

## Green corrosion inhibitors in various corroding media

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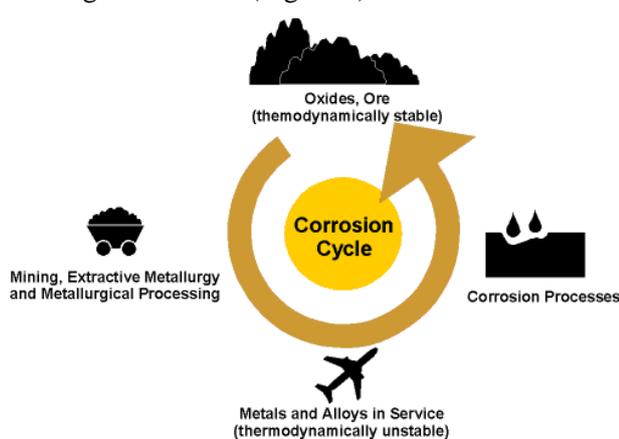
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Recently, development of green corrosion inhibitors is highly called for due to the increasing demands of green chemistry. Plant materials are ideal green candidates for toxic corrosion inhibitors. The review discusses the research work published on the use of different extracts such as leaf, root, stem, bark, pulp, fruit, etc. as corrosion inhibitors for metals in different corroding media. The inhibiting effect of these natural products as corrosion inhibitors for various metals has been evaluated by weight loss, hydrogen evolution, potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical frequency modulation techniques. The results revealed that most of the extracts act as mixed-type inhibitors. Thermodynamic parameters were calculated using adsorption isotherms. The surface morphology was studied by using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), FT-IR and X-ray diffraction (XRD). Quantum chemical calculations have been used to evaluate the structural, electronic and reactivity parameters of the inhibitors. Physisorption was reported as the probable mechanism for the adsorption of these extracts on the surface of metals. The inhibition action of these products was due to the formation of a protective film on the surface of metals.

**Keywords:** Corrosion, Biomaterials, Electrochemical Techniques, Inhibition

### INTRODUCTION

All natural processes tend toward the lowest possible energy states. Since corrosion is a natural process, metals such as iron, steel, etc., have a natural tendency to combine with other chemical elements that are available in the environment to attain their lowest energy states. To get this lower energy states, iron and steel normally combine with oxygen and water, both of which are available in the environments, to form hydrated iron oxides (rust) that is similar in chemical composition with that of the original iron ore (Figure 1).



**Fig. 1.** Corrosion cycle of steel

The word “corrode” is derived from the Latin *corrodere* which means “to gnaw to pieces”.

Corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and of its properties [1].

Corrosion occurs in different forms [1]. Classification is based on any one of three factors:

1. Nature of the corrodent: Corrosion may be classified as “wet” or “dry”.
2. Mechanism of corrosion: This involves either electrochemical or direct chemical reactions.
3. Appearance of the corroded metal: Corrosion is either uniform (the metal corrodes at the same rate over the entire surface) or it is localized (only small areas are affected).

Eight forms of wet corrosion can be identified based on the appearance of the corroded metal. These are a) Uniform (general) corrosion; b) Pitting corrosion; c) Crevice corrosion; d) Galvanic corrosion; e) Erosion corrosion; f) Inter-granular corrosion; g) De-alloying and h) Stress corrosion. This classification system is rather helpful in the study of corrosion problems.

The effects of corrosion in our daily lives are both direct and indirect. At home, corrosion is readily recognized on automobile body panels, charcoal grills, open-air furniture and metal tools. Painting such items will be one of the preventive maintenance approaches from corrosion [1]. Most

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dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion. Some consequences are economic and cause the following: i) replacement of corroded equipment; ii) overdesign to allow for corrosion; iii) prevent maintenance (painting); iv) shutdown of equipment due to corrosion failure; v) contamination; vi) loss of efficiency; vii) loss of valuable product; viii) damage of equipment [1].

According to a recent report by the National Association of Corrosion Engineers (NACE), the annual worldwide cost of corrosion is over \$ 2.5 trillion which constitutes about 4.2% of Gross Domestic Product (GDP) [2]. In India, the annual cost of corrosion is over 5,000,000 million Indian rupees (i.e. about \$ 100 billion), while in South Africa, the direct cost of corrosion is estimated to be around R 130 billion (i.e. about \$ 9.6 billion) [3].

Other social consequences are i) safety, for example, sudden failure can cause fire, explosion, release of toxic product and construction collapse; ii) health, for example, pollution due to escaping product from corroded equipment or due to a corrosion product itself; iii) depletion of natural resources, including metals and the fuels used to manufacture them and iv) appearance as when corroded material is unpleasing to the eye [1]. There are five methods of corrosion control: a) material selection; b) coatings; c) inhibitors; d) cathodic protection and e) design. Each method is defined here.

a. *Material selection:* Materials that are used for this type of corrosion control are often called high performance alloys, special metals, exotic alloys or exotic metals. Some metals hold the properties to withstand corrosive environments, alongside issues of pitting, stress corrosion cracking and more. These metals are more expensive than a standard stainless steel but they can provide strength within environments with acids, alkali, salts and sea water [1]. The general relation between the rate of corrosion, the corrosivity of the environment and the corrosion resistance of a material is:

$$\frac{\text{Corrosivity of environment}}{\text{Corrosion resistance of metal}} = \text{Rate of corrosive attack}$$

b. *Coatings:* Coatings for corrosion protection can be divided into two broad groups – 1) metallic (applying a more noble metal coating on an active metal) and 2) nonmetallic (organic and inorganic) coatings. The aim of the coatings of the two types is

the same, that is, to isolate the underlying metal from corrosive media [1].

c. *Inhibitors:* Corrosion damage can be prevented by the use of corrosion inhibitors [4, 5], which is the best way to prevent destruction or degradation of metal surfaces in corrosive media. The use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals. Corrosion inhibitors are chemicals either synthetic or natural which, when added in small amounts to an environment, decrease the rate of attack by the environment on metals.

d. *Cathodic protection:* It suppresses the corrosion current which causes damage in a corrosion cell and forces the current to flow to the metal structure to be protected. Cathodic protection can be achieved by two application methods – 1) an impressed current system (uses a power source to force current from inert anodes to the structure to be protected) and 2) a sacrificial anode system (uses active metal anodes, for example, zinc or magnesium, which are connected to the structure) [1].

e. *Design:* Corrosion often occurs in dead spaces or crevices where the corrosive medium becomes more corrosive. These areas can be eliminated or minimized in the design process. Where stress corrosion cracking is possible, the components can be designed to operate at stress levels below the threshold stress for cracking [1].

