol, Anonaine, Lanuginasine [42].

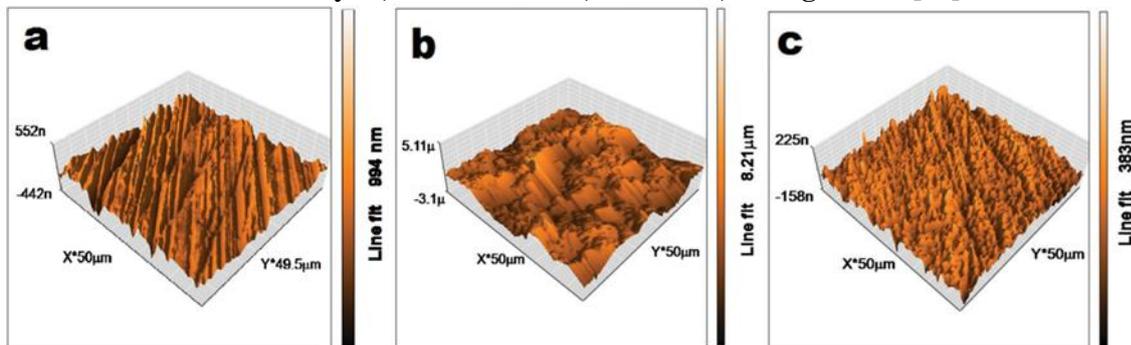


Figure 26. AFM images for (a) polished mild steel, (b) mild steel immersed in 1 N HCl, and (c) mild steel immersed in 1N HCl with 300 ppm of *Tephrosia purpurea*, containing phytochemical n-hexadecanoic acid [43].

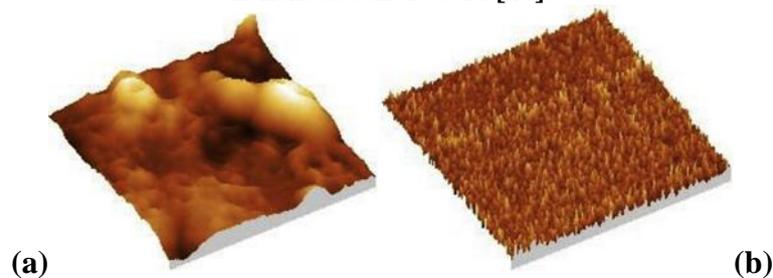


Figure 27. AFM images of (a) mild steel without inhibitors and (b) Green Eucalyptus leaf extract, which contain Ellagic acid, Eucalyptone, Macrocarpal A, Marcrocarpal E phytochemicals, mild steel immersion in 1M HCl media [47].

3.3.3 X-ray Diffraction (XRD):

One of the most versatile techniques for materials characterization is X-ray diffraction. When a material possesses atomic-scale periodicity or crystallinity, this is a useful tool for compound identification, and it's also used to figure out how metal coatings form in corrosive conditions [48,49].

The x-ray diffraction patterns of Mild Steel after 24hrs immersion in an acidic medium with and without Opuntiol isolated from the *Opuntia elatior* fruit extract are analyzed. Figure 28a and 28b show the procured x-ray diffraction patterns of the Mild Steel surface in the presence and absence of opuntiol in 1M hydrochloric as well as 1M sulphuric acid. The results indicated that mild steel is corroded by the development of Fe_2O_3 (a metal deterioration outcome) in an acidic environment. The absence of the Fe_2O_3 peak in the vicinity of opuntiol, on the other hand, strongly shows that opuntiol shields the MS exterior by providing a coating, preventing metal deterioration [20]. Likewise, the XRD patterns on the surface of the mild steel immersed in the test solutions of *Ficus hispida* leaves extract (Figure 29), which contains phytochemicals like stigmasterol in 1M HCl. The patterns in this plant extract demonstrate the presence of metal and metal oxide phases, as well as several properties that are explained by the usual Fe and FeCl_2 patterns. The strength of the peaks owing to iron alone is found in the presence of *Ficus hispida* leaves extract, which contains phytochemicals, which is fairly high when compared to the intensity of the peaks because of Fe only. As the diffraction intensities in this region are low, a little amount of Fe_2O_3 was found, indicating the avoiding of corrosion. These results clearly show the creation of an attached protective layer on the metallic surface in the occurrence of *Ficus hispida* leaves extract. This method could be useful for completing the interaction of phytochemicals in an extract with a metallic surface [25].

