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Review Article

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Studies on the anticorrosive effect of phytochemicals on mild steel, carbon steel, and stainless-steel surfaces in acid and alkali medium: A review

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Abstract: Phytochemicals are the natural active compounds present in plant sources that act as corrosion inhibitors for various metals subjected to different ecological situations. This phenomenon has inspired to do research work to find natural inhibitors for replacing synthetic chemical inhibitors for the alleviation of corrosion effects on various metals and alloys in aqueous medium. The phytochemical compounds like alkaloids, flavonoids, phenols, tannins, and coumarins from various plant sources, such as *Aleo vera, Polyalthia longifolia* (PL), *olive leaf extract, Phyllanthus amarus, Glycyrrhiza glabra, Salvia officinalis, Triticum aestivum, Ilex kukicha, etc.*, have the potential to overcome the corrosion effect prejudiced by acid, alkali, and microbially influenced corrosion on metallic surfaces. The adsorption chemistry reveals that the anti-corrosive effect on the metal surface is driven by the functional groups such as primary amide, hydroxyl, ester, carboxylic acid, and amino groups, followed by chemisorption and physisorption mechanisms, which are confirmed through the Langmuir Isotherm model and multi-layer isotherm model. The corrosion inhibition efficiency of plant extracts is majorly elucidated by electrochemical analysis (polarization, impedance and anti-corrosion effect), weight loss measurement, and surface characterization properties by atomic force microscopy and scanning electron microscopy-energy dispersive X-ray spectroscopy methods. The plant extract discussed in this review article obtained corrosion inhibition efficiency and current density (I_{corr}) by *Plantago ovation* at 60°C of around 94.4% and $10^{-5}\,\mathrm{A{\cdot}cm^{-2}}$, respectively. This review article discusses the various sources of corrosion and their mechanisms, different types of phytochemical compounds, the performance of the anti-corrosion effect, the adsorption mechanism of phytochemical constituents on metal surfaces and methods used for evaluating the inhibition process using computational tools.

Keywords: corrosion, phytochemicals, plant extracts, electrochemical analysis, metal surfaces

1 Introduction

1.1 Basics of corrosion and its chemistry on mild steel (MS), stainless steel (SS), and carbon steel (CS)

Corrosion and bio-corrosion are two different methods that lead to deterioration of metals and alloys by electrochemical reactions occurring in environments and biochemical reactions influenced by the microbial species, respectively. In addition, these two processes diminish the structural properties, surface properties of materials, and fluid flow properties in the pipelines and endeavor to contaminate the reactive products. The corrosion phenomena are mediated by the two most predominant reactions, such as (i) the evolution of hydrogen and (ii) the reduction of oxygen in acidic as well as in alkali conditions [1]. Due to

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the existence of acidic media, the metal and alloys are severely affected by corrosion or dissolution of metal because of the interfacial reaction arising between acids and metals. In some industrial processes, acid has been used for descaling, pickling, cleaning, and mill scale removal on the surface of the metals. It is relevant to remark that corrosion indemnities are more rampant in the progression of gaining untainted metals from its ores [2]. These practices custom awfully concentrated acidic solutions for the cessation of metals and creating surface defects or rust formation. In addition, sulfur and naphthenic acid are the perilous compounds that cause corrosion in oil and gas pipelines [3].

Several research studies stated that MS materials are mainly corroded by electrochemical reactions. During the oxidation process, the metals are liberated in their ionic form, in the anodic region, which releases the electrons and moves toward the cathodic junction. Notably, the cathode is the region where the reduction reaction has been taking place by the consumption of electrons [4]. The common chemical reaction executed during the dissolution of metal is given in Eq. (1).

$$M \rightarrow M^{n+} + ne^- \tag{1}$$

where M signifies the pure metallic form, M^{n+} represents the ionic form of metal, n states the valence of metal oxidized, and e^- is an electron. All through the iron corrosion, the metallic iron releases ionic form with two electrons at an anodic terminal which is postulated in Eq. (2). On the other hand, the cathodic reactions driven by the oxygen reduction in both acid and neutral or Alkali medium are given in Eqs. (3)–(5).

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2}$$

In acid medium,
formation of hydrogen:

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

Oxygen reduction in pH < 7

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{4}$$

Oxygen reduction pH ≧ 7

$$O_2 + 4H_2O + 4e^- \rightarrow 4OH^- \tag{5}$$

Especially, the gaseous form of hydrogen peers is a sporadic cathodic process in the presence of an acidic medium, whereas the reduction of oxygen is very common in any water medium interacting with air for a proceeding reduction reaction. In addition, the reduction of native metal ions and impurities (Fe^{3+}) is infrequent in some cases [5]. Besides, SS is one of the very important alloys that has been used in several applications due to its corrosion-resistant nature in normal atmospheric conditions. SS is majorly comprised of 12% chromium, which helps to resist rust formation in the form of metal hydroxides, nickel in diverse amounts, and the carbon is around 0.2–2.11% to achieve the features of SS by the development of an imperceptible chromium enriched oxide film on its surface. However, the SS is subjected to corrosion aggressively in high salt concentrations, biomedical transplants, forceful mechanical stress in bearings, turbines, and other chlorinated mediums. In naval surroundings, SS has been rusted because of pitting corrosion caused by the settling of airborne marine salts. Henceforth, environmental conditions such as temperature, relative humidity (R_h), moisture content, and concentration of salt are the major reasons for the formation of pitting corrosion on the SS surface. During the SS-chlorine interaction, the corrosion could be driven by the formation of a shrill chloride electron conducting layer at the lowest temperature because of condensation phenomena and also a high concentration of chlorinated layers are formed at high temperatures due to evaporation of the salt medium. Various literature attests that, due to the dew point of condensation and precipitation, a three-phase layer forms along with water droplets on SS exterior surfaces. In those conditions, the pitting corrosion assisted by chlorine varied with respect to the size and thickness of droplets because of the restricted cathode zone, possibly initiating the development of pits [6,7].

CS is another alloy, most preferably used in oil and gas transportation pipelines because of its good mechanical properties and cost-effective features. But CS is strongly instigated by pitting corrosion in the presence of carbon dioxide, hydrogen sulfide and organic acids like acetic acid, formic acid, and propionic acid [8,9]. The enigma of corrosion rises in CS majorly by the interaction of carbonic acid (weak acid) produced by the absorption of CO_2 with the water medium. Several studies observed that Iron(III) carbonate is the major corrosive compound engendered on the CS surface in the presence of carbon dioxide, which are mentioned in Eqs. (6)–(9).

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \tag{6}$$

$$CO_{2(aq)} + H_2O_{(aq)} \leftrightarrow H_2CO_3 \leftrightarrow H^+ \leftrightarrow HCO_3^- \tag{7}$$

$$2H^+ + 2e^- \leftrightarrow H_2 \tag{8}$$

$$2H_2CO_3 + 2e^- \leftrightarrow 2HCO_3^- + H_2 \tag{9}$$

Bockris *et al.* [10] depicted that the oxidation of metallic iron was a pH-reliant reaction. Literature shows that the dissolution of iron from the anodic region has declined more than pH 4. Furthermore, the disbanding of

Fe in CS interacted with CO_2, which ended with the formation of $Fe(CO)_3$ and hydrogen gas as a by-product as represented in Eq. (10). Also, the carbonated form of iron gets precipitated when the scales are generated at high temperatures and pH conditions [11–15].

$$Fe_s + CO_{2(g)} + H_2O \rightarrow Fe^{2+} + CO_2^{3-} + H_{2(g)} \qquad (10)$$

1.2 Biocorrosion mechanisms of MS, SS, and concrete

Biocorrosion is a metal deterioration process, influenced by the formation of biofilm by certain microbial species through cathodic depolarization and galvanic coupling mechanisms on metals. During the cathodic depolarization, the sulfate-reducing bacteria present on the metal surface utilize cathodic hydrogen molecules *via* a hydrogenase enzyme, which converts sulfate compounds into hydrogen sulfide [16]. This mechanism covers water dissociation reaction, cathodic reaction, and hydrogen oxidation. The corrosive molecules of hydrogen sulfide interact with metal ions, which produce metal sulfides by galvanic coupling, resulting in severe biocorrosion. Besides, the deposits of metals at the bottom induce differences in aeration, concentration of the salt, and pH of the solution. Additionally, the breakdown of corrosion inhibitors and degradation of coating compounds promote corrosion and enhances the growth of bacterial species. Various types of microbial species lead to biocorrosion on several metal surfaces, like carbon steel, nickel, chromium-coated carbon steels, aluminum (Al) alloys, *etc.* [17]. Moreover, literature states that more than 2.5 trillion USD has been spent around the globe, which is approximately 34% of the world gross domestic product, to overcome the corrosion impact on metal surfaces [18].

Generally, sulfate-reducing bacteria (SRB) are capable of corroding CS in the presence of sulfite or sulfate ions under anaerobic conditions. These bacterial species can persist in the corrosion process at approximately up to 80°C and are very energetic in less acidic environmental conditions. The microbial influenced corrosion causes pitting corrosion in water pipelines, sprinkler lines, fuel tanks, cooling tanks, *etc.* The SRB have more potential to corrode SS alloys, nickel-based alloys, and rapidly attack Al alloys [19]. The common mechanism held between water and air, the reaction possessed by bacterial species, and the overall reaction occurring in CS are mentioned in Eqs. (11)–(18) and also schematically represented in Figure 1.

Water dissociation:

$$8H_2O \rightarrow 8H^+ + 8OH^- \qquad (11)$$

Metal dissolution (anodic reaction):

$$4Fe \rightarrow 4Fe^{2+} + 8e^- \qquad (12)$$

Cathodic reaction:

$$8H^+ + 8e^- \rightarrow 8H \qquad (13)$$

The reaction proceeded by bacterial species in an anaerobic medium

Conversion of sulfate:

$$SO_4^{2-} \rightarrow S^{2-} + 4O \qquad (14)$$

Cathodic polarization:

$$8H^+ + 8e^- \rightarrow 4H_2 \qquad (15)$$

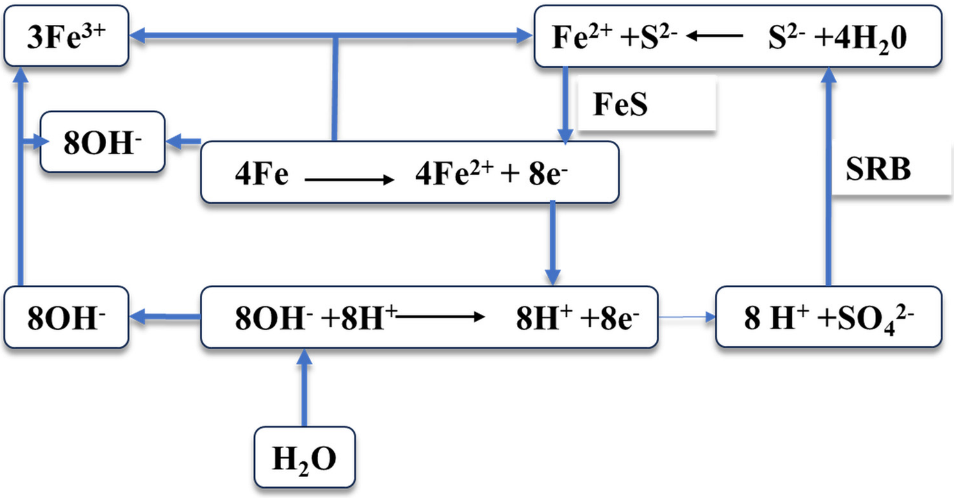


Figure 1: Biocorrosion mechanism on CS in the presence of SRB under anaerobic conditions [19].