#### *Mechanism of corrosion*

Literature survey revealed that many of the organic compounds (as well as the compounds extracted from plants) used as corrosion inhibitors are heterocyclic compounds that contain polar functional groups such as OH, OCH<sub>3</sub>, Cl, NO<sub>2</sub>, CN, CH<sub>3</sub>, and NH<sub>2</sub>, as well as unsaturated (double and triple) bonds that can serve as adsorption sites using a lone pair or  $\pi$ -electrons [3, 6]. These heterocyclic compounds adsorb on metallic surface through their active sites. The adsorbed inhibitor molecules shield the metal surface from direct attack by corrosive ions, and the organic compound is said to inhibit metallic corrosion [3, 6].

All metals exhibit the tendency to readily oxidize. A tabulation of the relative strength of this tendency is the galvanic series. The knowledge of a metal's position in this series helps in selecting an appropriate metal in structural and other applications. In a corrosion cell, the electron produced by the corrosion reaction will be consumed by a cathodic reaction. The electron and the hydrogen ions react to form atomic hydrogen and then molecular hydrogen gas. The formed hydrogen

gas tends to inhibit further corrosion by forming a very thin gaseous film at the surface of the metal. This film thus reduces the corrosion rate. Dissolved oxygen in water will react with the hydrogen, converting it to water thus destroying the film, which continues the corrosion. Other corrosion accelerating factors are pH value and temperature [7, 8].

It is often observed that the presence of electron-donating groups such as OH, NH<sub>2</sub>, CH<sub>3</sub>, and OCH<sub>3</sub> increases the inhibition performance, while presence of electron-withdrawing substituents such as NO<sub>2</sub>, CN, COOH, COOC<sub>2</sub>H<sub>5</sub> decreases the inhibition efficiency of organic molecules [9].

In order to reduce the threat caused by the corrosion of industrial installations, several steps have been adopted. However, one of the best options available for protecting metals against corrosion involves the use of corrosion inhibitors. Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys in contact with aggressive environments [10, 11]. These inhibitors can be adsorbed onto metal surfaces, block the active sites and decrease the corrosion rate. The adsorption ability of inhibitors onto the metal surface depends on the metal's nature and the chemical composition of electrolytes, as well as on the molecular structure and electronic characteristics of the inhibitor's molecules [12].

Inhibition efficiency of corrosion inhibitors increases with increase in concentration of active components as it is directly proportional to the number of electron-withdrawing or electron-donating groups present in the inhibitor [13]. Presence of heteroatoms, polar functional groups and  $\pi$ -electrons as active centers in a particular compound makes it an effective corrosion inhibitor [14, 15] because these heteroatoms or  $\pi$ -electrons facilitate electronic interactions between metal surface and inhibitor.

Corrosion inhibitor's safety and environmental issues arisen in industries have always been a global concern. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to the kidneys or liver of terrestrial and aquatic organisms or disturb their biochemical processes or enzyme systems [16]. Therefore, it is desirable to look for environmentally safe corrosion inhibitors.

Recently, a new type of corrosion inhibitors is being developed to meet the terms with the environmental regulations on industrial consumption and development; thus natural products, pharmaceutical ingredients and environment-friendly products have gained much attention as substances for green corrosion inhibitors

that have high inhibition efficiencies [17, 18]. The exploration of natural products of plant origin as inexpensive and eco-friendly corrosion inhibitors is an essential field of study. In addition, plant products are biodegradable, low-cost, readily available and renewable sources of materials. The most common natural substances used are plant extracts [19, 20].

#### *Important parameters for extract preparation*

Nowadays, development of green inhibitors is very much wanted because of the increasing demand of green chemistry. Because of natural and biological origin along with their ecofriendly isolation, plant extracts can be considered as green and sustainable materials as corrosion inhibitors for metals and alloys corrosion in aggressive media including HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and HNO<sub>3</sub> [21]. There are several methods available in literature for preparation of plant extracts. The parameters that should be considered during the preparation of plants extracts are described briefly.

*Solvents for extraction:* Choice of the suitable solvents for extraction is very important for effective extraction since the solvent diffused into plant tissue, solubilized and finally extracted the compounds (phytochemicals) present over there [22, 23]. Literature survey reveals that water is the best solvent owing to its simplicity, ready availability, non-toxic nature, non-flammable, non-hazardous and inexpensive properties [24-27]. However, preparation of some plant extracts requires organic solvents like ethanol and methanol.

*Extraction temperature:* Temperature has a very marked effect on the effective plant extract preparation. A very low temperature limits the effective solubility of the phytochemicals while very high temperature causes the decomposition of the active constituents (phytochemicals). Generally, extraction is carried out in the temperature range of 60 – 80 °C in order to find optimal extraction yield [28, 29].

*Plant drying temperature:* Plant materials are allowed to dry at room temperature in shade. This type of drying requires several days, weeks, even months; therefore, oven drying can also be used.

*Advantages and limitations:* Extracts of natural plants are environmentally friendly, nontoxic and relatively less expensive. They are easily biodegradable also. However, this biodegradability limits the storage and long-term usage of plant extracts. However, it is proposed that the decomposition of plant extracts by microorganisms can be prevented by addition of biocides such as sodium dodecyl sulfate and N-cetyl-N,N,N-trimethyl ammonium bromide. If plant materials are

used as corrosion inhibitors, to prevent the corrosion of metals, the plant kingdom will slowly diminish; metals will be protected at the cost of destruction of plant kingdom [30].

#### Mild steel

Mild steel, also known as plain-carbon steel, is the most common form of steel because of its relatively low price while it provides material properties that are acceptable for many applications such as different engineering applications for the production of some automobile components, structural shapes, pipelines, construction materials and transportation [31, 32]. Mild steel is known for its high carbon content of about 0.2% to 2.1%, manganese (1.65%), copper (0.6%), silicon (0.6%). It is produced from steel which is extracted from pig iron. It has outstanding ductility and toughness, high machinability and weldability which make its applications possible in engineering fields [20, 33, 34]. It can be hardened by heat treatment. It is used for the production of lightly stressed machine fittings, turbine motors, railways axels, pipes and drums. The mild steel is chosen as it is accessible and easily fabricated with high tensile strength [35].

Mild steel structures corrode as a result of electrochemical reaction with the environment. In most industries, maintenance operations such as pickling, cleaning and descaling are carried out to prolong the life span of the mild steel structures. But aggressive acidic media used for such operations often corrode the mild steel structures [36, 37]. Considering the viability of mild steel and its high cost of production and installation, several steps are taken to prolong its life period.

Extracts from *Pisidium guajava*, *Punica granatum*, *Ginko biloba*, *Tinospora crispa*, *Ficus carica*, *Uncaria gambir*, *Phyllanthus amarus*, *Murraya koenigii*, *Justicia gendarussa*, *Hibiscus sabdariffa* and *Zenthoxylum alatum* have been studied as corrosion inhibitors for mild steel in various acidic media [38-43].

The potential of *Tinospora crispa* as a corrosion inhibitor of mild steel in 1 M HCl has been determined [44]. Both water and acetone – water extracts of the plant were found to be good mild steel corrosion inhibitors in 1 M HCl. The maximum percentage of inhibition efficiency was obtained at the concentration of 800 ppm (water extract) and 1000 ppm (acetone-water extract). Based on a SEM photograph, it was found that the mild steel specimen in 1 M HCl has a rough surface due to localized attack of HCl thus forming a rust product on the surface. When a maximum concentration of the inhibitor is added, the mild steel surface becomes

significantly smooth and comparable to untreated mild steel surface.