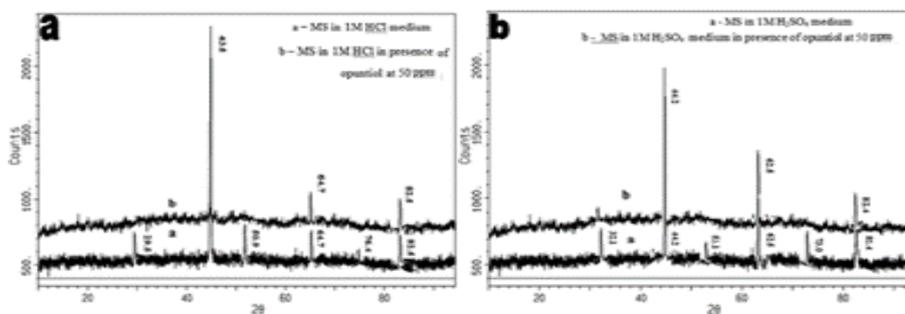


Figure 28. (a) XRD pattern of the film formed on mild steel in 1M HCl with and without Opuntiol phytochemical from *Opuntia elatior* fruit Extract. (b) XRD pattern of the film formed on mild steel in 1M H_2SO_4 with and without Opuntiol phytochemical from *Opuntia elatior* fruit Extract [20].

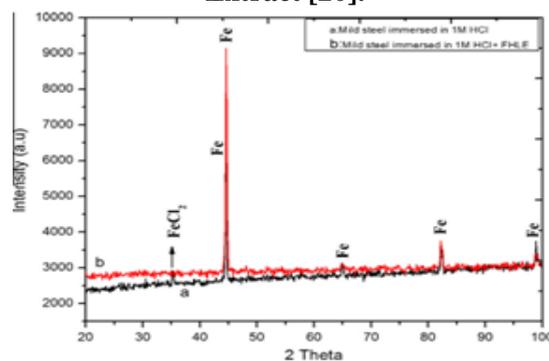


Figure 29. XRD pattern of (a) mild steel in 1M HCl and (b) mild steel in 1M HCl in the presence of *Ficus hispida* leaf extract which contains its phytochemical Stigmasterol [25].

3.3.4 X-ray photoelectron spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) was used to examine the surface to validate the assumption of physisorption and chemisorption, as well as to determine the type of the organic thin-film formed on the metal surface [19].

For instance, the XPS of a very effective (Laurhydrazide N'-propane-3-one) environmentally acceptable corrosion inhibitor for mild steel corrosion in 5M HCl at higher temperatures is shown in Figure 30. After immersion in 5M HCl with $370\mu\text{molL}^{-1}$ of Laurhydrazide N'-propane-3-one (LHP) O at 20 °C, the adsorbed inhibitor XPS survey and high-resolution XPS analysis of C, O, and N are demonstrated for mild steel. The C1s are broken down into three distinct peaks. The deconvolution of the O1s spectrum also yields three peaks. On the contrary, the deconvolution of the N1s spectrum peak results in two peaks around 399.8 and 402.3 eV. Therefore, XPS authorizes the presence of the adsorbed Highly efficient (Laurhydrazide N'-propane-3-one) LHP eco-friendly corrosion inhibitor on the metallic surface [50]. Also, x-ray photon spectroscopy reviews, as well as optimal-definition spectra from a steel surface with *Brassica oleracea* L. fruit extract, are shown. In surveys (Figure 31 a and d), the N peaks are observed. The reason is due to extracting constituent induction. As a result, a complex layer is produced to protect Q235 steel from corrosion [51]. Likewise, the XPS studies were carried out on the metal surface where the phytochemical act as a corrosion inhibitor is also analyzed. The phytochemicals are extracted from their plant extract. The x-ray photon spectroscopy of C 1s, O 1s, and Fe 2p_{3/2} for the Mild steel after immersion for 4hrs in 1 molL⁻¹ hydrochloric acid having 400 mgL⁻¹ methanolic extracts of *Artemisia pallens* (Asteraceae) and its active phytochemicals, arbutin is displayed in Figure 32. The C1s spectra of methanolic extract, as well as arbutin-processed Mild steel, were deconvoluted into 3 peaks, showing the presence of 3 synthetic variants of carbon atoms on the Mild steel surface (Figures 32a and b). O1s spectra deconvolution may be divided into three primary peaks. Three peaks emerge from the deconvolution of the high-resolution Fe 2p_{3/2} spectrum. The peak intensity of the Fe 2p spectra of crude methanolic extract processed Mild steel is lower than that of arbutin processed Mild steel, implying the formation of a thin layer on the mild steel surface due to the high adsorption of the crude methanolic extract [19].