Precipitation (metal sulfides):

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \qquad (16)$$

Precipitation (metal hydroxide):

$$3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2 \qquad (17)$$

Overall reaction

$$SO_4^{2-} + 4H_2 \rightarrow H_2S + 2H_2O + 2OH^- \qquad (18)$$

In the case of corrosion occurring on SS by bacterial species, several studies depicted that iron-oxidizing bacteria like *Gallionella ferruginea* and *L. ochracea* are the well-known bacterial species that grow in deposits of iron oxides and flakes under aerobic conditions by utilizing energy released during the conversion of Fe^{2+} to Fe^{3+} significantly. The chemistry of the corrosion process is represented in Eq. (19), stating that the bacterial species convert divalent iron into trivalent iron at neutral pH conditions with by-products of hydroxides and their metabolites. In some cases, extracellular proteins produced by the bacteria have been attached to the surface of the metal with high chlorine content and form ferrite chloride along with HCl, which leads to pitting corrosion on weld joints. In addition, the colonization of iron oxidizing bacteria, dissolution of iron, interaction of chlorides, and conversion of ferrous to ferric are major reasons leading to pitting corrosion [20,21].

$$3Fe^{2+} + \frac{1}{2}O_2 + (2 + X) + H_2O \rightarrow Fe_2O_3XH_2O + 4H^+ \qquad (19)$$

Biocorrosion can also happen in concrete sewer pipelines under aerobic conditions by the well-established bacterial species *Thiobacillus ferroxidans*. This bacterium can oxidize sulfur, sulfide, and H_2S into sulfuric acid. The liberated acid corrodes the steel and concrete and produces calcium sulfate and bi-carbonates. Additionally, the SRB reduce sulfur and form hydrogen sulfide under anaerobic conditions. Beneath the water level, the microbial species attach to the wall and form a slime layer. The oxygen liberated from the sewage can to penetrate to a particular depth of the slime layer, which helps the rapid breakdown of organic compounds in the presence of aerobic bacteria. Underneath the slime film, sulfate reducing bacteria oxidize carbon and interact with sulfate to produce sulfide ions and carbon dioxide as a by-product, as denoted in Eq. (20). After that, the sulfide again comes back to sewage and the hydrogen sulfide is retained in the solution. During the time of turbulent flow, the H_2S escapes and undergoes an oxidation process to produce sulfuric acid by the sulfur oxidizing bacteria [22]. Eventually, the sulfuric acid interacted with concrete and breakdown into hydrated calcium sulfate, calcium sulfate, and bi-carbonates, as shown in Eqs. (21) and (22) and schematically given in Figure 2. The list of SRB following the types of mechanism is given in Table 1.

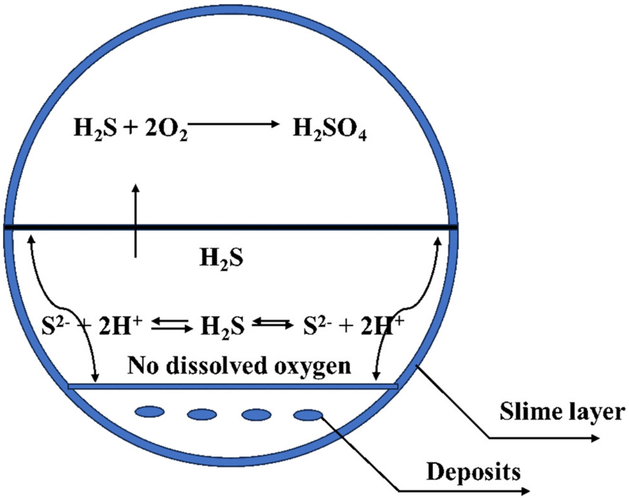


Figure 2: Biological mediated corrosion in concrete systems [23].

$$SO_4^{2-} + 2C \rightarrow S^{2-} + CO_2 \qquad (20)$$

$$H_2S + O_2 \rightarrow H_2SO_4 \qquad (21)$$

$$CaCO_3 + Ca(OH)_2 + 2H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O + CaSO_4 + H_2CO_3. \qquad (22)$$

1.3 Traditional corrosion inhibitors

Traditional inhibitors can lessen the effect of corrosion on metal surfaces under corrosive conditions at a specific ideal concentration of inhibitor material. The chemical compound, which prevents oxidation or reduction on metal surfaces, is called an inhibitor [18].

Specifically, corrosion inhibitors enhance its activity by

1) The establishment of interaction with corrosive material can reverse the state of the material into a noncorrosive nature.
2) Development of a defensive layer over a metallic surface preventing it from deterioration.

The inhibitors are classified as inorganic(II) and organic inhibitors (OIs), where their subtypes are classified based on interactions like cathodically, anodically, and mixed-type inhibitors [3]. Chemical compounds such as NO_2, PO_4, OH, molybdates, sodium chromates, and SiO_4 are the anodic inhibitors, while the oxides and salts of

Table 1: List of aerobic and anaerobic bacterial species that cause biocorrosion on metal surfaces

Sl. no	Microorganism	Cell wall	Method of corrosion	Aerobic/anaerobic	Ref.
1	*D. desulfuricans*	Gram negative G-ve	Sulfur reducing	Anaerobic	[24]
2	*D. vulgaris*	G-ve	S^{2-} reducing	Anoxic	[25]
3	*D. thermophilus*	G-ve	Sulfur reducing	Anaerobic	[26]
4	*D. bearsil*	G-ve	Sulfur reducing	Anaerobic	[27]
5	*D. baculatus*	G-ve	S^{2-} reducing	Anoxic	[28]
6	*D. africanus*	G-ve	Sulfur reducing	Anaerobic	[29]
7	*D. gigas*	G-ve	Sulfur reducing	Anoxic	[30]
8	*Desulfotomaculum species*	G-ve	S^{2-} reducing	Anaerobic	[31]
9	*Desulfomicrobium salsuginis*	G-ve	S^{2-} reducing	Anaerobic	[32]
10	*Desulfomicrobium aestuarii*	G-ve	Sulfur reducing	Anoxic	[33]
11	*Desulfomicrobium baculatum*	G-ve	Sulfur reducing	Anaerobic	[34]
12	*Desulfobulbus propionicus*	G-ve	S^{2-} reducing	Anoxic	[35]
13	*Desulfobacter hydrogenophilus*	G-ve	S^{2-} reducing	Anaerobic	[36]
14	*Desulfococcus biacutus*	G-ve	S^{2-} reducing	Anaerobic	[37]
15	*Desulfococcus multivorans*	G-ve	Sulfur reducing	Anoxic	[38]
16	*Desulfococcus oleovorans*	G-ve	S^{2-} reducing	Anoxic	[39]
17	*Bacillus cereus*	Gram positive	Nitrate reducing	Aerobic	[40]
18	*Acidithiobacillus thiooxidans*	Gram positive	Sulfur oxidizing	Obligate aerobic	[41]
19	*Thiomonas intermedia*	G-ve	Sulfur oxidizing	Obligate aerobic	[42]

antimony, As, and Bi can be used on the cathodic area of solution and considered as cathodic inhibitors [42]. In addition, the OI can accomplish the adsorption phenomenon on the surfaces of metals by (i) hydrolysis of organic compounds, where insoluble metal salts are deposited on metal surfaces. (ii) The interaction between π-electrons of aromatic compounds or electron pairs of elements such as oxygen, sulfur, and nitrogen and metal species with vacant d-orbitals [27].

Traditionally, reduction is carried out by the polarization of metal species and the formation of thin film around the metal surfaces by organic amines, imidazolines (IMs), and Schiff bases [43,44]. Liu and Zheng [45] described that the hydrophobic and hydrophilic nature of functional groups existing in the IM is responsible for the inhibition of corrosion on metal surfaces. Furthermore, the work done by Li *et al.* [46] depicted the effect of IM on the crevice corrosion of N80 carbon steel, revealing that the efficiency of inhibition is directly proportional to the concentrations of inhibitors. Additionally, the compound that has jasmine or methylamine groups double bond between C and N, known as Schiff base, can bind with metal surfaces and diminish corrosion by preventing the interaction of anticorrosive agents with the metal [47]. Yuce *et al.* [48] delineated that organic amines have hydrolysis resistance, biodegradability, and stability of functional groups as exceptional corrosion inhibitors. In recent decades, researchers have developed artificial corrosion inhibitors made up of inorganic or artificially developed organic corrosion inhibitors. The inhibition compound 2-amino-4-methylthiazole synthesized and developed by Li *et al.* [46] showed an excellent effect on metal corrosion as it forms a covering layer by physical adsorption, which prevents corrosion on low carbon steel [49]. Avdeev *et al.* [50,51] observed and stated the impact of unsaturated bonds of aldehydes concerning inhibitor concentration on carbon steel under HCl and H_2SO_4 medium. In addition to that, 2-cyclohexanecyclo-hexanone has a substantial inhibition effect in hydrochloric acid medium with an efficiency of <90% [51].

Despite the above corrosion inhibitors, some drugs have been used to inhibit corrosion. Ostapenko *et al.* [52] observed that drugs like 2-clohexenylcyclohexanone have cathodic and anodic sites, which can inhibit corrosion on metal surfaces such as steel with an efficiency of about 92–96%, respectively. Bashir *et al.* [53] depicted that the phenobarbital-named drug acts as an active inhibitor with 95% inhibition efficiency, and the $C_5H_3ClN_4$ (chlorinated pyrimidine) acts as an effective forbidden on corrosion of steel metal in an acidic environment and also the minor rise up in concertation of drugs can affect the efficiency of inhibiting characteristics [54,55]. Likewise, the mechanism of inhibition was well labeled by the Langmuir adsorption isotherm through the experimentation of varying initial concentrations of corrosion inhibitors from the pyridine derivatives and phenylhydrazine. Several authors elucidated and analyzed corrosion inhibitors based on Langmuir isotherm, which includes compounds formed by quinoxaline and pyrazine derivatives showing mixed-type inhibition in nature. The inhibition effects on metals like copper and CS in nitric acid and hydrochloric acid have been studied using drugs, namely, Amikacin Disulfate, Esomeprazole and Lansoprazole, and acrylamide methyl ether, respectively [56]. Some of the drugs used for resisting corrosion are given in Table 2. The current review article discusses about various types of phytochemical compounds (natural inhibitors) and their extraction methods for effective separation of phytocompounds. In addition, this article attests to the inhibition characteristics of phytochemicals (alkaloids, flavonoids, phenols, tannins (Tas), and glycosides) on CS, SS, and MS in acid, alkali, and also in biological medium. Likewise, this article gives a brief discussion about natural corrosion inhibitor with respect to the effect of solvent on phytochemical compounds, the effect of temperature and resistance nature of phytocompounds extracted from seeds and leaves. This review article also depicts the basic knowledge on the applications of computational analysis to understand the interaction mechanisms between metal surface and phytochemical compounds.

1.4 Green corrosion inhibitors

These inhibitors are naturally derived compounds with minimal or no harmful environmental effects. Highly toxic corrosion inhibitors, which are used traditionally, have a noticeable effect on damaging environmental conditions. To reduce the toxic effect, these eco-friendly green corrosion inhibitors possess various types are listed in Figure 3.

1.5 Types of phytochemicals from plant extract

The plants contain various types of phytochemicals as a part of their metabolic activities. The biodegradable and environment-friendly plant extracts can be separated with more straightforward and cost-effective extraction, formulation, and application, which fascinates researchers to develop and investigate plant extracts as a corrosion inhibition agent. Phytochemicals such as phenolics, saponins, terpenoids, alkaloids, flavonoids, TAs, and essential oils have reactive groups with metal ions, and they formulate a defensive layer on the superficial area of metals, which leads to inhibit the corrosion effect on metal surfaces [70].

1.5.1 Alkaloids

This phytochemical is biosynthetically derived from amino acids and is present in various structural forms isolated from plants and found in 20% of plant species. Alkaloids like papaverine, strychnine, quinine, and nicotine are considered corrosion inhibitors based on the interactive nature of phytochemicals with metal ions. The alkaloid structures contain heteroatoms like nitrogen and oxygen associated with double bonds, which endorse the adsorption between metals and GIs. It can form protective coverage along with metal surfaces through adsorption.