Corrosion inhibition of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> by leaves and stem extracts of *Sida acuta* was studied using chemical and spectroscopic techniques at 30 – 60 °C [45]. The inhibition efficiency increases with increasing extracts concentration and is more pronounced for the leaves compared to the stem extract. The corrosion inhibiting effect is attributed to phytochemical components such as saponins, flavonoids, alkaloids, organic acid and anthraquinones in the leaves and tannins, alkaloids and anthraquinones only in the stem extracts. Atomic absorption spectroscopy (AAS) was used to determine the amount of the iron from the bulk of the metal into the electrolyte in the absence and presence of the extracts of *Sida acuta*. The results obtained indicate that there was a decrease in the amount of dissolved iron in the presence of inhibitors.

The anticorrosion activity of *Citrus aurantifolia*, *Bitter leaf root*, *Piper nigrum*, *Musa paradisica* and *Nicotiana tabacum* was studied [46-48]. Corrosion inhibition has also been investigated for the extracts of *Swertia angustifolia*, *Ricinus communis* (Castor) leaves for mild steel in acidic media [49-51]. Herbs such as *Bread fruit*, *Ligularia fischeri*, *Phyllanthus amarus*, palm oil and aloe vera gel were used as a new type of green inhibitors for steel acidic corrosion [49-51]. The corrosion behavior of mild steel in 0.5 M HCl and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in presence of *Eriobotrya japonica* leaf extract was studied [52]. The inhibitive action of *Gundelia tournefortii* leaf extract on mild steel corrosion in 2 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> solutions was studied [53]. Cathodic and anodic polarization curves show that this extract is a mixed-type inhibitor in both acidic media.

Use of *Amaranthus* extract, as mild steel corrosion inhibitor, in a pickling paste with H<sub>2</sub>SO<sub>4</sub> has been investigated [54]. All measurements (corrosion current, polarization and cathodic polarization) showed that *Amaranthus* extract has excellent inhibition properties for mild steel corrosion in a 4 N H<sub>2</sub>SO<sub>4</sub> solution. It is found that the *Amaranthus* leaves extract is uniformly adsorbed over the surface. The inhibition is due to the film formation onto the metal/acid solution interface. The extract polarizes the cathode and acts as a cathodic inhibitor. SEM micrographs prove that further corrosion is prevented due to the formation of protective layer. Inhibited pickling acid in the paste form can be conveniently applied on large structures, as well as on small tools to be pickled / cleaned. Corrosion inhibition of an extract of rice husk ash on mild steel in 1 M HCl and H<sub>2</sub>SO<sub>4</sub> was investigated

[55]. Anticorrosion activity of *Tiliacora acuminata* leaf extract as a corrosion inhibitor in 1 M HCl has been investigated [56].

The inhibitive action of *Chromolaena odorata* stems extract, in various concentrations, against mild steel corrosion in a 1 M NaCl solution was studied using weight loss, potentiodynamic polarization methods and scanning electron microscopy [57]. Maximum inhibition efficiency of 99.83% was obtained, at 303 K, for an extract concentration of 3000 mg/L. Adsorption energies were lower with inhibited solutions than in uninhibited solutions, suggesting a decrease in mild steel corrosion rate, while Gibbs free energy, enthalpy and entropy of adsorption indicate that the adsorption process was spontaneous and endothermic in nature. The SEM and Langmuir adsorption isotherm studies suggested that the mechanism of corrosion inhibition occurred through an adsorption process. The inhibition action of lignin extract is due to the presence of hydroxyl and carbonyl groups.

Bitter leaves extract was studied as an inhibitive agent in HCl medium for the treatment of mild steel through pickling [58]. Thermometric, gravimetric and potentiodynamic polarization methods were employed in the study. The analysis of bitter leaves extract by gas chromatography revealed the presence of 96 g/mole of 2,4-hexadienal; 96 g/mole of 3,4-heptadiene; and 170 g/mole of 2-decenoic acid as the predominant chemical components. It is found that the activation energy for the corrosion inhibition process ranged from 39.831 to 77.533 kJ/mole, while the heat of adsorption ranged from 16.093 to 30.224 kJ/mole. These values showed that exothermic and spontaneous adsorption of the extract on the mild steel followed the physical adsorption mechanism. Maximum inhibition efficiency of 85.4% was obtained in this study. It was found that this extract is a suitable additive for pickling, cleaning and descaling operations.

The inhibitive action of *Piper guineense* (uzuza leaf) extract on the corrosion of mild steel in a 2 M H<sub>2</sub>SO<sub>4</sub> medium has been studied using the weight loss method [59]. The gel extract, obtained by rigorous grinding and squeezing of the leaves, was used for the weight loss determination at various concentrations at temperatures of 303 K, 313 K and 323 K. The result showed that corrosion inhibition increases with increasing concentrations of the extract showing greater efficiency at higher temperatures of 313 K and 323 K. The methanolic extract of *Aquilaria malaccensis* leaf was confirmed to inhibit the corrosion of mild steel in 1 M HCl [60]. The leaf extract acted as a mixed-type cathodic inhibitor.

Inhibitive and adsorption properties of the ethanol extract of *Phyllanthus amarus* for the corrosion of mild steel in H<sub>2</sub>SO<sub>4</sub> were investigated using gravimetric, thermometric and gasometric methods [61]. Thermodynamic consideration indicates that the adsorption of the extract is exothermic and spontaneous. A physical adsorption mechanism is proposed for the adsorption of the ethanol extract of *Phyllanthus amarus* on mild steel surface. The corrosion behavior of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the presence of apple, *Malus domestica* and *Bonduc*, *Caesalpinia bonducella* leaf extracts was investigated [62]. The main components present in the extract are bonducellin and quercetin.

Lignin, a polyhydroxy compound, was extracted from the black liquor of pulp and paper industry and its inhibition efficiency on mild steel corrosion by sulfuric acid was investigated [63]. The corrosion inhibition efficiency increases with an increased concentration of lignin, up to 1000 ppm. The inhibitive effect of the aqueous extract of leaves of *Polyalthia longifolia* on the corrosion of mild steel was studied using the weight loss method at temperatures of 303 and 318 K [64]. The adsorption of the extract was spontaneous and occurs according to Flory-Huggins adsorption isotherm.

The effect of the extract of *Musa paradisiaca* on corrosion inhibition of mild steel in aqueous 0.5 M sulfuric acid was investigated [65]. Polarization measurement indicates that *Musa paradisiaca* acts as a mixed-type inhibitor and the inhibition efficiency decreases with rise in temperature. The stem extracts of *Bacopa monnieri* [66] and *Momordica charantia* fruit extract [67] were examined as corrosion inhibitors of mild steel in 1 M HCl medium.