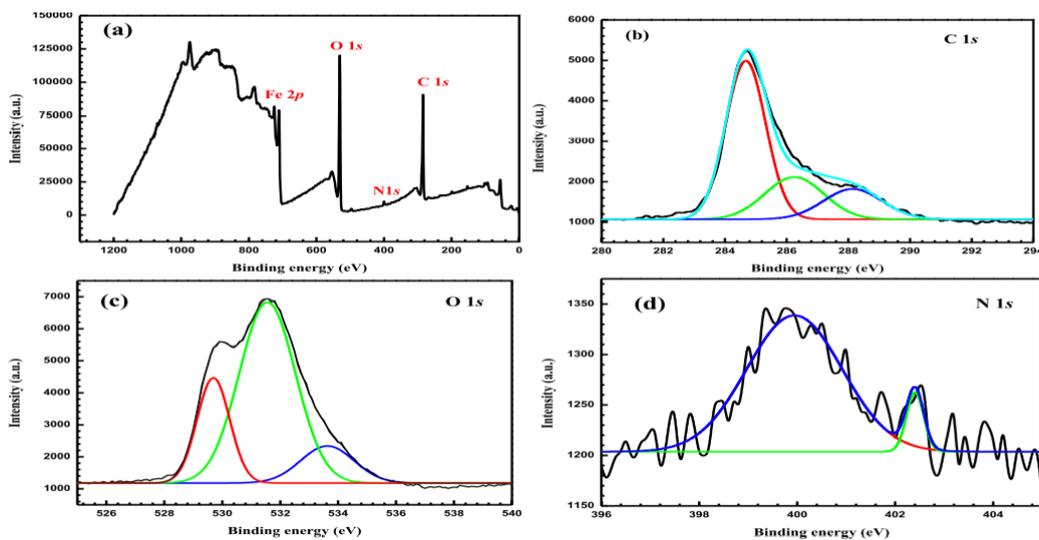


Figure 30. (a) XPS survey scan composition of the Mild steel immersed in 5M HCl with $370 \mu\text{mol L}^{-1}$ of Laurhydrazide *N'*-propan-3-one (LHP) at 20°C for 24hrs and the profiles of (b) C 1s, (c) O 1s, and (d) N 1s [50].