1.5.2 Flavonoids

Flavonoids are a group of secondary metabolites that originate in a variety of plants. The structure of flavonoids

Table 2: List of drugs used to resist corrosion on metal surfaces

Sl. no.	Name of the compound	Description	Ref.
1	Augmentin	Brass in acidic media	[57]
2	Azithromycin	Presence of copper in NaCl salt solution	[58]
3	Antibiotics	Different metals	[59]
4	Ambroxol	MS in 1 M HCl	[60]
5	Amitriptyline	Steel in an acidic medium at different concentrations	[61]
6	Amlodipine besylate		
7	Expired Asthalin	Acidic media	[62]
8	Atenolol and nifedipine	Corrosion of HCl	[63]
9	Atorvastatin and fresh atorvastatin		[64]
10	Benzosulfonazole	Chemisorptions for inhibition	[65]
11	Biotin drug		[66]
12	Expired Carvedilol	Followed both physisorption and chemisorption on the surface	[67]
13	Clozapine	In nitric acid and sulfuric acid	[68]
14	Cefuroxime Axetil, Cefixime, and Cefadroxil	CS in HCl	[69]

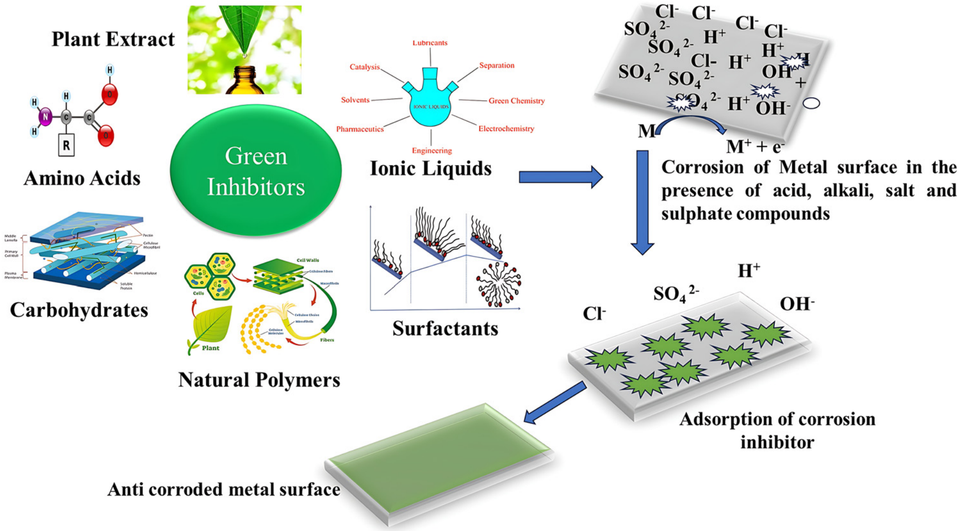


Figure 3: Schematic representation of different types of green inhibitors (GIs).

contains 15 carbon atoms organized in a benzene ring structure along with a carbon-oxygen bridge. The structural positions and antioxidant effects are the unique features of these molecules that make them special. Subtypes of flavonoids are chalcones, flavones, iso-flavonoids, flavanones, anthoxanthins, and anthocyanins. Some of these phytochemicals are responsible for yellow, red, and purple-red coloration in plant species [71]. According to Thacker [72], flavonoids are efficient inhibitors and show promising adsorption on zinc metal surfaces. The mixed type and temperature-dependent inhibition effect of flavonoids possess the capability to restrict corrosion on metal surfaces. The flavonoid derivatives such as naringenin, morin hydrate, and 6-hydroxy flavone are analyzed with various mechanistic properties and stated as suitable inhibitors for corrosion on metal surfaces where the electron delocalization through aromatic rings and minimal electron-withdrawing groups on aromatic rings are involved. The recent study delineated that the hydroethanolic extracts (HE) *Ammi visnaga* and *Zee mays* give a synergetic effect on the reduction in corrosion effect on MS in the presence of 1 M HCl medium. Based on the result obtained from electrochemical studies, the inhibition of corrosion by the HE, Zee mays, is very effective due to the flavones present in the flavonoids. Similarly, HE, *Ammi visnaga,* also reduces the impact of corrosive nature because of the condensed form of TAs (catechin). The chemistry of the process reveals that the restriction of corrosion by catechin and flavone is assisted by the chelation mechanism on the metal surface, due to the availability of oxygen in the adsorption center, benzyl group, hydroxyl ions, ketonic group, carbonyl groups, and electron-rich bonds present in both phytochemicals. The ligands form a strong coordination bond formation between metal and inhibitor by the existence of free heteroatoms and by the non-binding sites of the metal surface [73].

1.5.3 Terpenoids

Terpenoids are a significant and assorted group of phytochemicals. Adefegha *et al.* [74] stated that terpenoids are components of essential oils. The derivatives of terpenoids contain oxygen molecules, which are produced by mevalonate pathways in plants. Generally, it contains five-carbon isoprene units (C5, C10, C15, C20, C25, and C30) such as hemiterpenes, monoterpenes, sesquiterpenes, diterpenes, sesterterpenes, triterpenes, *etc.* It has also been proved that terpenoids possess antioxidant properties. Samal *et al.* [75], in the paper titled Expounding Lemonal Terpenoids Act, as a corrosion inhibitor for copper metal, analyzed and put forward the chemistry of inhibitors on the surface of metals, specifically copper, and suggested that terpenoids isolated from lemon extract have high potential to resist the oxidation of copper surfaces.

1.5.4 Phenols

Phenolic compounds are the richest secondary metabolites found in plants. They are produced by the interaction of shikimic acid and pentose phosphate through phenylpropanoid metabolization. The structure of such compounds includes benzene rings with single or multiple hydroxyl substituents, and they can be divided into simple to highly polymerized compounds. Phenols are antioxidants in nature and can prevent various oxidative stress-associated diseases [76]. Lakshmi *et al.* [77] reviewed that the phenols are effective corrosion inhibitors and their derivatives show a compelling anticorrosive nature on various metal surfaces. The compounds like phenols containing OH and NH_2 functional groups can interact and impel electrons on metal surfaces. An obstruction in metal oxidation or a protective layer covering are the primary reasons for exhibiting the anticorrosive properties of phenolic compounds. Chung *et al.* [78] demonstrated the antioxidant and anticorrosive effect of phenol compounds extracted from *Tragia involucrata L*. and examined the protective nature of phenols on CS metal surfaces against corrosion. Likewise, the phenolic compounds extracted from *Ammi visnaga* show synergetic effects on MS (MS) metal surfaces. The investigation states that phenolic compounds are effective against corrosion, and their efficacy could be improved with a rise in the concentration of phytochemicals [79].

1.5.5 TAs

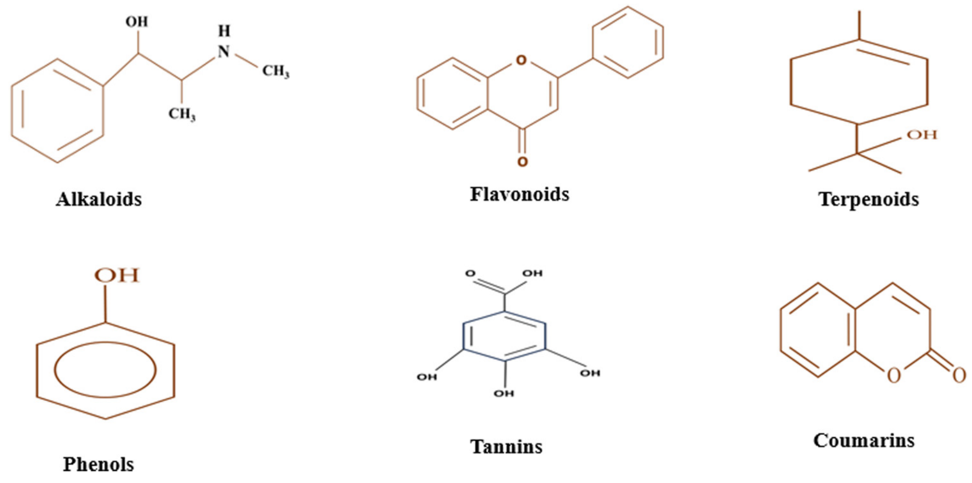
Plants contains a very diverse and high molecular weight phytochemical named TAs, and it is present during plant metabolism in both free and condensed form [80]. TAs are the most efficient inhibitor by forming ferric tannate film on the MS surface to inhibit corrosion. Additionally, tannic acid serves as a cathodic-type inhibitor, and the interaction mechanism is followed by the elimination of reactive compounds through cathodic reduction during both wet and dry cyclic conditions because of FeOOH adhesion on MS surfaces. In the assessment of TA as an effective corrosion inhibitor on the alloy of Al, the hydroxyl and carbonyl groups containing oxygen atoms, which can donate a single pair of electrons to the metal species, and aromatic π-bonds provide electrons that can form a protective layer on the metal surface, results in the reduction in corrosion of Al. Moreover, the film is nontoxic to the environment [81].

1.5.6 Glycosides and coumarins

Coumarins are the family of benzopyrones (1,2-benzopyrones, or 2*H*-1-benzopyran-2-ones), containing oxygen molecules in their heterocyclic. Bandeira *et al.* [82] explored coumarin-based corrosion inhibitors on MS, and their derivatives were synthesized and evaluated. The major phytocompounds like 3-(3-benzyl-4-hydroxy-2-thioxo-3,4-dihydro-2*H*-1,3-thiazin-6-yl)-8-methoxy-2*H*-chromen-2-one and 3-(3-benzyl-4-hydroxy-2 thioxo-3,4-dihydro-2*H*-1,3-thiazin-6-yl)-2*H*-chromen-2-one are found out that coumarins involved in mixed type of corrosion inhibition. The compounds prevent the attack of chlorine ions on metal, by forming a non-crystallized defensive layer on the surface of the metal. The inhibition efficiency achieved by these derivatives is found to be 93.59 and 92.17%, respectively. The molecular structure of different phytochemicals are clearly mentioned in Figure 4.

2 Various methods to extract phytochemicals from plant extracts

Various available works of literature attest that plants and components, such bark, peel, flower, root, seed, and fruits



Alkaloids

Flavonoids

Terpenoids

Phenols

Tannins

Coumarins

Figure 4: Molecular structural representation of various phytochemicals.

Table 3: Different types of extraction process for the separation of plant extracts [92]

No.	Types of extraction methods	Advantages	Major instructions
1	Separation of plant extract by SE	Enhanced energy competence, more production, easy to recover the extract with less time	SE sometimes affects the properties of plant extracts with respect to solvent polarity, solvent ratio, extraction time, and temperature
2	Microwave-assisted extraction	Less reaction time and reduces the damage of active phytochemical compounds	Microwave has symbiotic effect on both thermal heating and breaking of bonds, whereas other extraction methods does not have such characteristics
3	Enzyme-based extraction	Appropriate technique intended for liberating confined constituents, improved inclusive yield	Permitting for the consumption of almost the whole plant
4	UAE	High effective method for extracting plant yield more than 99.9% in certain studies, with any damage of Phyto compounds	UAE process aids to leach both organic as well as inorganic products with high efficiency

have different types of phytochemicals such as flavonoids, saponins, terpenoids, alkaloids, organic acids, and alkaloids, which can significantly be used as a green corrosion inhibitor [83]. Besides, phytochemicals are synthesized primarily from the leaves by the absorption of sunlight, water, and carbon dioxide [84]. The most common functional groups found in phytochemicals are amide, hydroxyl, carboxylic acid, amino, and hydroxyl, which contribute to the corrosion inhibition process through monolayer or multilayer adsorption phenomena [85]. Solvent extraction (SE), microwave-assisted extraction, enzyme-assisted, and ultrasonic-assisted extraction (UAE) are the major methods currently used for the effective separation of phytochemical from plant extracts. The major instructions and advantages of various extraction methods are given in Table 3 and the steps involved in the extraction process are represented in Figure 5.

3 Analytical methods used to understand the corrosion system

The primary methods to understand corrosion behavior are weight reduction measurements, electrochemical methods, and surface analysis. The techniques included in the electrochemical analysis are linear polarization resistance, impedance analysis, Tafel extrapolation techniques, and

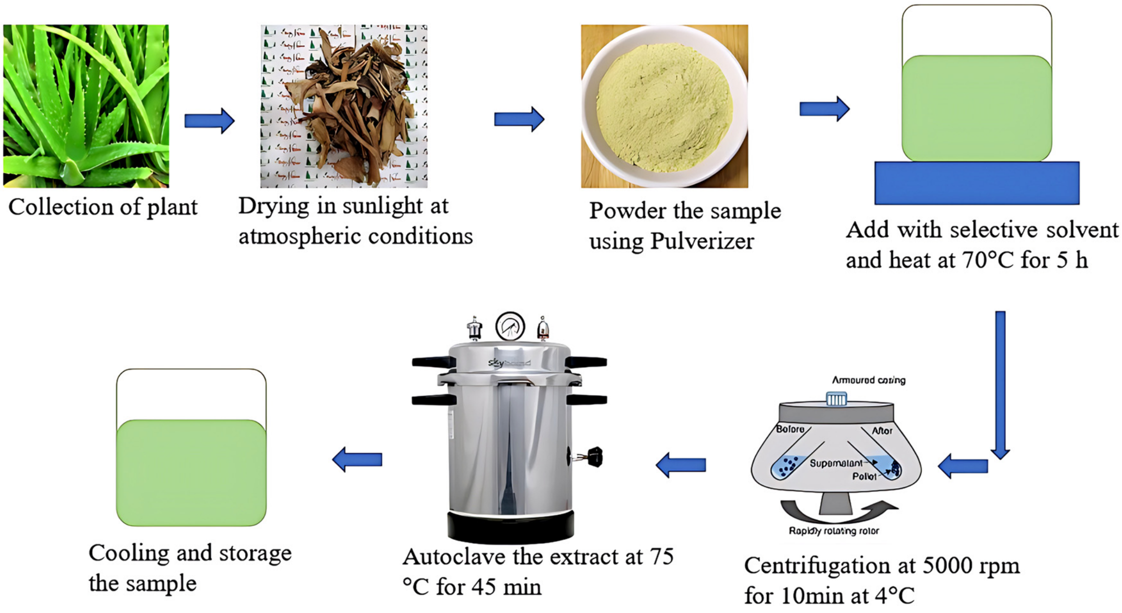


Figure 5: Schematic representation of steps involved in the extraction of phytocompounds.

electrochemical noise [86]. However, among all the electrochemical noise techniques, it is rarely used to spot the localized forms of corrosion by observing drift and irregularity in current and voltage noise signals [87–89].