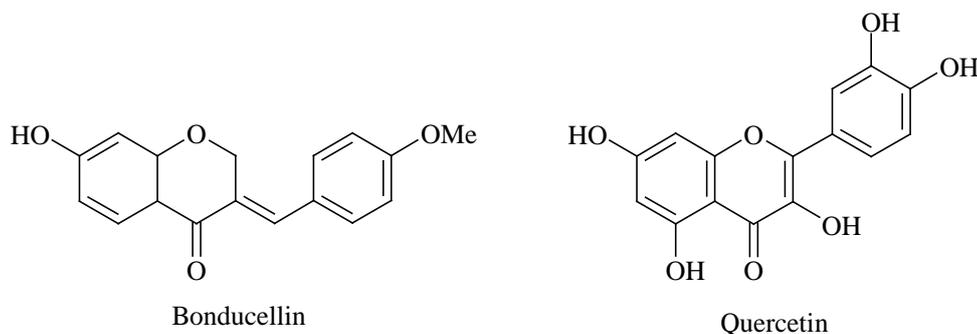
To improve the corrosion inhibition potential of *Anogessius leocarpus* gum exudates for mild steel in acidic medium, corrosion inhibition efficiencies of the gum, KI, KCl and KBr were studied [68]. Aqueous extracts of the leaves of *Anthocleista djalonensis* have been investigated as nontoxic corrosion inhibitors for mild steel in acidic environments [69]. Polarization study indicates that the adsorbed organic matter extract inhibited the corrosion process via mixed-inhibition mechanism, affecting both the anodic metal dissolution reaction and the cathodic hydrogen evolution reaction. The use of *Grewa venusta* root extract as corrosion inhibitor with mild steel was investigated [70] using gravimetric and electrochemical techniques in 1.0 M hydrochloric acid. Chemical compounds identified in the ethanol distillate of *Grewa venusta* extract by GC-MS analysis is given in Table 1. The adsorption

of the extract molecules on the mild steel surface obeys Langmuir adsorption isotherm. The results showed that the inhibitor acted as a mixed-type inhibitor.

Essential oil of *Juniperus phoenicea* extracted by distillation has been tested as inhibitor for the corrosion of mild steel in 1 M acidic media [71]. The inhibition efficiency was found to increase with the oil content, attaining 83% at 1500 ppm. This oil acts as a mixed-type inhibitor. The inhibition performance and mechanism of *Houttuynia cordata* extract for the corrosion of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> were investigated [72]. The extract of *Butea monosperma* has been examined to check the inhibitory effectiveness of mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> [73]. The *Butea monosperma* extract consists of stigmasterol β-D-glucopyranoside [74]. The corrosion inhibition of mild steel in HCl medium with pawpaw leaves extract as inhibitor has been reported [75]. *Cleome droserifolia* extract and

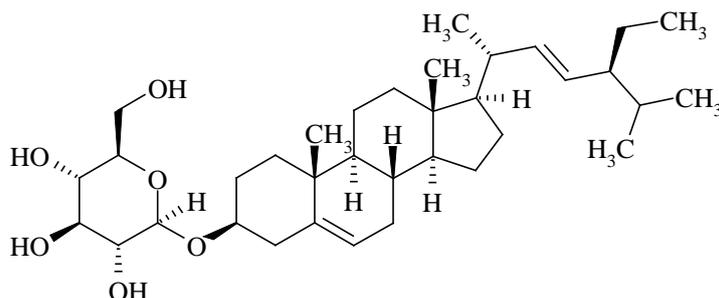
coffee husk were investigated for their capability to prevent mild steel corrosion in 1 M HCl [76, 77]. The *Mentha piperita* essential oil has been investigated as corrosion inhibitor for mild steel in 1 M HCl [78]. The oil has the following major compounds: 1-(p-fluorophenyl) anthraquinone, methenolone, selina-3,7(11)-diene and longifolene, as shown below.

The inhibition efficiency was modeled and optimized using response surface methodology. Annatto extract was investigated as a cheap and ecologically friendly corrosion inhibitor in acidic medium [79]. Thermodynamic models provided evidence of spontaneous physical and chemical adsorption mechanism with the evolution of heat. Phytochemical screening of this extract has revealed the presence of tannins, saponins, flavonoids, terpenoids, phenolics, anthraquinones, steroids, proteins and carbohydrates with no alkaloids [80]. Bixin and norbixin carotenoids (Figure 2) have been isolated from the extract [81, 82].



**Table 1.** Chemical compounds identified in the ethanol distillate of *Grewia venusta* extract

Peaks	Extract	Compound name	Molecular formula	Molecular weight g/mol
1	<i>Grewia venusta</i>	2-Pentanone, 4-methoxy-4-methyl	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	130
2		4H-Pyran-4-one, 2,3-dihydro-3	C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>	144
3		1,2,3-Propanetriol, mono acetate	C <sub>5</sub> H <sub>10</sub> O <sub>4</sub>	134
4		4H-Pyrazole, 3-t-butylsulfanyl-4	C <sub>9</sub> H <sub>10</sub> F <sub>6</sub> N <sub>2</sub> S	292
5		Dodecanoic acid, 3-hydroxy	C <sub>12</sub> H <sub>24</sub> O <sub>3</sub>	216
6		Hexadecanoic acid, 15-methyl	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	284
7		Octadecanoic acid, stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	284
8		Cyclohexanol, 3,5-dimethyl	C <sub>8</sub> H <sub>16</sub> O	128
9		1,9-Nonanediol, dimethanesulfonate	C <sub>11</sub> H <sub>24</sub> O <sub>6</sub> S <sub>2</sub>	316