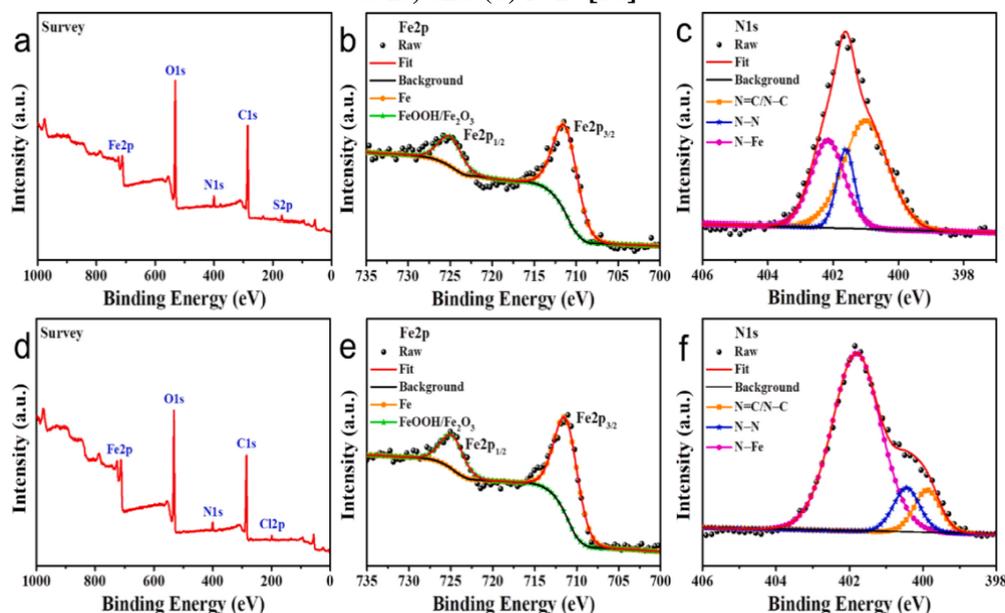


Figure 31. XPS Survey and high-resolution spectra from the steel surface with the fruit of *Brassica oleracea* L. extract containing Fe2p, and N1s, (a), (b), (c) in H_2SO_4 , (d), (e), (f) in HCl [51].

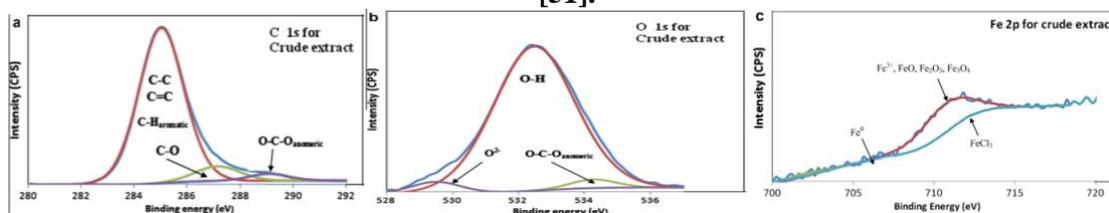


Figure 32 a, b, and c: The XPS deconvoluted profile for (a) C 1s, (b) O 1s, and (c) Fe 2p for mild steel surface after immersion for 4 hrs in 1 mol l^{-1} HCl solution containing 400 mg l^{-1} of the crude methanolic extract of *Artemisia pallens* at 30°C [19].

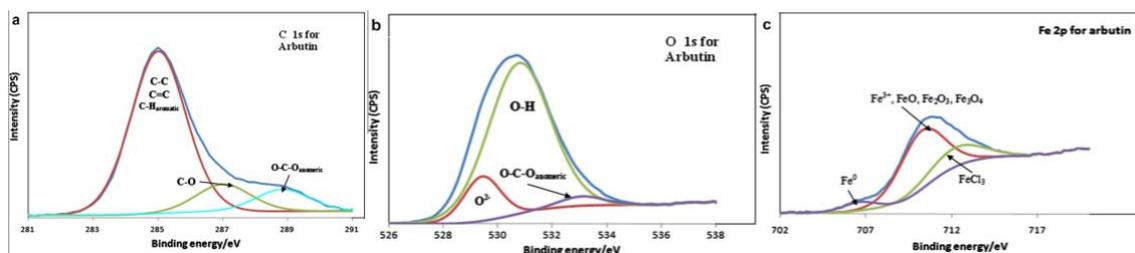


Figure 33 a, b, and c: XPS deconvoluted profile for (a) C1s, (b) O1s, and (c) Fe 2p for mild steel surface after immersion for 4hrs in 1 mol l⁻¹ HCl solution containing 400 mg l⁻¹ of arbutin at 30°C [19].

3.3.5 Electrochemical / Electron Frequency Modulation (EFM):

Electrochemical / Electron frequency modulation (EFM) is a non-destructive electrochemical technology that may estimate the corrosion current value directly and efficiently using only a short polarising signal and no prior knowledge of Tafel slopes. This method has the advantage of combining corrosion rate, Tafel parameters, and causative factors into a single data set, making it a good choice for online corrosion monitoring. A potential perturbation signal comprised of 2 sinusoidal waves is implemented to any corroding metals to evoke an existing reaction utilizing electron frequency modulation. This method is furthermore utilized to precisely explore metal deterioration criteria for a wide range of metals & electrolytes. Noise may alter the measurement if the causality factors are not between 2 and 3. If the correlation factor's value nears the threshold, there is a link between the perturbation as well as the response signals, and the information can be acknowledged. If CF-2 and CF-3 are in the 0–2 and 0–3 ranges, respectively, the EFM results are valid. Any deviation from the anticipated value in the causation factor could be caused by a too-small perturbation amplitude, inadequate spectrum frequency resolution, or a non-functioning inhibitor [52,53].