3.1 Estimation of weight loss

Before the analysis of weight loss measurement, the metal surface was polished by different abrasive papers, then rinsed and washed with polar (water, acetone, and ethanol) solvents, and dried at atmospheric temperature. After that, the weight of the metal specimens is measured using an optimized and most sensitive electronic weighing balance before being rinsed in the biocides. To address the weight loss, the properly eviscerated corroded metal specimen has to be exposed to the plant extracts for a fixed time of exposure [90]. Eventually, the efficacy of corrosion resistance can be assessed by measuring the difference in mass of the metal specimen before and after the interaction of phytochemicals. The rate of corrosion is elucidated by the weight loss observed over time, which can be represented by different units (mils per year or inch per year (py), millimeters per year (mm/year), and mg·dm^{-2}. The effectiveness of corrosion frequency was determined by Eqs. (23)–(25). To elucidate the rate of corrosion by weight loss, a research article result was inferred in Figures 6 and 7, provided that the corrosion rate and inhibitor efficiency variation, concerning inhibitor concentration, and temperature [91].

$$\text{Weight loss } (\Delta W) = W_1 - W_2 \tag{23}$$

$$\text{Corrosion rate (CS)} = K\frac{\Delta W}{\text{DAT}} \tag{24}$$

$$\text{Inhibition efficiency (IE)} = \frac{W_0 - W_1}{W_0} \times 100 \tag{25}$$

where W_0 and W_1 are the mass of the metal before and after interacting with biocides, CR is the corrosion rate (mpy), K is the constant (2.83106 for mpy), D is the density of metal (7.86 for CS), t is the reaction time (hours), and A is the reacting or interacting area (cm^2).

3.2 Electrochemical analysis by potentiodynamic polarization (PDP) method

In this electrochemical method, the rate of corrosion and inhibition rate have been evaluated by gauging the current densities anodically and cathodically by using a three-electrode system (reference electrode: standard hydrogen or silver chloride, auxiliary electrode: platinum, and working electrode: respective corroded metal). The reference electrode quantifies and resists the system's voltage(v), and the counter electrode enumerates the current(i). The open circuit potential (E_{ocp}) of the respective metals varied when the electrochemical reactions proceeded. During the Tafel analysis, the potential will be applied to carry out both oxidation and reduction, and the observed current density will be used to elucidate the changes in corrosion before and after the interaction of inhibitors. Eventually, the percentage of corrosion was determined by comparing the current densities observed before and after

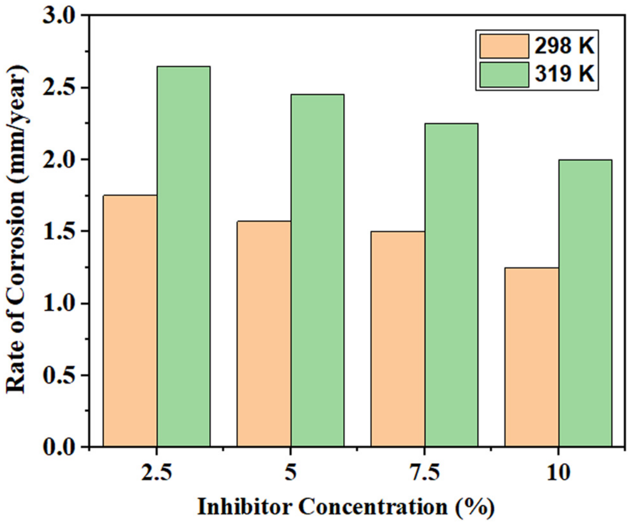


Figure 6: The corrosion rate of MS coupons in the presence of *Elaeis guineensis* extract in 1 M HCl at different temperatures [93].

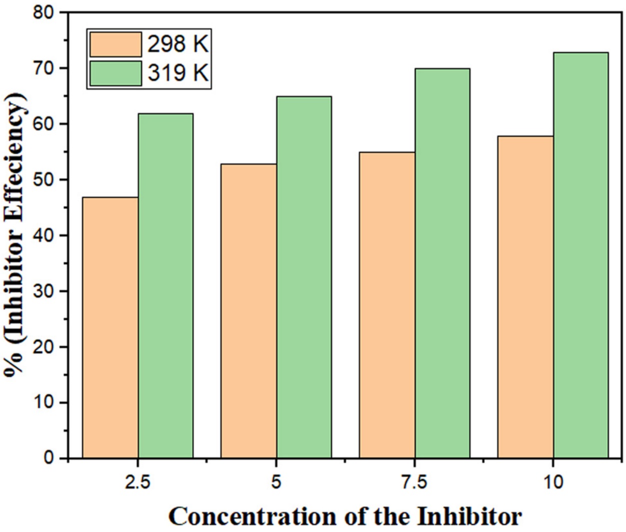


Figure 7: Inhibitor efficiency of MS coupons in the presence of *Elaeis guineensis* extract in 1 M HCl at different temperatures [93].

interaction with the plant extract (inhibitor). The percentage of efficiency and corrosion can be evaluated by the following equations [92,93]. For the betterment of understanding, polarization and impedance results obtained from the study by Baskar *et al.* [95] were used for discussion. In this work, the polarization studies were carried out with varying inhibitor concentrations from 50 ppm to 250 ppm of *Trochodendron Aralioides* extract in the presence of an acid medium. Figure 9 reveals that the rate of corrosion decreases by increasing the concentration of the inhibitor. This is reflected in the reduction in current density from −0.5 to −1.5 A·cm^{-2}, which is concerned with the potential shifting of −0.7 to −0.85 V. In addition to that, the Tafel plot confirms that the interaction between the extract and the metal surface followed physisorption (Gibbs free energy is positive).

$$\text{Inhibition efficiency (\% IE)} = \frac{I_{O-I}}{I_O} \times 100 \qquad (26)$$

$$\text{Corrosion rate (CR)} = \frac{I_{\text{corr}} \times \text{Eq}}{F} \qquad (27)$$

where I_O is the current density before interaction with inhibitor (A·cm^{-2}), I' is the current density after interaction with inhibitor (A·cm^{-2}), I_{corr} is the current density after the oxidation and reduction process (A·cm^{-2}), F is the Faraday's constant and Eq: Equivalent mass of metal (g).

3.3 Electrochemical impedance spectroscopy (EIS)

EIS is a very effective electrochemical evaluation of the surface properties of the electrode and kinetics through impedance results. In this study, a three-electrode system was used with a potential change of 5–50 mV of AC voltage, with a frequency range of 10^5–10^{-2} Hz. EIS typically measures the impact of solution resistance and capacitive resistance, observed before and after the interaction of plant extracts on the metal surface using the Nyquist plot. Additionally, the Nyquist plot referred to in Figures 8 and 9 attests that intensification of extract amount profiles two significant observations: (i) with a decrease in solution resistance and (ii) momentous surface coverage and an increase in the resistance of charge transfer by increasing the inhibitor concentration.

$$\text{Inhibition efficiency (\% IE)} = \frac{1 - R_{\text{ct}}}{R_{\text{ct}}} \times 100 \qquad (28)$$

$$\text{Corrosion rate (CR)} = \frac{I_{\text{corr}} \times \text{Eq} \times 10 \times 3.15 \times 107}{\text{FD}} \qquad (29)$$

R^{*}_{ct} and R_{ct} are the resistance of charge transfer before and after interaction with the inhibitor.

3.4 Scanning electron microscopy (SEM)

SEM is typically used to address the microscopical and nano-level changes on the surface of the metal specimen before and after interaction with the corrosion inhibitor. From Figure 10 (Shasuzzaman *et al.* [94]), delineated the anticorrosive nature of *C. Tagal* extract in the presence of 1 M HCl on the MS surface.

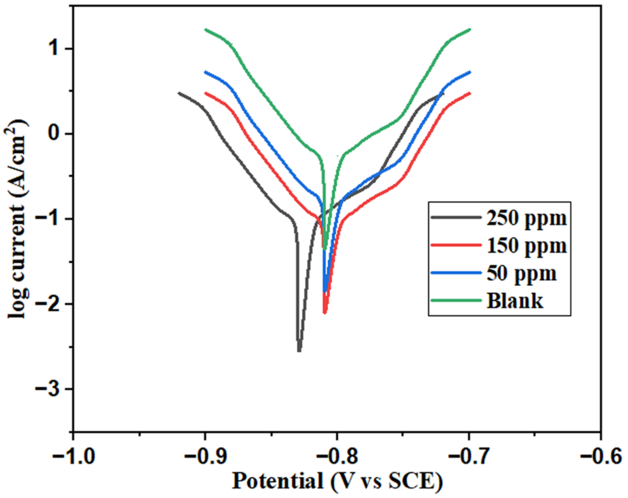


Figure 8: Polarization studies on testing the anticorrosive nature of *Trochodendron Aralioides* in the presence of 1 M HCl on a MS surface [95].

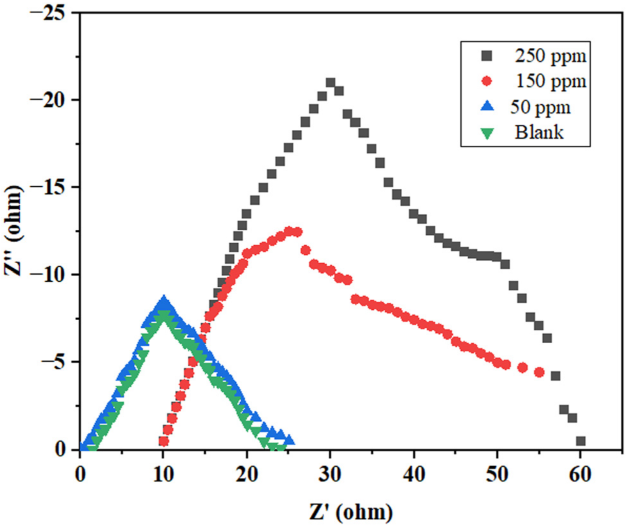


Figure 9: Electrochemical impedance for MS in the HCl medium along with *T. Aralioides* plant extract [95].

4 Discussion on the anticorrosive effect of natural inhibitors on SS, MS, and CS in acid and alkali medium

The corrosion mechanism clearly depicts that metal corrosion has prevailed during acid, neutral and base pH conditions under aerobic and anaerobic conditions. Metal hydroxides, metal carbonates, and metal sulfates are the major products exhibited in acid/base medium as well as in microbially influenced corrosion processes. In chemical corrosion, the phytochemicals tend to reduce the formation of hydroxides, chlorines and, in the case of bio-corrosion, the phytochemicals should act as antibacterial and anti-corrosive against hydroxides, sulfates, and carbonates. Besides, the inhibition effect on the metal surface is predominantly executed by two steps: (i) adsorption of corrosion inhibitor and (ii) formation of protective film and hindering the active sites by the heteroatoms, pi- electrons, and aromatic rings. In most of the research work, the irreversible nature of inhibitor and metal interaction is postulated by adsorption models. The adsorption models evaluate the negative Gibb's free energy, to understand whether the adsorption mechanism is spontaneous or not, by using Eq. (30).

$$\Delta G^{O}_{\text{ads}} = -55.5\ \text{RT} \ln K_{\text{ads}} \tag{30}$$

where R ($\text{J·mol}^{-1}\text{·K}^{-1}$) is the universal gas constant, T (K) is the absolute temperature, K_{ads} is the adsorption equilibrium constant, and 55.5 is the concentration of solution in mol·L^{-1}. The negative $\Delta G^{O}_{\text{ads}}$ above $-40\ \text{kJ·mol}^{-1}$ denotes the interaction between metal and inhibitor followed by chemisorption, less than $-20\ \text{kJ·mol}^{-1}$ tends to physisorption, and -20 to $-40\ \text{kJ·mol}^{-1}$ concludes that the interaction is mixed adsorption.