Stigmasterol  $\beta$ -D-glucopyranoside

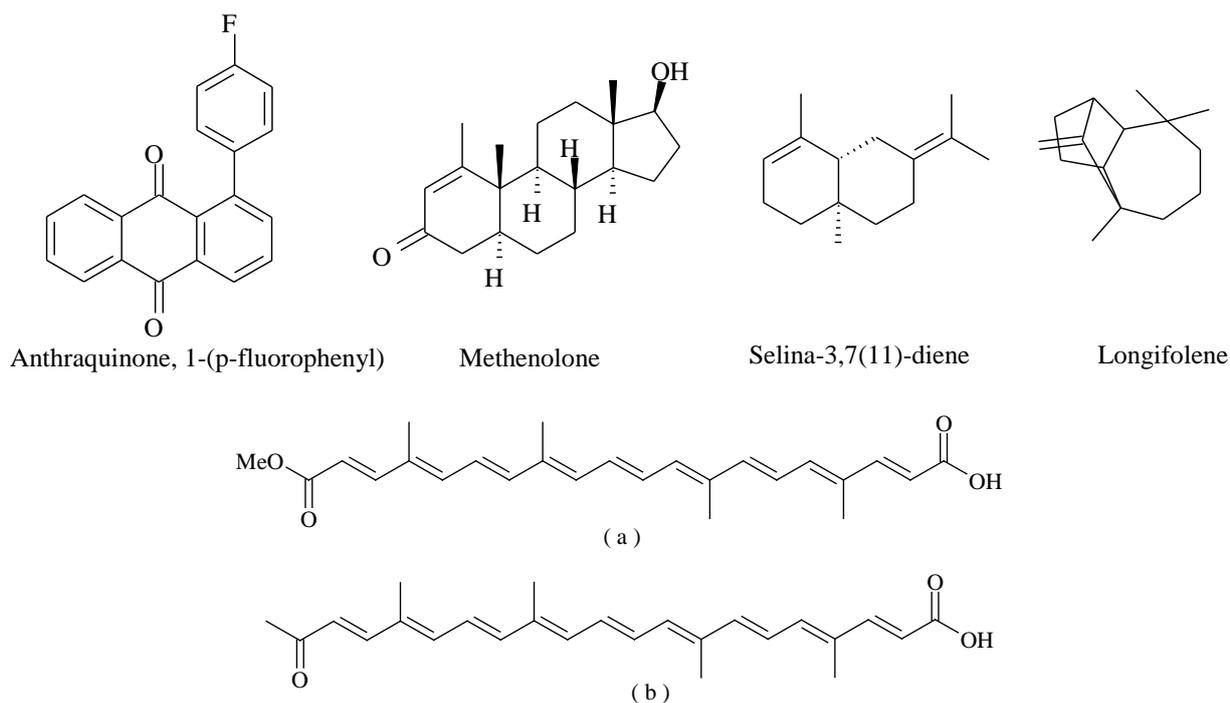


Fig. 2. Molecular structures of (a) bixin and (b) norbixin

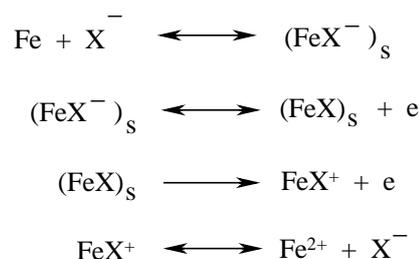
*Thymus sahraouian* essential oil [83] and *Viburnum sargentii* Koehne fruit extract [84] as new corrosion eco-friendly inhibitors have been used to protect mild steel in 1 M HCl. The methanol extracts from the leaves of *Pistacia terebinthus* L. [85] and extracts of *Acacia tortilis* leaf and bark [86] were tested as corrosion inhibitors for iron in a 3% NaCl solution and sea water, respectively. The influence of berberine extract (roots extract of *Coptis chinensis*) on corrosion of carbon steels in 3.5 wt.% NaCl solution saturated with CO<sub>2</sub> was evaluated [87].

The inhibition of the corrosion of mild steel in 1 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> by *Spirulina platensis* has been studied at different temperatures such as 303 K, 313 K and 323 K by the weight loss method, potentiodynamic polarization method, electrochemical impedance spectroscopy measurements and SEM analysis [88]. From the results, the mode of adsorption is found to be physisorption.

It has been found that the leaves and stem extracts of *Sida acuta* inhibited the acid-induced corrosion of mild steel [89]. Addition of iodide ions enhances the inhibition efficiency to a considerable extent but decreases with rise in temperature. Adsorption of the extracts was found to obey Freundlich adsorption isotherm. Inhibition mechanism is deduced from the temperature dependence of the inhibition efficiency, as well as from assessment of kinetic and activation parameters that govern the processes.

The inhibitive action of ethanol extracts from leaves, bark and roots of *Nauclea latifolia* (NLE) on mild steel corrosion in H<sub>2</sub>SO<sub>4</sub> solutions at 30 – 60 °C has been studied [90]. The mechanism of extracts action can be different, depending on metal, the medium and the structure of the inhibitor. One possible mechanism is the adsorption of the inhibitor, which blocks the metal surface and thus does not permit the corrosion process to take place [91].

The observed corrosion inhibition of mild steel in H<sub>2</sub>SO<sub>4</sub> solutions can be explained by the adsorption of components of NLE on the metal surface [92]. Various mechanisms have been proposed for the inhibition of metallic corrosion in acid media [93, 94]. According to the mechanism, if a molecule or ion, X<sup>-</sup>, is adsorbed on the steel surface, a surface complex forms in the anodic process and the complex is then desorbed from the surface.



where s represents ion or compound at the surface. In general, if the adsorbed molecule / ion on the surface complex is stable, the corrosion of steel

is inhibited. Therefore, it can be concluded that the adsorption of the phytochemical components of the plant extract leads to the formation of a stable surface complex, which blocks the active sites on the surface of the metal thereby reducing the corrosion rate. Increase in the concentration of the phytochemicals increases the amount of the surface complex resulting in greater inhibition of the corrosion.

The *Jatropha curcas* seeds oil was tested as an iron corrosion inhibitor in an acidic medium [95]. The electrochemical measurements show that this seed oil is a mixed-type indicator. The inhibition efficiency increases with higher inhibitor concentrations to attain a maximum value of 97% at 250 ppm. The inhibition effect of *Mentha pulegium* extract on the acid corrosion of carbon steel in 1 M HCl solution was studied [96]. The inhibition action of *Salvia officinalis* [97], *Strychnos nux-vomica* [98], *Ilex paraguariensis* [99], *Cucumis sativus* [100], aqueous brown onion peel extract [101], *Eulychnia acida Phil.* [102], leaf extract of *Khaya senegalensis* [103] and *Salvia hispanica* [104] on carbon steel corrosion in acid media was investigated. Extract of *Juniperus procera* [105], both treated and untreated date palm tree waste [106], *Jasmine tea* [107], *Pulicaria undulate* [108], *Curcuma longa L.* [109], *Prunus persica* [110], *Lawsonia inermis* [111] and *Nerium oleander* [112] have been investigated as corrosion inhibitors for carbon steel in acidic media.

The alcoholic extracts of eight plants, namely *Lycium shawii*, *Teucrium oliverianum*, *Ochradenus baccatus*, *Anvillea garcinii*, *Cassia italica*, *Artemisia sieberi*, *Carthamus tinctorius* and *Tripleurospermum auriculatum*, were studied for their corrosion inhibitive effect on mild steel in 0.5 M HCl media using the open circuit potential (OCP), Tafel plots and A.C. impedance methods [4]. OCP values in the presence of plant extracts shifted to more positive potential with time compared to those of acid solution. This slight OCP displacement (~10 mV) in the presence of plant extracts suggests that all the plant extracts act as mixed-type corrosion inhibitors. The lowest  $I_{corr}$  values observed in the presence of extracts of *Artemisia sieberi* and *Tripleurospermum auriculatum* suggest that these two plant extracts possess stronger inhibitive properties in comparison to other studied plant extracts. The addition of alcoholic extracts of all the plants in aggressive media either shifts the corrosion potential ( $E_{corr}$ ) values slightly toward positive side or remains constant but alters both anodic and cathodic Tafel slope values indicating that the presence of extracts inhibits both cathodic and

anodic reactions and the extracts can be classified as mixed corrosion inhibitors [113].