For instance, the EFM of azelaic acid dihydrazide (Figure 34) shows that CF-2, as well as CF-3, possess conventional numbers of 2.0 and 3.0, respectively. These findings reveal that inhibitor molecules bind to the mild steel surface physically rather than chemically and that rising temperature speeds up both metal dissolving and inhibitor molecule desorption. [52]. EFM Intermodulation spectrums of carbon steel in 1M HCl acid solution with various Modazar drug doses are also shown (Figure 35). Increases in the studied inhibitor concentrations increase the inhibition efficiency $IE_{EFM} \%$, which can be measured as follows:

$$IE_{EFM} \% = \frac{1 - i_{corr}}{i_{corr}^0} \times 100 \text{-----}[6]$$

where i_{corr}^0 and i_{corr} are corrosion current densities without and with different concentrations of inhibitors, respectively [53].

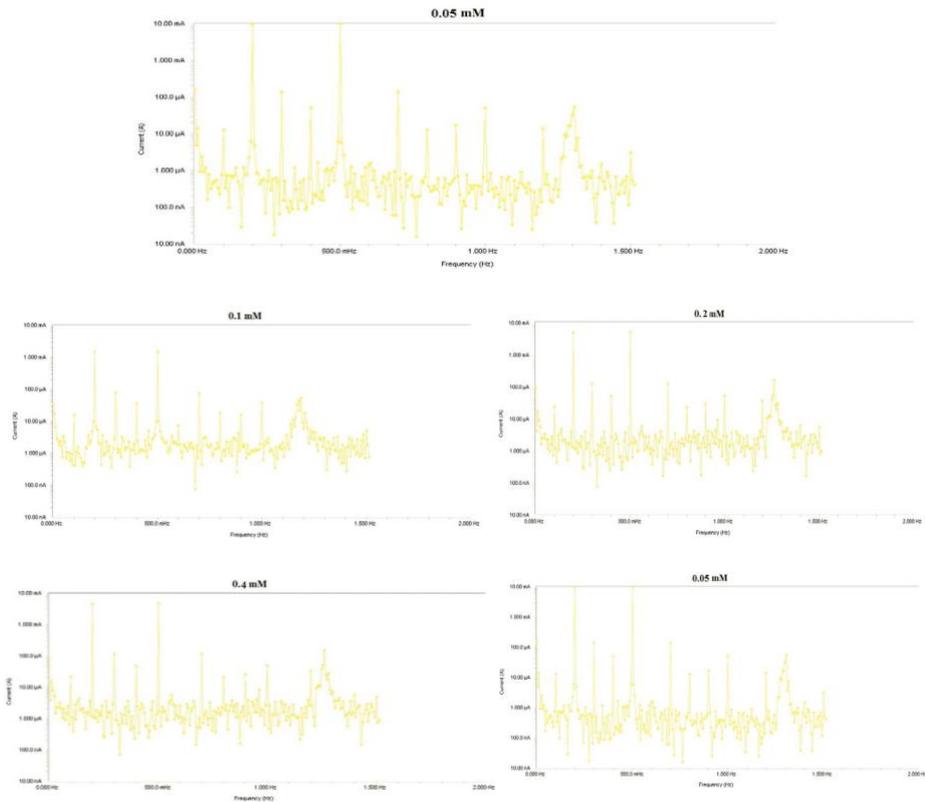


Figure 34. EFM spectra of mild steel in 1M HCl in the absence and presence of different concentrations of the azelaic acid dihydrazide corrosion inhibitor [52].