CS is one of the major metals, effectively used for the production of high viscous (oil) and gas carrying pipelines, because of its high mechanical strength and cost-effective characteristics. But CSs are highly damaged by pitting corrosion in the presence of sulfate, CO_2, and weak acids. The weak acids are formed by the reaction between carbon dioxide and water medium. Several studies stated that the phytochemical compounds, addition of solvents with phytocompounds, plant extracts from leaf, polyphenols and polysaccharides has an eminent potential to resist the corrosion on CS in acid medium, salt medium, and also gas phase medium.

The combination of a polar solvent along with a corrosion inhibitor enhances the effectiveness of inhibition because it enhances the stability and decreases the viscosity of the inhibitor. These two properties increase the affinity of biocides on metal surfaces for resisting corrosion consequences. The anticorrosive effect of PE prepared with ethanol and the addition of potassium iodide on CS Q-235 in the presence of $0.5\ \text{mol·L}^{-1}$ sulfuric acid medium. The researcher investigates the effectiveness of PE by weight loss measurement, electrochemical analysis (EIS), and PDP. The obtained result concluded that the PE gives a 99% anticorrosive effect against CS in the presence of the lowest concentration of KI. Due to the electronegativity of I^-, the attachment of the inhibitor is very strong and irreversible. In addition, the impedance study and polarization study confirm that an increase in KI concentration reduces the solution resistance to around 1.86 ohms and I_{corr} (5.59×10^{-5}) A·cm^{-2}, which is more favorable for inhibitor and metal interactions, due to the elevation of negative surface charge of inhibitor [96]. In addition, the adsorption of PE on CS is mediated by physisorption or through electrostatconcentration, which interactions, as configured in Figure 11.

The leaves have more phytochemical compounds than the other parts of the plant because of high water absorption, sunlight, and carbon dioxide. The potential of corrosion inhibition capability of olive leaf extract (OLE) was tested by varying its concentration (from 50 to

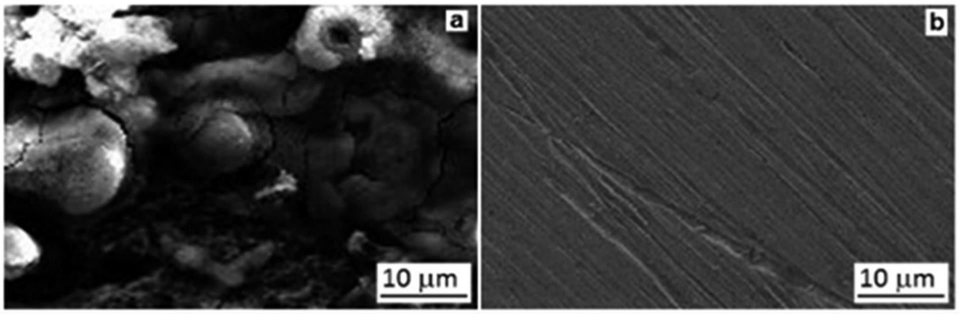


Figure 10: Scanning electron micrograph of MS in the (a) presence of 1 M HCl and (b) 600 parts per million of *C. Tagal* extract along with acid [94].

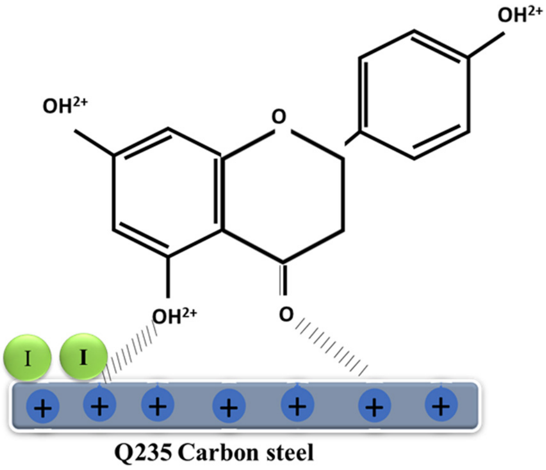


Figure 11: Mechanism of interaction between GI (parsley extract, PE) on the metal surface [96].

300 mg·L^{-1}) on CS in the presence of carbonated chloride solution (30 g·L^{-1} NaCl, 0.1 g·L^{-1} $NaHCO_3$, and 0.1 g·L^{-1} $CaCO_3$) using polarization studies and electrochemical impedance. The high performance liquid chromatography studies reveal that the OLE extract comprises various aromatic compounds like oleuropein, vanillin, hydroxytyrosol, luteolin, *etc.* These aromatic compounds restrict corrosion behavior because of their aromatic nature. The Tafel analysis concludes, that the OLE extracts can mitigate the reduction reaction in the cathodic region. Because of that, the cathodic current was drastically reduced. The lessening of cathodic polarization is clearly reflected in the changes obtained in the I_{corr} from 107.70 to 4.56 A·cm^{-2} [97,98].

Polyphenols are effective phytochemicals used for surface handling and coatings for the protection of metals in the presence of acid and alkali mediums. Furthermore, the polyphenols are fewer toxic substances that can easily separate from the plant source. These Phyto compounds can create complexation with metals and form insoluble metal complexes. Chen *et al.* [99] studied the inhibition effect of *Ilex kukicha* (IK) concentration, which varied from 0.1 to 4%. It was tested on CS with 3.5 wt% NaCl saturated with carbon dioxide. In addition, the Fourier-Transform Infrared spectroscopy (FTIR) studies reveal that polyphenols, such as flavonoids, triterpenoid, one isoflavone, three flavanols, one dihydro flavanol, and anthocyanidins have functional groups like carboxyl, hydroxyl, C–O, and C═C, can reduce corrosion effect. The electro impedance studies and theta frequency studies admit that the addition of IK to the NaCl medium increases the resistivity of chloride interaction and charge transfer, respectively. It is mainly due to the interaction of a lone pair of electrons with an oxygen molecule and conjugated double bonds present in the flavonoids. The maximum percentage of anti-corrosive effect exhibited by IK was found to be 96.53%. The open circuit potential studies revealed that the corrosion current declined from 35.986 to 1.17 A·cm^{-2} at 3.5% IK concentration. Likewise, the performance of the inhibition effect of *Morus alba pendula* (MAP) leaf extract on a steel surface in 1 M HCl medium was analyzed at 25°C. The gained result clearly stated that the presence of flavonoids like Morusin, kuwanon C, and kuwanon G, phenolic acids, and pyrrole alkaloids has significant corrosion inhibition with 93% efficiency. Also, they found that the addition of KI along with the flavonoids increases the efficiency of inhibition by around 96%, obeying monolayer coverage of adsorption Jokar *et al.* [100].

Some scientific studies have proved that polysaccharides also can reduce the corrosion effect because of long polymeric chains, more heteroatoms with high electronegativity, enriched conjugated pi bonds, and more adsorption capacity against metal surfaces. Based on this information, Mobin and Rizvi [101] investigated the corrosion inhibition effect of polysaccharides isolated from *Plantago ovata* (PO) on CS in 1 M hydrochloric acid solution. The studies depicted that the mucilage of the plant extract comprised of polysaccharides such as arabinose (galacturonic acid) and rhamnose xylan (AX) has anticorrosive characteristics of CS in an acidic medium. The surface characterization and the quantum level changes also indicate that the inhibition of corrosion is mainly due to the formation of a protective layer by saccharides on metal surfaces. Also, they found that the efficacy of inhibition depends upon the temperature and concentration of plant extract, and the amount of phytochemical adhered to the metal was around 935.4 ppm. Eventually, the maximum percentage of anticorrosive effect achieved by the PO was around 94.4% at 60°C. The impedance and Tafel analysis denoted that the interaction of chlorine on the metal surface is highly resisted by PO extract and the current density was reduced from 10^{-3} to 10^{-5} A·cm^{-2}, respectively.

Alibakhshi *et al.* [102] studied the influence of mixed types of inhibition on MS in the existence of 1 M HCl using *Glycyrrhiza glabra* extract. The performance of corrosive inhibition was analyzed by polarization and impedance studies, atomic force microscopy (AFM), and goniometer to analyze the surface changes and contact angle properties of the inhibitor. From the polarization studies, they observed that the current density declined from 260 to 40.2 μA·cm^{-2} by adding 800 ppm of inhibitor, which shows an efficiency of 88% inhibition. Furthermore, the topographical analysis delineated that the surface adsorption of organic compounds such as Glycyrrhizin, Licochalcone A, 18β-Glycyrrhetinic acid, Licochalcone E, and Glabridin,

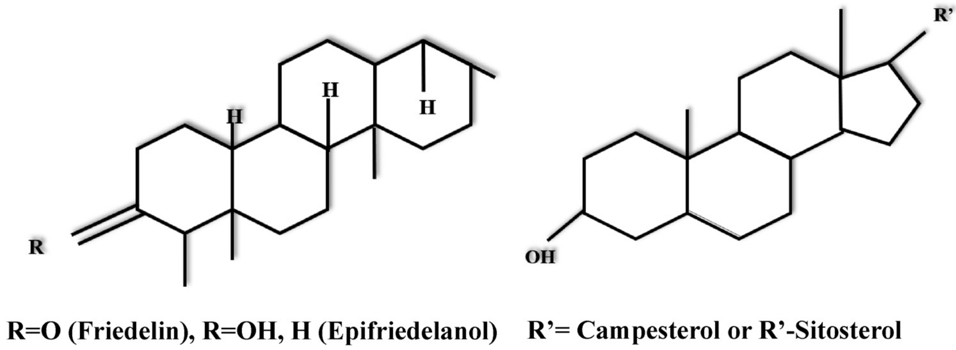


Figure 12: Schematic representation of chemical structures of some phytochemicals found in FE [115].

Liquiritigenin creates a protection layer and reduces the corrosion on metal surfaces.

El-Etre and El-Tantawy [103] analyzed the inhibitive efficiency of pitting corrosion on CS, nickel, and zinc using *Ficus extract* (FE). The proficiency of the anticorrosive nature was examined using various measurements such as potentiostatic and polarization techniques. The result depicted that the FE has the potential to decrease the deterioration rates of the three metals in acidic and alkaline nature. From the characterization studies, the researchers found that the extracts comprised different types of phytochemicals like friedelin, epifriedelanol, and nitinol sterols, which are mentioned in Figure 12.

In another research work, Philip *et al.* [104] tested the anti-corrosion effect of cashew nutshell (CSNL) at 80°C on CS in the presence of carbon dioxide. The pH of the inhibitors depends on the structure of the inhibitor shown in Figure 13, as well as the metal corroding nature and the active types of reactive analytes existing in the inhibitor. A similar kind of investigation was carried out by Philip *et al.* [105] concerning pH (4–6) resulting in 3% NaCl along with saturated CO_2 at 30°C. It is observed that the corrosion inhibition increases as the pH increases from 4 to 6, resulting in a reduction in current densities when the oxidation process is not anodically polarized. In addition to that, the occurrence of phenoxide in CSNL suggestively reduces the corrosion in CO_2 dissolved alkali medium. The obtained result delineated that the phytocompounds has been attached on metal surface by the mechanism of adsorption followed by weak forces of interaction between the cationic metal outer layer and anionic-charged phenoxide ions, as schematically shown in Figure 14.

Eventually, these studies delineate that the functional groups such as hydroxyl, carbonyl, acetyl present in the phytocompounds have given a significant impact on resisting the corrosion against pitting formation. In addition, the glycosides and aldehydes in the polysaccharides also work as inhibitors on CS against the chlorine ion. Moreover, the attachment of polyphenols such as flavonoids, phenolic compounds, glycosides has effectively reduced the corrosion current during oxidation and reduction on CS surface by forming a film over the metal surface.