The corrosion rate of mild steel in 1 M  $H_2SO_4$  in the absence and presence of different concentrations of *Lannea coromandelica* leaf extracts was determined [114]. Maximum inhibition efficiency was found to be 89% at 250 mg/L (308 K). The impedance parameters such as  $R_s$ ,  $R_{ct}$ ,  $C_{dl}$  and  $f_{max}$  derived from Nyquist plots are given in Table 2. The charge transfer resistance increased with an increase in the concentration of inhibitor in acid solution.

**Table 2.** Electrochemical impedance parameters for mild steel in 1 M  $H_2SO_4$  in the absence and presence of *L. coromandelica* leaf extract

$C_{inh}$ (mg/L)	$R_s$ ( $\Omega cm^2$ )	$R_{ct}$ ( $\Omega cm^2$ )	$C_{dl}$ (F/ $cm^2$ )	% IE
0	2.2	3.7	$2.9 \times 10^{-2}$	-
50	2.9	24.5	$6.7 \times 10^{-4}$	84.9
100	4.3	38.1	$2.4 \times 10^{-4}$	90.7
150	4.4	39.9	$1.6 \times 10^{-4}$	92.2
200	4.8	47.3	$1.1 \times 10^{-4}$	93.8
250	5.4	60.1	$1.0 \times 10^{-4}$	93.8

FT-IR spectrum of the extract shows an absorption band at  $3431\text{ cm}^{-1}$  (associated hydroxyl) overlapped with the strong stretching mode of N-H. The  $1635\text{ cm}^{-1}$  band was due to stretching mode of C=O. The peaks at  $2073\text{ cm}^{-1}$  could be assigned to stretching mode of  $-C=N$ . The peaks at  $1465\text{ cm}^{-1}$  could be attributed to the stretching mode of aromatic substituted N=N. These observations confirmed that the leaf extract contains a mixture of natural products. The FT-IR spectrum of the adsorbed protective layer formed on mild steel surface indicates some additional peaks and some peaks shifted to the higher frequency region. This information provides that some interaction / adsorption had taken place over the metal surface. The N-H stretching shifted from  $3431$  to  $3423\text{ cm}^{-1}$  indicated the coordination of inhibitor with  $Fe^{2+}$  through the N atom of the N-H group. The shifting of C=O stretching from  $1635$  to  $1734\text{ cm}^{-1}$  confirms that there is a strong interaction between the extract and the mild steel surface. All these results confirmed the adsorption of inhibitor on the surface of the mild steel [115].

Peaks at  $2\theta = 35.5^\circ, 59.9^\circ, 71.7^\circ$  in the XRD patterns suggested the presence of iron oxide and a very small amount of brown film of  $Fe_2O_3$  for the mild steel immersed in  $H_2SO_4$ . In the XRD patterns of mild steel immersed in the test solution containing 250 mg/L of the leaf extract, the peaks due to iron appeared at  $2\theta = 44.6^\circ$  and  $65.5^\circ$  which indicated the absence of oxides of iron ( $Fe_2O_3$ ,  $Fe_3O_4$  and  $FeOOH$ ). This result was in good agreement with the observations made by Addoudi [116].

AFM surface examination reveals that the mild steel exposed to 1 M H<sub>2</sub>SO<sub>4</sub> has a considerable porous structure with large and deep pores whereas in the presence of inhibitor the mild steel surface appears more flat, homogeneous and uniform which indicated that the extract provides an appreciable resistance to corrosion.

The phenolic (OOMW-Ph) and non-phenolic (OOMW-NPh) fractions of the extract of olive oil mill wastewaters were evaluated as a corrosion inhibitor of steel in molar hydrochloric acid [117]. Olive mill wastewater is a natural source with high amounts of bioactive substances with attractive properties [118] such as polyphenolic mixtures with different molecular weights [119]. In olive mill waste, hydroxytyrosol, tyrosol and oleuropein are the major phenolic components [119-121]. The inhibition efficiency of an aqueous extract of *Eclipta*

*alba* leaves in corrosion of carbon steel in sea water has been evaluated [122]. The active compound in an aqueous extract of *Eclipta alba* extract is wedelolactone (Figure 3). The inhibitive action of the argan press cake extract against corrosion of steel in a 1 M HCl solution was investigated [123]. Polarization studies showed that this extract was a mixed-type inhibitor with predominant cathodic effectiveness and its inhibition efficiency increased with the inhibitor concentration but decreased with rise in temperature. The inhibition of steel in hydrochloric acid and sodium chloride solutions by *Nicotiana* leaves extract was investigated [124]. The chemical constituents in *Nicotiana glauca* are anabasine, glutamic acid and 7-dehydrocholesterol [125].

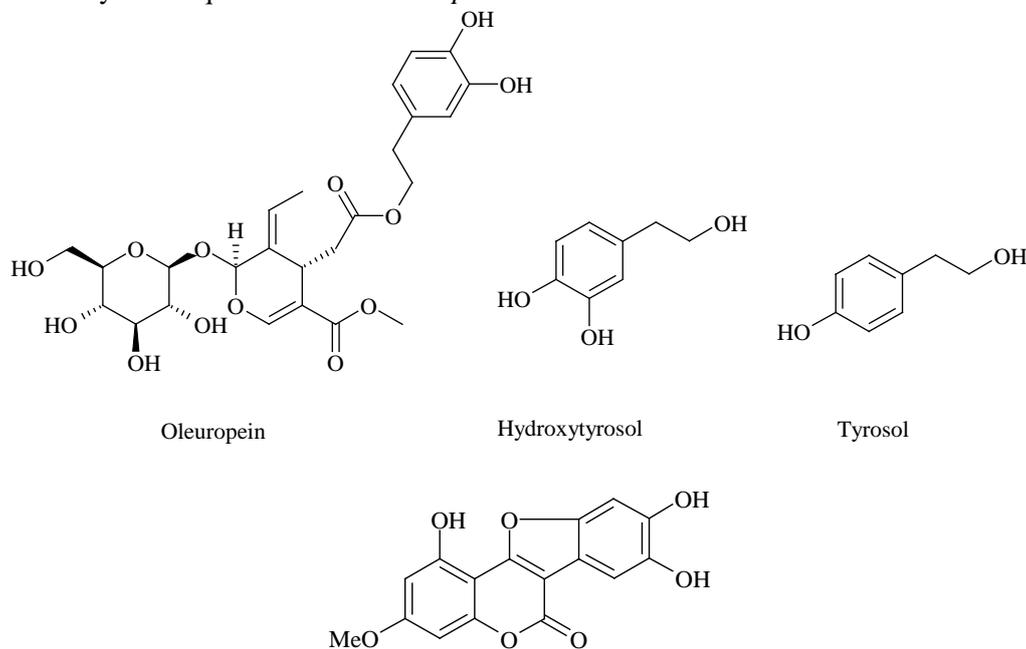
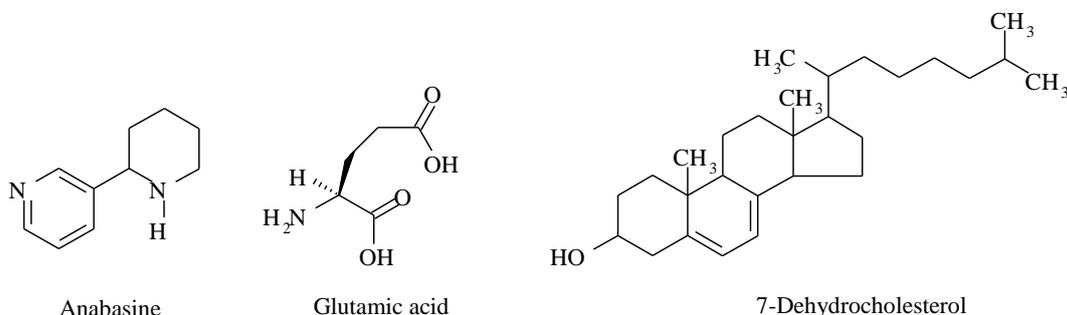