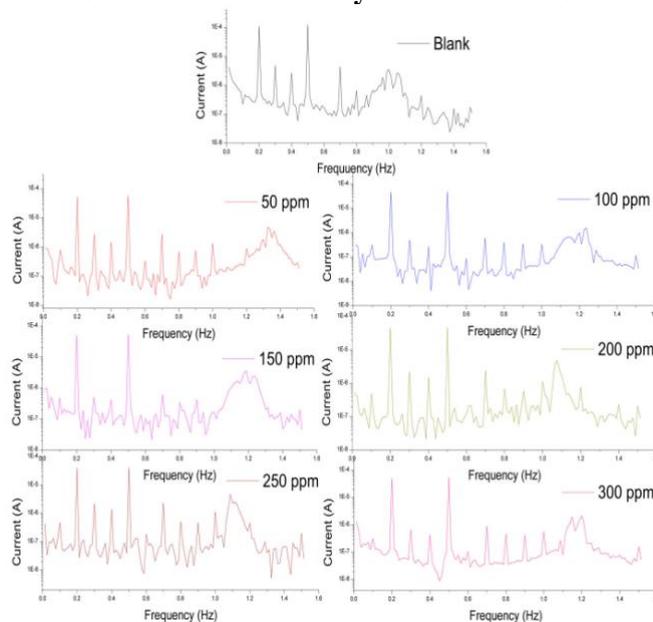


Figure 35. EFM spectra for C-steel in 1M HCl in the absence and presence of various concentrations of Modazar drug [53].

Therefore, EFM studies are also supported for phytochemicals of the plant extracts which are used as an inhibitor for the metals for quickly determining the corrosion current value without preliminary information of Tafel slopes.

4. Summary and conclusion:

In this review article, phytochemicals as an inhibitor in the field of corrosion inhibition systems using plant extracts are surveyed. All types of inhibitors, such as drugs, chemical compounds, ionic liquids, Surfactants, natural polymers, natural oils, and plant extracts, have already been applied where their non-toxicity has been indirectly confirmed. All types of inhibitors utilized resulted in a reduction in corrosion rate but to various degrees.

Table 2: Comparative analysis of different types of corrosion inhibitors:

INHIBITOR	INHIBITION EFFICIENCY (%)	ENVIRONMENTAL EFFECT
Chemical compounds	80% - 98%	Comparatively higher
Lanthanide salts	87.53% - 98.21%	Comparatively higher
Ionic liquids	79% - 99%	Low
Drugs	94% - 97%	Low
Plant extracts	87% - 95%	Negligible
Phytochemicals	>90%	Negligible

Plant extracts are considered a great eco-friendly replaceable source for noxious and overpriced inhibitors. Different plant parts (bark, stem, root, seeds, fruits, and leaves) are suitable for the inhibition process. These extracts are enriched with different types of phytochemicals that protect the metal surface by forming the thin film layer after adsorption. Plant extracts contain a variety of phytochemical components, but only a few specific phytochemical components are responsible for metal protection, which may be determined by using instruments like Gas Chromatography-Mass Spectroscopy. According to certain research, phytochemicals derived from plant extracts are commercially accessible as corrosion inhibitors. Among the different phytochemicals that stimulate the adsorption process (e.g., organic acids, flavonoids, catechins, alkaloids, and co-enzymes), phenolic compounds are the most effective. However, because they contain varying types and quantities of phytochemicals, their inhibitory efficacy varies. Plant extracts have corrosion inhibition efficiency of more than 60%, with the majority of them

at 80–90%. The most difficult task is to create an extract or isolate the primary component with a better than 90% inhibitory efficiency. We saw an increase in corrosion resistance when we used the phytochemicals from the plant extraction and easily know the component behind that process to take place. According to a literature review, many extracts have lately been evaluated as metal deterioration inhibitors in acidic environments. However, there are data on the non-corrosive impact of plant extracts in aqueous-oriented electrolytes. Hence, the use of extracts as metal deterioration inhibitors needs to be investigated. Concentration, extraction solvent, temperature, and immersion duration are just a few of the variables that may be investigated while evaluating a plant extract as a corrosion inhibitor. Electrochemical techniques (Electrochemical Impedance study, Electrochemical Frequency Modulation) and studies like Weight loss method or Gravimetric method, Scanning Electron Microscope, X-ray Diffraction, X-ray photoelectron spectroscopy, Atomic Force Microscopy, Gas Chromatography-Mass Spectroscopy, Nuclear Magnetic Resonance spectroscopy, Fourier transfer Infrared spectroscopy, Ultraviolet-Visible Spectroscopy were evaluated.

Despite suffering from some shortcomings, specific compounds can be isolated and studied, intending to produce them in the large quantities required for the industry.

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