In case of corrosion, MS is majorly corroded by the electrochemical reaction between the metals as well as environmental factors. Particularly, the vapor or gaseous state of hydrogen ions leads to form metal hydroxide acid medium. This reaction is common in any water medium. Several literatures state that the carbonyl, hydroxyl, acetyl and methylated gropes present in the phytocompounds

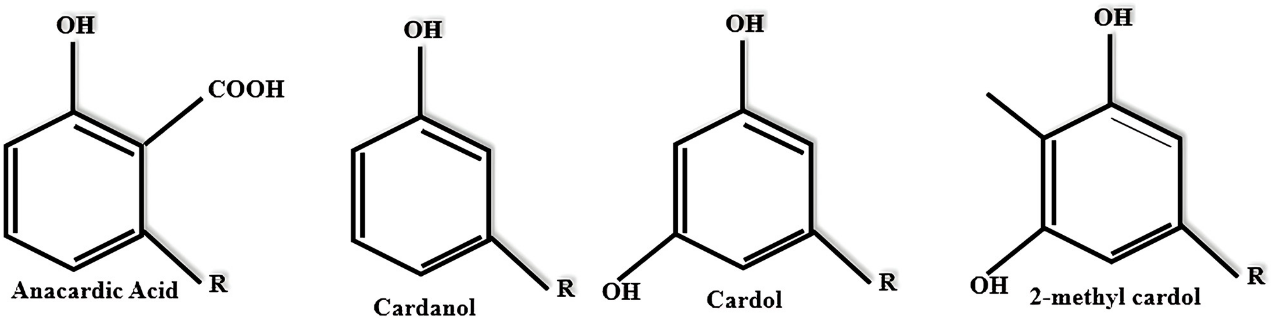


Figure 13: Molecular structures of the organic compounds present in CNSL [104,105].

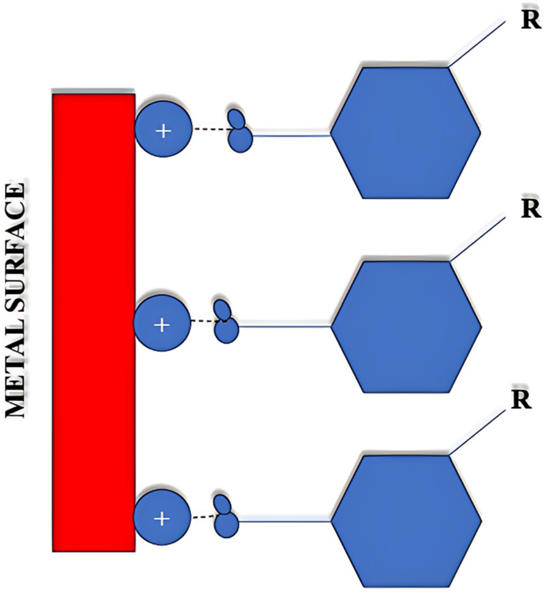


Figure 14: Mechanism followed by CSNL during adsorption on a metal surface [104].

can resist the corrosion behavior on MS surface effectively in acid medium. In addition to that, the fatty acids, alcohols, cellulose, xylanase, and polyphenols extracted from the plant seeds play a vital role in the inhibition of corrosion effect. Okewale and Adesina [106] elucidated the inhibition effect of *Theobroma cocoa* (TC) plant extracts on MS in the presence of 1M HCl solution medium. The author tested the inhibitor's performance and its characteristics through electrochemical methods and FTIR studies. The inhibition effect of TC was analyzed by varying concentrations from 0.5 to 3%. The FTIR results confirm that the aromatic, carboxyl, and alkyl groups are responsible for interaction on metal surfaces with weak bonds. The impedance and open circuit potential studies attest that the flavonoids present in the extract reduce the flow of conductivity and the current density was anodically reduced from 0.06 to 0.005 $A\cdot cm^{-2}$. The observation states that the complexation of TC on the metal surface denied the oxidation process due to the decline in donating unpaired electrons by oxygen molecules. Moreover, the rate of corrosion is reduced inversely concerning temperature because of the vaporization of phytochemicals. The attachment of phytochemicals on metal surfaces followed physisorption with an activation energy between 63.28 and 97.55 $kJ\cdot mol^{-1}$, respectively. However, the bark of the TC shows a less inhibition effect on CS, which is 18.23% less efficient than the benzotriazole drug Barreto *et al.* [107].

In addition, Carvalho *et al.* [108] and other researchers analyzed the corrosion inhibition effect using cocoa bean shells (CBS) on MS in an acidic medium. The maximum anticorrosive efficiency achieved by TC seed is around 97.92% in 1.77 $g\cdot L^{-1}$ concentration of inhibitor; however, the low concentration of inhibitor exhibits better results of about 96.03% at 0.44 $g\cdot L^{-1}$. In addition, the researcher proposed that CBS is a great alternative inhibitor for toxic traditional inhibitors, which is 600-fold less costly.

In addition, an increase in temperature also enhances the anti-corrosive effect. This is mainly because of higher diffusion rate of inhibitors and decreasing resistivity for electron transport in electrolyte solutions. The corrosive nature on MS and Al surfaces by using *Phyllanthus amarus* (PS) leaf extract at different temperatures. The study revealed that phytochemicals can reduce the oxidation of metals when the temperature increases beyond a certain point. Furthermore, the efficiency of inhibition is effective against acidic media on MS at around 95% and for Al is around 76%, respectively, at 60°C. In addition, the isotherm studies confirm that the phytochemicals adsorbed on the surface of metals followed monolayer coverage of adsorption [109,110].

Furthermore, in a study by Rahal *et al.* [111], the adsorption capacity and corrosion inhibition property of *Abelmochus esulentes* (AE) and *citrus maxima* (CM) were examined on MS using 0.5 M HCl medium, through electrochemical analysis and characterization studies. The experimental findings such as corrosion voltage (−448 and −410 mV), anodic Tafel constant of around (78 and 49), cathodic Tafel constants (10 and 86), and corrosion current of about (0.096 and 0.108 $A\cdot m^{-2}$) at 0.6 and 0.7 ppm of AE and CM confirmed that the plant sources AE and CM effectively resist the corrosion effect in MS. The obtained corrosion current values depicted that the amount of corrosion current observed in the presence of plant extracts is comparatively lesser than the control in both the inhibitor systems, which clearly ensure that the AE and CM are effective corrosion inhibitors at low acid concentration. FTIR results that, the carbonyl group, hydroxyl groups, and primary amine are the major functional groups present in the phytocompounds, which have the capability to restrict the formation of hydroxide on MS surface, clearly admitted from XRD result. Similarly, Abdel-Gaber *et al.* [112] observed that the phytochemical compound (Citronellal) extracted from eucalyptus has the potential to act as a corrosion inhibitor on MS in 0.5 M sulfuric acid and 0.5 M orthophosphoric medium. The presence of carbonyl, hydroxyl, acetyl, and methylated groups in citronellal behaves different pathway to resist the corrosion in sulfuric acid medium and H_3PO_4 medium. In sulfuric acid medium, the corrosion was restricted by preventing the dissolution mechanism by the phytocompounds. In case of orthophosphoric acid system, the corrosion inhibitors form a film on a strong black phosphate film, which resist the corrosion effect. The Tafel studies stated that, the I_{corr} existed on the MS surface in H_2SO_4 and H_3PO_4 acid medium was drastically reduced from 2.86 to 0.46 $A \cdot m^{-2}$ and 0.98 to 0.34 $A \cdot m^{-2}$ in the presence of phytocompounds, respectively. Besides, the quercetin present in the willow leaf extract act as a corrosion inhibitor on MS in 0.5 M HCl system as well as in 0.1 M nitric acid system. The maximum amount of inhibition efficiency achieved by the willow leaf extract was found to be 82 and 91%, respectively [113].

Examined corrosion resistance on MS surface pipelines used in oilfields by using an extract from *Griffonia simplicifoliay* (GS) separated from the seed and its leaves [114]. The observed result attested that the presence of O and N sites has more affinity on metal surfaces, which forms a shielding layer on the MS surface and is accountable for inhibition. Additionally, another set of studies revealing the use of different types of solvents in the extraction process shows a significant inhibition behavior in 1 M HCl medium. The percentage of inhibition efficiency achieved by the vegetal extract was found to be 95.86 and 82.14% in leaves and their seeds, respectively, at 30°C. Moreover, this diverse type of inhibition process followed Temkin adsorption isotherm, which confirms the molecular interaction between the plant extract and metal surface by weak forces of interaction.

The *sunflower seeds* (SFS) have huge amounts of long chain fatty acids, alcohols, carbohydrates, cellulose, xylanase furfural, and triterpenic alcohols, flavonoids along with a smaller number of proteins. All these compounds have heteroatoms like oxygen and nitrogen, capable of interacting with a metal surface which forms a film that prevents the corrosive conditions in an acid medium. *Cocoa pod Husk-Ficus exasperata* (CHF) used as an inhibitor on steel metal shows a maximum inhibition efficiency of around 95.42%, mainly due to resisting the loss of Fe^{2+} ions and maintaining the stability on the surface of the metal [115]. Farhadian *et al.* [116] investigated the anticorrosive effect of SFS on MS surface on 1 M HCl medium. The corrosion inhibition rate was delineated by using various potentiodynamic, impedance analysis, and UV-vis methods. They observed that the adsorption phenomenon was followed by the Langmuir adsorption isotherm with an inhibition efficiency of 98% at 400 ppm in 1.0 M HCl medium. Likewise, Ituen *et al.* [114] examined corrosion inhibition using sunflower extract in a 15% hydrochloric acid medium at a high temperature. Eventually, the obtained result showed a significant reduction in corrosion, up to 98% at 60°C and 93% at 80°C. From the review, it is observed that the presence of nitrogen and oxygen atom endeavors to resist the corrosion by forming a shielding layer on MS surface, even at high temperatures. The heteroatomic interactions led by these two atoms effectively reduces the formation of metal hydroxides during electrochemical reaction.

Generally, SS has been easily corroded in a high salt environment. Literature defines that at high temperatures with low relative humidity, the chloride forms a layer on SS, which deliberately causes pitting corrosion severely. The anticorrosive nature of plant extract collected from *Triticum aestivum* (TS) has several phytochemical compounds, such as *Lariciresinol, Metaresinol, Hisokinin, and S-stigmasta-dion-3beta-ol*, which have free heteroatoms responsible for interaction between metal and inhibitor. Besides, the research work analyzes the electrochemical behavior, surface properties, effectiveness of inhibitor, and adsorption mechanism. The result depicted that the plant extracts showed 90% inhibition against the HCl medium on SS, because of the interaction of heteroatoms present in the inhibitors. The adsorption of inhibitors follows both physisorption and retro-donation (donation of electrons to fill d-orbital of metal) explained in Figure 15. Also, the corrosion rate drastically decreased from 39.01 to 3.1 $mg \cdot cm^{-2}$ as the concentration of plant extract increased from 1 to 4 $g \cdot L^{-1}$, respectively. The SEM and AFM micrographs confirm the inhibition effect on the SS surface. The Tafel studies show a significant decrease from −6 to −8 $A \cdot cm^{-2}$ in the I_{corr} (current density) after the addition of inhibitors on the metal surface [117].

Bouyanzer and Hammouti [118] studied the anticorrosive consequence of *Artemisia* (AA) extract on the steel surface in the inorganic acid medium between the temperatures of 298 and 353 K using bulk mass loss and polarization approaches. Eventually, the corrosion effect significantly decreases with an efficiency of 95 and 99% at 298 and 353 K, respectively, at an initial concentration of 10 $g \cdot L^{-1}$ of AA. In addition to that the efficacy of the anticorrosion effect

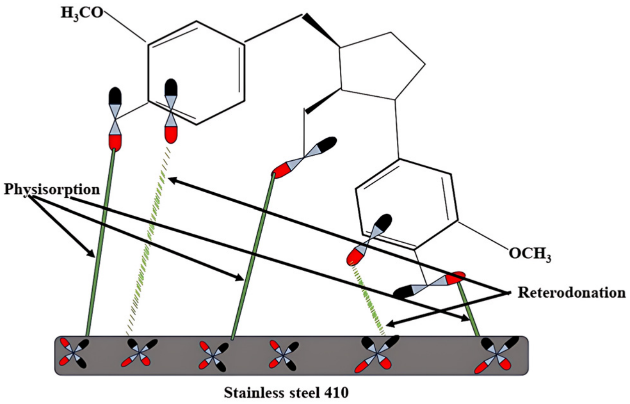


Figure 15: Molecular interaction of TS extract on SS surface [117].

increases concerning temperature and follows the Langmuir adsorption model. Bouyanzer and Hammouti [118] observed the same kind of results when they used AA oil in the presence of HCl and H_3PO_4. The obtained result clearly stated that AA has more consideration as a hopeful antimalarial drug and davanone Figure 16, which can form a complex with the Fe(II)-davanone complex.