Fig. 3. Wedelolactone



The corrosion inhibition of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution by the extract of *Litchi Chinensis* was studied by weight loss method, potentiodynamic polarization and electrochemical impedance spectroscopy [126]. The results show that the litchi

peels extract acts as mixed-type inhibitor. The extraction of *Zea mays hairs* (*Z. mays*) was carried out by Soxhlet and ultrasound techniques and through solvents. The extracts were rich in polyphenols. The inhibiting effect of the extracts on

mild steel corrosion in 1 M HCl solution was investigated by electrochemical measurements [127].

Essential oil from fennel (*Foeniculum vulgare*) was tested as inhibitor on carbon steel in 1 M HCl [128]. The main constituents are limonene and  $\beta$ -pinene (Figure 4).

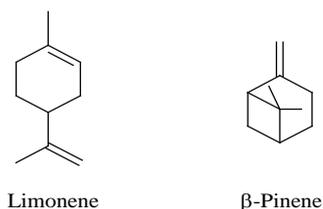
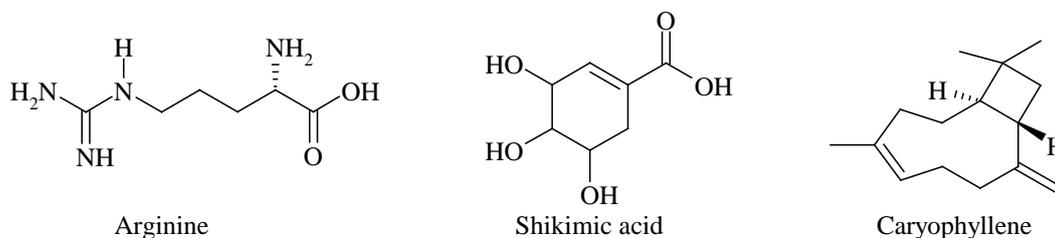


Fig. 4. Molecular structures of limonene and  $\beta$ -pinene

Corrosion inhibition of carbon steel in  $\text{CO}_2$ -saturated chloride-carbonate solution by the olive leaf extract has been studied [129]. The olive leaf extract achieves high corrosion efficiency as a



Under normal conditions, reinforcement steel is protected by the formation of a passive film mainly composed of Fe(II) / Fe(III) oxides, due to the high alkalinity of the concrete pore solution (pH around 13) [140]. However, the passivity breakdown becomes easy when the chloride ions reach a threshold value in the pore solution and/ or the pore solution drops from its normal values to values approaching neutrality (pH around 9) due to the carbonation of concrete [141]. The effect of *Chamaerops humilis L.* extract on the behavior of reinforcement steel in a carbonated concrete pore solution (pH = 9) was studied [142]. The results show that the plant extract has a beneficial effect on the development of a passive layer. The corrosion mechanism of *Morinda lucida* leaf extract admixtures on concrete steel rebar in saline / marine simulating environment was investigated [143]. Two naturally derived Welan gum and Neem gum have been tested as corrosion inhibitors against the steel reinforced in concrete in NaCl media at different time intervals [144].

#### Aluminium

Aluminium is the third most abundant element and the most abundant metal in the earth's crust.

mixed-type inhibitor. The activity of the extract from the peel of fuji apples (*Malus domestica*) was studied as a potential corrosion inhibitor for carbon steel in a saline medium [130]. *Rose*, *Gardenia* and *Solanum violaceum* extracts were used as corrosion inhibitors of steel in acidic medium [131]. The corrosion inhibition characteristics of the extracts of *Salvadora persica* [132], Coconut leaf [133], *Tobacco rob* [134], Red onion seeds and peels [135], *Raphanus sativus L* [136], *Coleus forskohlii* leaf [137] and *Pinus massoniana* needle [138] on corrosion of steel in acidic medium were investigated. The extract of *Pinus massoniana* needle has arginine, shikimic acid and caryophyllene as major constituents.

Reinforcement steel corrosion in concrete has received considerable attention. It has been identified as the primary cause of deterioration in concrete structures [139].

Aluminium plays an essential role in automobiles, packaging, utensils, pipelines, etc. Aluminium is a reactive metal [145], aluminium and aluminium alloys are extensively used in industry in a variety of aggressive aqueous environments covering a wide range of pH. Aluminium is usually protected by a thin oxide film, whose solubility is negligible in neutral solutions (pH 4.0 – 8.5) at room temperature provided the solution does not contain activating anions whereas heavy corrosion is observed both in acidic and alkaline media [146]. Anodizing in sulphuric acid solution can produce a protective oxide layer [147]. According to Obot *et al.* [148], a general mechanism for the dissolution of Al metal would be given as in the following equations:



The controlling step in the metal dissolution is the complexation reaction between the hydrated cation

and the anion present, equation 3. In the presence of chloride ions, the reaction will correspond to equation 5 and the soluble complex ion formed increases the metal dissolution rate which depends on the chloride concentration:



The corrosion of Al [149] in alkaline solution has been studied in the presence of some plant extracts [150] such as *Gum Arabic* [151], *Pachylobus edulis* and *Raphia hookeri* [152], *Fenugreek* leaves [153], *Calendula officinalis* flower [154], *Sansevieria trifasciata* [155], *Mangrove tannins* [156], *Ocimum basilicum* [157], *Ocimum gratissimum* [158], lignin from wheat straw [159], *Neolamarkia cadamba* bark extract [160] and *Vigna unguiculata* [161].