For instance, Agwa *et al.* [119] tested the inhibition effect of *Aloe barbadensis* (AB) by varying inhibitor concentration (10, 20, 30, 40, and 80%) on corroded steel specimens in the presence of SRB (1.7×10^3cfu·mL^{-1}) and iron oxidizing bacteria (4×10^3 cfu·maL^{-1}) at neutral pH condition. The authors found that the pH of the SRB system was dropped to 6.5 and the conductivity was drastically reduced from 3,150 to 200 µS·cm^{-1} after 4 weeks, because of restriction of cathodic polarization and, on the other hand, the conductivity was increased from 100 to 2,820 µS·cm^{-1} after 28 days. Finally, the result shows that 80% inhibitor concentration gives a significant anticorrosive effect on steel metal specimens in the presence of SRB and iron oxidising bacteria was around 89 and 66%, respectively.

In another study, Vaidhyanathan *et al.* [120] focused on mitigating microbial-influenced corrosion by SRB by using *Polyalthia longifolia* plant extract (PLAE). This research work was carried out by using SRB isolated from the marine milieu to examine the corrosion effect by using Autolab PGSTAT 302 potentiostat at sweeping potential from −0.3 to 0.2 V with a scan rate of around 0.5 mV·s^{-1}. The SEM studies indicate that the PLAE extract has more anti-bacterial activity against SRB, which causes damage to its cell membrane and reduces the growth of the bacterial species. Also, the Tafel investigation elucidates that due to the anti-microbial activity, the cathodic polarization was resisted and I_{corr} was reduced from 4×10^{-6} to 4.2×10^{-7} A·cm^{-2}. The FTIR analysis revealed the presence of the methyl group, hydroxyl, amide I, and sulfate group on the cell membrane and are cleaved by PLAE. In another research work, Bhola *et al.* [121] delineated that the neem extract (NE) shows a good inhibition effect on corrosion surface mediated by SRB like *Desulfovibrio africanus*, *Desulfovibrio alaskensis*, and *Desulfomicrobium* sp. Along with that the topography analyses by FE-SEM and electrochemical studies attest that 4% of NE can reduce more than 50% of corrosion on pipeline steel surfaces. A similar kind of study has been carried out by Hart and James [122] to attest the anticorrosive nature of CS and SS pipelines used in the oil atmosphere by *Allium sativum* (garlic extract) as a GI in the existence of *Bacillus subtilis* A1 and *Streptomyces parvus* B7. The studies were carried out by varying inhibitor concentrations from 100 to 200 ppm at neutral pH conditions. The authors detected that the minimal concentration of 100 ppm is enough to achieve 81 and 75%, an anticorrosive effect on CS and SS, respectively. The significant corrosion resistance offered by garlic extract is mainly due to the presence of sulfur compounds (S^{2-}), antimicrobial, and anti-oxidative properties of inhibitor. In addition, the garlic extract has formed a higher affinity protective layer on both CS and SS due to the higher electronegativity of the sulfur compound, stating that the adsorption was followed by monolayer coverage of adsorption. Likewise, Parthipan *et al.* [123] observed that the presence of sulfur-enriched compounds such as diallyl disulfide (DAD, $C_6H_{10}S_2$) and 2-furan carboxaldehyde, 5-(hydroxymethyl) -($C_6H_6O_3$), trisulfide, di-2-propenyl, and Di-*N*-Decyl sulfone assist the anticorrosive effect around 81 ± 3% and 75 ± 3% in conventional process while 72 ± 3% and 69 ± 3% are attained in the occurrence of mixed bacterial consortia for CS and SS, respectively. The statistical analysis of various plants is shown in Figure 17 (Table 4).

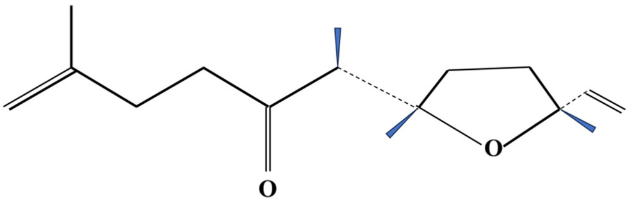


Figure 16: Chemical structure of AA extract [118].

5 Computational modeling in corrosion inhibition assessment

Enactment of computational knowledge like Density function theory (DFT) and Molecular dynamics (MD) are the most effective, economical, and user-friendly technique for the assessment of corrosion. This modeling does not need any chemical synthesis data to understand the molecular interactions. These models help to identify the reactive limitations and inhibition effect of any phytochemical's effects before the experimental analysis. In addition to that, the DFT clearly demonstrates the active site of the compounds accountable for molecular interactions with metal topography [139]. By means of MD and MSS (Molecular simulations), the alignment of inhibitors on metal can be easily elucidated. Due to the unfavorable economic conditions and toxic effects of chemical compounds, scientists and industrialists are giving more concentration to the application of computational modeling on

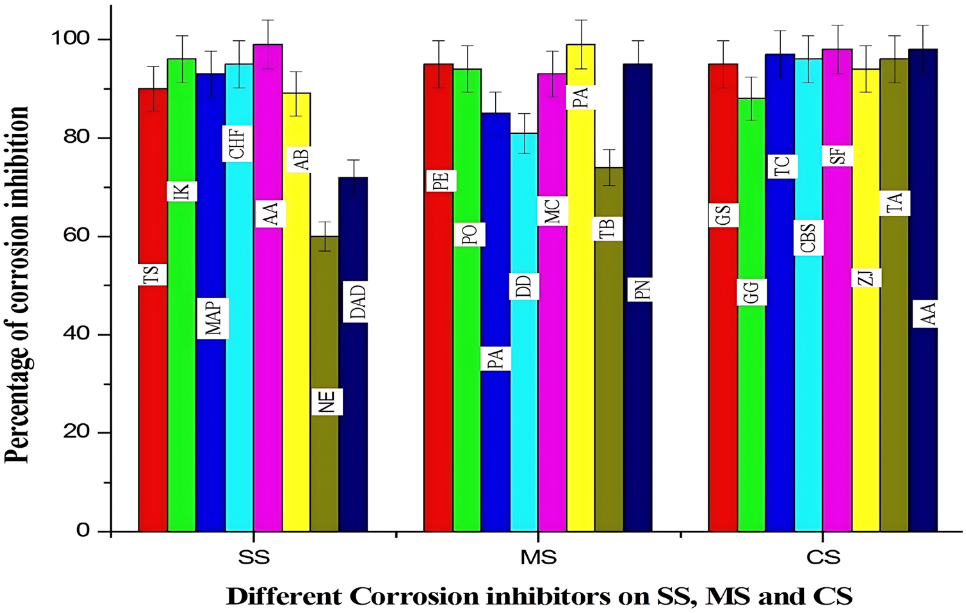


Figure 17: Statistical data representation of various plants and its effectiveness of corrosion inhibition on SS, MS, and CS [96–122].

Table 4: Comparison of corrosion inhibition efficiency of synthetic OI and natural inhibitor

Synthetic OIs	Natural inhibitors	Medium	Metal	Inhibitor efficiency (%)		Ref.
				Synthetic OIs	Natural inhibitors	
5((6-Methyl-2-oxo-2*H*-chromen4yl) thiomethyl)-2((*N*-(3-methylquinoxalin-2(1*H*)-one)yl)methyl) 1,3,4oxadiazole	*GS*	1 M HCl	MS	72.69	95.86	[114,124]
Rabeprazole sulfide	*PS*	1 M HCl	MS	89.91	88	[110,125]
2-chloro 3-formyl quinoline	*TC*	0.5, 1 M HCl	MS	66.03	97.92	[111,126]
2-chloro-*N*-(1-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline-3-carbonothioyl) propanamide	*CBS*	1 M HCl	MS	95.50	96.42	[108,127]
2-methoxy-*N*-(1-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline-3-carbonothioyl) acetamide	*Sunflower*	1 M HCl	MS	91.33	98	[116,127]
N-(1-methyl-2,4-dioxo-1,2,3,4-tetrahydroquinazoline-3-carbonothioyl) propionamide	*Cocoa pod*	1 M HCl	MS	86.71	94.7	[115,127]
Triazolyl-benzimidazolone derivatives (TB-CH_2Ph)	*Trochodendron Aralioides*	1 M HCl	MS	90.4	96.42	[128]
Triazolyl-benzimidazolone derivatives (TB-NO_2Ph)	*Aquatic Artichoke*	1 M HCl	MS	95.7	98.7	
3-phenyl-2-thioxo-2,3-dihydro1*H*-quinazolin-4-one	*TS*	1 M HCl	SS	74	90	[117,129]
3-amino-6-bromo-2-thioxo-2,3- dihydro-1*H*-quinazolin-4-one	*IK*	1 M HCl	SS	62	96.5	[106,129]
Pyrazolone derivative	*MAP*	0.5, 1 M HCl	SS	72	93	[100,130]
3-[*E*-phenyldiazenyl]-2,4 pentandion	*CHF*	1 M HCl	SS	61	95.42	[115,130]
N-benzyl-*N*-(4-chlorophenyl)-1*H*-tetrazole-5-amine	*Artemesia* (AA)	1 M HCl	SS	98.6	99	[103,130]
3-oxo-2-(phenyldiazenyl) pentanenitile	*AB* (AB)	1 M HCl	SS	69	89	[119,130]
Ethyl 2 cyano-2 (mtolyldiazenyl) acetate	*NE*	1 M HCl	SS	76	60	[121,130]
Oxazole derivatives	*DAD*	1 M HCl	SS	91	72	[130]
1-((4*S*,5*R*)-2,4,5-tris(2,5-dimethoxyphenyl)-4,5-dihydro-1*H*-imidazol-1-yl)ethan-1-one (25MAC-C)	*PE*	1 M HCl	CS	86	95	[96,131]
Tris(4-ethoxyphenyl)-4,5-dihydro-1*H*-imidazole	*OLE*	1 M HCl	CS	98.3	94.4	[97,132]
Imidazole derivatives	*IK*	1 M HCl	CS	96.5	95	[99,133,134]
HZ-OH (hydroxylated hydrazone derivatives)	*Momordica charantia*	1 M HCl	CS		93.51	[135,136]
HZ-Me (methylated hydrazone derivatives)	*Platanus acerifolia*	1 M HCl	CS		99.86	[135,137]
HZ-Cl (Chlorinated hydrazone derivatives)	*Taxus baccata*	1 M HCl	CS		74.56	[135,138]

effective anti-corrosive reactants. The domain of quantum electrochemistry is the combination of quantum mechanics, electrochemistry, and electrodynamics. Generally, the Hohenberg–Kohn DFT theorems elucidate that the DFT stresses on the electron density (ρ(r)) attesting the distribution of electrons within the atom and molecules. The quantification of electron density enumerates the evidence of the reactive nature of the chemical species. Besides, the Hohenberg–Kohn theorems conclude that the ground state of an electronic system is the function of electron density.

The DFT theory clearly states that the performance of new corrosion inhibitors is evaluated by the theoretical measurement of energies of higher occupied molecular orbital (E_{HOMO}), lower unoccupied molecular orbital (E_{LUMO}), polarizability of molecules (α), and limitations of dipole moment (μ). The higher values of E_{HOMO} and lower values of E_{LUMO} represent, the corrosive resistance of OIs has shown a significant affinity towards metal surfaces effectively. Obot *et al.* [140] investigated the effectiveness of two pyrazoline derivatives, namely, 2-(4-(4,5-dihydro-3-(4-methoxyphenyl)−1*H*-pyrazol-5-yl)phenoxy) acetic acid (PYR-1) and 2-(4-(4,5-dihydro-3-p-tolyl-1*H*-pyrazol-5-yl)phenoxy) acetic acid (PYR-2) as a corrosion inhibitor for MS in the presence of HCl. The DFT modeling result enumerates that the value of (E_{HOMO}) for PYR-1 is −3.904 eV and (E_{LUMO}) for PYR-2 is −4.098 eV. It confirms PYR-1 has less negative than PYR-2, and concludes that iron has more strongly interacted with PYR-1 than PYR-2.

Noticeably, HOMO and LUMO molecular orbitals are in charge of the donation of electrons and the acceptance of electrons, respectively. It is vital to indicate the contact between metals with inhibitors depending upon charge sharing. Consequently, the Frontier molecular orbital (FMO) picture is used to measure the relative electron transfer during the donation and retro-donation process. Obi-Egbedi *et al.* [141] investigated the anti-corrosive effect of two different carbohydrate-based pyrazole (i) (*E*)−5-amino-3-(4-methoxyphenyl)-*N*′-(1-(4-methoxyphenyl)ethylidene)–1Hpyrazole-4-carbohydrazide [AMPC] and (ii) (*E*)−5-amino-*N*′-(4-chlorobenzylidene)–3-(4-chlorophenyl) −1Hpyrazole-4-carbohydrazide [ACPC] tested on MS in 15% HCl medium by evaluating electronegativity (χ), dipole moment (μ), chemical hardness (η), global softness (S), and charge of the electron (ΔE). The result states that the value E_{HOMO} is higher than E_{LUMO} because of donating electrons to the d-orbital of iron. In addition, both inhibitors have a higher energy gap between the higher occupied molecular orbital and the lower unoccupied molecular orbital in a vacuum. It concludes that the adsorption of inhibitors follows both physisorption and chemisorption. Finally, it has been confirmed that the AMPC inhibitor has more potential than ACPC. Likewise, in the same environment, other researchers [142,143] tested the inhibition capacity of *N*′-[(1Z)-phenyl methylene]−2-(quinolin-8-yloxy) acetohydrazide (PQA) and *N*′-[(1*Z*)−4-chlorophenylmethylene]−2-(quinolin-8-yloxy) acetohydrazide (CPQA). The obtained data clarify that the E_{LUMO} of PQA is less negative (−1.651 eV) than the E_{HOMO} of CPQA (−5.04 eV) with dipole moment of 4.32 D and ΔE (3.389 eV), indicating that the PQA has more adsorption property on MS than CPQA.

In a recent study, Haldhar *et al.* (2021) [144] discussed the corrosion resistance efficacy of the three different phytochemicals such as Kuguacin-F (K-F), Cucurbitane triterpenoid (CT), and Pentanol cucurbitacin (PC) extracted from *M.* charantia. The path of interaction and the collaboration of electrons and inhibition effect between the phytochemicals on CS have been evaluated by various quantum chemical parameters: electronegativity (χ), dipole moment (μ), chemical hardness (η), global softness (S), charge of the electron (ΔE), and the values of E_{HOMO} and E_{LUMO} from the DFT/B3LYP/6-31G + (d,p) method. The obtained result delineates that the energies of higher occupied molecular orbitals (E_{HOMU}) of CT > K-F > PC are around −3.17, −4.12, and −9.12 eV, due to the huge ability to transfer the electron on the CS surface, respectively. Similarly, the PC achieved an E_{LUMO} of about −2.17 eV for the high donating capability of electrons on the surface of iron. The changes in charge of electrons (ΔE) in CT are less than the other two phytochemicals because of its significant complexation phenomena with high affinity on metal surfaces. Furthermore, the MD simulation studies revealed that the selected phytochemicals interacted at the adsorption site of [1 1 0] on the iron surface by the unpaired electrons present on benzene rings, molecular oxygen, sulfur, and nitrogen atoms [145]. The adsorption of inhibitors on metal surfaces increases the coating thickness and surface contact by very near iron atoms present in the flat orientation of the molecular structure of the metal surfaces. The strength of affinity induced by the inhibitors on metal surfaces has been articulated by the values of adsorption energy. In this study, the maximum adsorption energy achieved by hydrogen bonding, bromine, and methyl oxide is around −336.9, −380.3, and −413.4 kJ·mol^{-1}, which states that the adsorption is spontaneous. In another research work carried out by Abuelela *et al.* [146], they investigated the impact of inhibitor effects of phytochemicals (ellagic acid [EA], gallic acid [GA], and malic acid [MA]) extract *Terminalia bellerica* fruit in the presence of water medium, acid medium, and sulfate medium. The adsorption study and the structural analysis were optimized by the Adsorption Locator module (Material Studio 7.0) and the structural properties were optimized by the compass force field. The electrostatic interaction and weak forces of interaction were elucidated by the Ewald summation technique and atom-based procedure, respectively. The interaction chemistry between the functional groups of phytochemical compounds and metallic atoms has been evaluated based on global reactivity conditions, natural bond orbital analysis, and local reactivity along with Monte Carlo simulation.

Generally, organic molecules tend to react in elemental form as well as ionic form of metals because of their π-electrons and unpaired heteroatoms. The lowest molecular interaction energy and lesser ionization behavior can be easily adjusted in the neighborhood of d-orbitals of transition metals. The electron-donating nature and its capability can be evaluated by various quantum chemical parameters like ionization potential, electronegativity, chemical harness, and electron affinity. Moreover, Zhang and Musgrave [145] state that the B3LYP method determines the eigenvalues of E_{HOMO} with an error value of 3.10 eV, and also that this method could not be able to accurately predict the eigenvalues of E_{LUMO}. Consequently, finding the accurate value of the band gap is a big task. Therefore, in this study, the researcher used a time-dependent B3LYP for estimating the energy gap, reduction in error in eigenvalues of HOMO, and accurate assessment of LUMO. The different chemical characteristics can be evaluated by this computational analysis. The equations used for different chemical interaction process is listed in Eqs. (31)–(37).

(i) The formulae used for finding corrected HOMO eigenvalue is

$$(-\text{HOMO})_{\text{corr}} = A + B(-\text{HOMO})_{\text{cal}} \tag{31}$$

where $A = 1.42$ and $B = 1.20$

$$\text{LUMO} = \text{HOMO} + E_{\text{gap}} \tag{32}$$

(ii) Electronegativity

$$\gamma = -\mu = \frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \tag{33}$$

(iii) Chemical hardness

$$\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \tag{34}$$

(iv) Global softness

$$S = \frac{1}{\eta} \tag{35}$$

(v) Global electrophilicity

$$\omega = \frac{\mu^2}{4\beta} \tag{36}$$

(vi) Back donation

$$\Delta_{\text{back donation}} = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{8} \tag{37}$$

(vii) Number of electrons transferred

$$\Delta N = \frac{X_{\text{Me}} - X_{\text{IN}}}{2(\eta_{\text{Me}} - \eta_{\text{IN}})} \tag{38}$$

The energy band gaps attested by GA, MA, and EA are found to be 5.44, 7.562, and 4.813 eV, respectively. In addition, EA has a greater corrosion inhibitory effect on metal surfaces than MA and GA due to its smaller energy gap and the presence of π-electrons and unpaired heteroatoms of carboxylic acid and the oxygen atom. Besides, the chemical hardness (η) has been calculated from the addition of two parts of the energy band gap, divided by electronegativity. Low values of η (2.4, 2.7, and 3.7) for GA, MA, and EA, respectively, ensure the most efficient candidate for adsorbing on metal surfaces.

The natural bond orbital analysis delineates the order of donating characteristics of electrons involved during inhibitor-metal interactions. Moreover, this analysis elucidates bond type, occupancy of electrons, type of hybridization, energy levels, and orbital characteristics [147]. The obtained result clearly states that the second lone pair of the 27th oxygen atom has a stronger affinity with the steel surface. However, the GA adsorbed on the metal surface by sharing electrons through the third and fourth positions of the carbon atoms present in the GA. Eventually, the 16th position of the second lone pair oxygen atom from malic acid has a higher electron-donating capability during the interaction. Eventually, the estimation of local reactivity ensures that the active sites in the functional group present in phytochemical entities interact with metal atoms to resist the corrosion effect. The local reactivity regions can be mapped by a molecular electrostatic potential model [148,149]. The obtained result shows that carboxylic and oxygen atoms in the selected phytochemical compound have a moderate electron charge density, which is responsible for the interaction on the metal surface. In addition, the Monte Carlo simulations supported the adsorption characteristics at the molecular level between metal-inhibitor interactions. EA from the *Terminalia bellerica* fruit extract has more reactivity and high binding energy, followed by flat and parallel adsorption phenomena. The inhibitory characteristics of *Jacaranda mimosifolia* extract, along with copper oxide nanoparticles, were investigated on corroded CS surfaces in the presence of 10^{-2} M HCl. The inhibition proficiency has been analyzed by potentiometric studies, and theoretical investigations have been carried out for phytochemical compounds: glucosidic ester, apigenin 7-b-glucoside (A7-BG), and jacaglabroside C (JC) interactions on CS topography using DFT tools. The computational studies revealed that the JC compound shows significant dipole–dipole interactions. Similarly, the E_{HOMO}, E_{LUMO}, and low ionization values conclude that the A7-BG gives a better corrosion inhibition effect than the other two compounds. The minimum values of chemical softness define that JC has a greater propensity to accept the electron with more stability during interactions. The Mulliken charges result clarifies that the negative charge of the carbonyl group exhibits more corrosion-resisting action on metal surfaces [150].

6 Future aspects and challenges of natural inhibitors

In general, plants are one of the richest sources for extracting natural corrosion inhibitors such as flavonoids, saponins, TAs, phenols, alkaloids, terpenoids, and coumarins. In addition, these phytocompounds are considered to be the most prevalent natural inhibitors because of its ecofriendly, cost-ineffective, high availability, and quick separating character. In pipelines, storage tank, acid medium, and saline conditions, corrosion has a severe impact on metal surfaces in aerobic and anaerobic conditions. So, the synthetic or chemical inhibitors are not able to resist the corrosion for a long time. But the plant extracts act as a very good corrosion inhibitor for a prolonged duration due to their chemical structure and interaction nature. Furthermore, the researchers developed corrosion inhibitors from the mixture of polymers such as chitosan and starch with plant extracts. These mixtures enhance the resistance against abiotic and biotic conditions. Similarly, the addition of nanoparticles such as silver oxide, copper oxide, and zinc oxide in plant extracts and addition of biopolymers, namely, polylactic acid and polyhydroxyalkanoates in phytochemicals reduces the corrosion effect. The combination of phytocompounds and functionalized coating increases the antimicrobial, antifouling, and self-healing properties on the interior and exterior surface of pipelines, petroleum tanks, water storage, acid storage tank, sewage tanks, cement walls *etc.* But the inhibition characteristics of phytocompounds are not prominently constant in the presence of carbon dioxide, hydrogen sulfide, predominantly at high temperatures. In future, the phytochemical-based corrosion inhibitors will be developed for reducing the corrosion effect on coating, production of nanocomposite-based natural inhibitors, biopolymer-based inhibitors, especially for high-temperature process. In addition, the effect of inhibition can be predicted by the computational analysis in advanced level in molecular perspective.

7 Conclusion

i) The corrosion mechanism depicts that MS, steels, and CS get corroded in both acidic and basic or neutral mediums in the form of iron hydroxide, chromium hydroxide, nickel hydroxide, manganese hydroxide, and iron carbonate.
ii) The bio-corrosion chemistry addressed that the MS, SS, and concrete are corroded in the presence of aerobic *(Thiobacillus ferroxidans)* and anaerobic species (SRB), forming iron hydroxide, iron sulfides, and hydrated form of calcium, respectively.
iii) Phytochemical compounds can be extracted by SE, microwave-assisted extraction, enzyme-assisted extraction, and UAE process.
iv) Various plant sources like A*leo vera, sulfur-enriched plants, PL, OLE, PS, etc.*, show significant anticorrosive properties against acid and alkali medium on MS, SS, and CS due to the various phytochemicals like alkaloids, Tannis, polyphenols, and flavonoids. In addition, the adsorption isotherm studies conclude that the interaction was followed by physisorption, chemisorption, and retro-donation mechanisms.
v) Computational studies enumerate the interaction mechanisms between metals and inhibitors can be confirmed by quantifying the values of E_{HOMO}, E_{LUMO}, energy band gap, electronegativity, dipole moment, chemical hardness, global softness, and charge transfer of electrons. The calculated values can give a clear idea about inhibitor preference, adsorption affinity, and molecular interactions through FMO.
vi) The global reactivity conditions, natural bond orbital analysis, and local reactivity, along with Monte Carlo simulation, could be used to evaluate E_{HOMO}, E_{LUMO}, energy band gap, electronegativity, electron density, and binding energy behavior in metal-inhibitor interaction. In addition, the Mullikan charge analysis gives a clear idea about the charges of different phytochemical compounds.
vii) The theoretical and experimental studies delineate that functional groups like oxygen, sulfur, nitrogen, and methylene groups are responsible for the interaction of metal surfaces.

viii) Phytochemicals like terpenoids, flavonoids, saponins, glycosides, polyphenols, and alkaloids are naturally observed in various plant sources, which can be used as corrosion inhibitors. The inhibitors form a defensive layer on metal surfaces and resist the further oxidation process. These GIs are promising alternative inhibitors that can be used in various industries like metal processing, prevention of corrosion in pipelines, oil and gas, and restricting the corrosion damage in machines and exterior surfaces of ships. These natural inhibitors reduce 30% of the capital cost used to overcome the corrosion effect.

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