The corrosion inhibition of *Ficus tricopoda* gum was investigated [162]. The gum was found to be a good adsorption inhibitor for the corrosion of Al in  $\text{H}_2\text{SO}_4$  solution. The adsorption of the gum was

found to be endothermic at a critical concentration of 0.3 g/L and exothermic at concentrations above the critical limit. Corrosion behavior of Al in 0.1 M HCl, 0.1 M  $\text{HClO}_4$  and 0.05 M  $\text{H}_2\text{SO}_4$  solutions was studied using lupine extracts [163]. The results showed that the lupine extract is effective in the order  $\text{HClO}_4 > \text{HCl} > \text{H}_2\text{SO}_4$ . The chemical composition of lupine extract is represented in Figure 5. Corrosion inhibition of Al by the extract of *Trigonella foenum graecum L* was studied in 1 M HCl acid solution [164]. An inhibition efficiency of 88.6%, 84.41% and 75.77% was obtained by the addition of 1400 ppm of the extract using three solvents, DCM, ethanol and pentane, respectively. The potentiodynamic curves show that the decrease of Al corrosion in the presence of the extract mainly acts by a mixed process with an anodic tendency for both extracts with ethanol and with pentane while the extract with DCM showed a cathodic tendency.

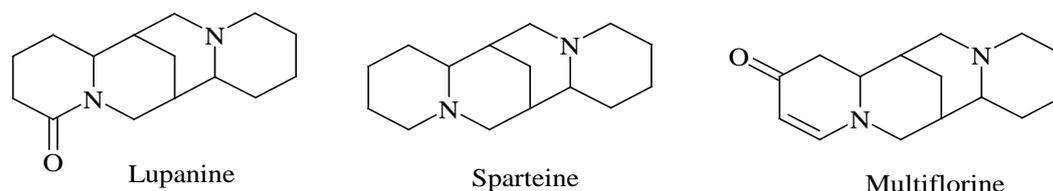


Fig. 5. Chemical composition of lupine.

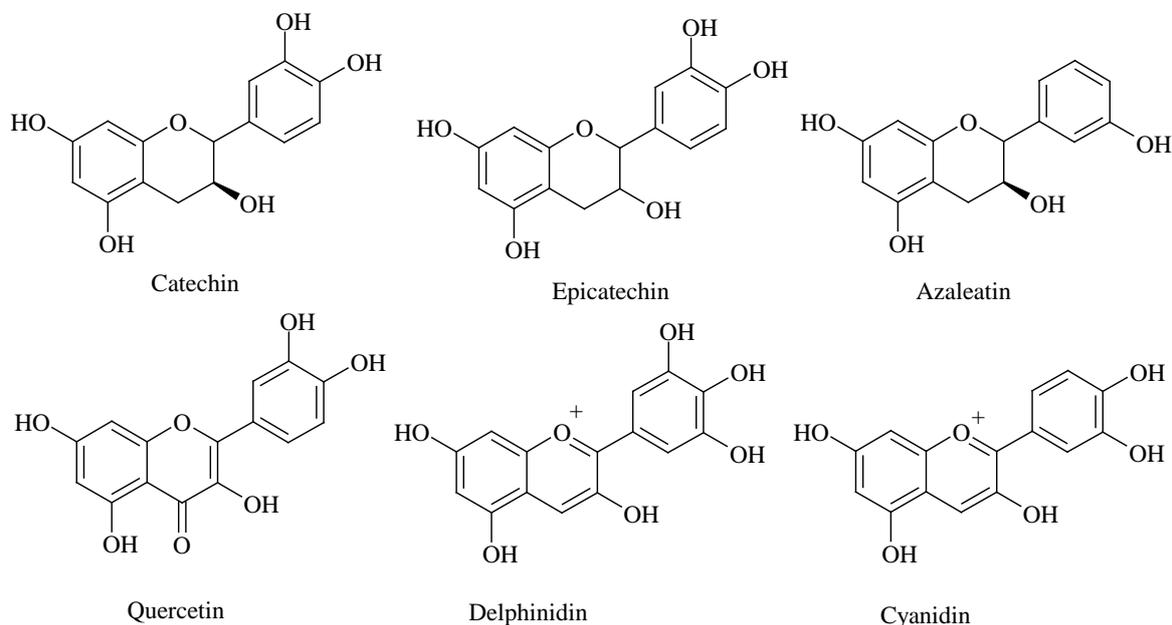


Fig. 6. Structures of *Cashew nut testa* tannin components

The inhibitive effects of *Treculia Africana* leaves extract [165], essential oil from *Mentha spicata* [166] and *Psidium guajava* [167] in the corrosion of Al in HCl solution were studied. The extract interaction with the metal surface was found to obey Freundlich and El-Awady adsorption isotherms.

*Asparagus racemosus* was used as a corrosion inhibitor of Al in acidic medium [168]. Steroidal saponin-shatavarin and sarsasapogenin are the active constituents of *Asparagus racemosus*. The thermometric and gravimetric analyses of Al corrosion control in HCl medium have been

performed using *Ricinus communis* extract [169]. The results showed that the extract contains phytochemicals such as alkaloids, cardiac glycosides, flavonoids, phenolics, phytates, saponins and tannins. *Cashew nut testa tannin* has been found to inhibit the corrosion of Al in HCl solutions [170]. It was found that *cashew nut testa tannin* is a cathodic inhibitor. The structures of the various components of this nut are given in Figure 6.

The *Psidium guajava* leaf extract was assessed as a corrosion inhibitor for a double thermally-aged Al-Si-Mg alloy in 3.5% weight NaCl solution [171]. Aluminium alloy corrosion behavior in 0.5 M HCl solution was studied using the ethanolic extract of *Cordia dichotoma* seeds [172]. The effect of the extract of *Lupinus varius L.* on the corrosion of Al in 1 M NaOH solution was investigated [173]. A first-order kinetic relationship with respect to Al was obtained with and without the extract from the kinetic treatment of the data. *Glycine max* extract was used as a corrosion inhibitor for Al alloy in 1 M HCl [174]. The corrosion inhibition of Al by *Ipomoea involcrata* (IP) in 1 M NaOH was studied [175]. The plant has been shown to contain mainly *d*-lysergic acid amide (Figure 7).

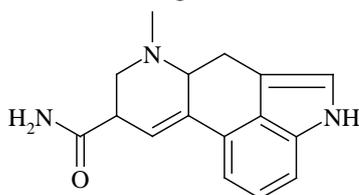


Fig. 7. Chemical structure of *d*-lysergic acid amide

The corrosion rate of aluminium was assessed by the H<sub>2</sub> evolution rate in the absence and presence of different concentrations of IP at 30 °C. The introduction of the plant extracts resulted in the reduction of the rate of H<sub>2</sub> gas evolution as compared to the blank. The study indicates a decrease in the protective nature of the inhibitive film formed on the metal surface at higher temperatures [176] which suggests a physical adsorption mechanism. Physical (electrostatic) adsorption takes place when inhibition efficiency decreases with increase in temperature [177]. The extracted compounds contain heteroatoms such as oxygen, nitrogen and aromatic rings with  $\pi$ -bonds in their molecules, which serve as adsorption sites onto the metal surface.

Increased activation energy in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface [178]. The negative  $Q_{\text{ads}}$  values ranging from (-11.09 to - 8.95 kJ/mol) indicate that the degree of surface coverage decreased with rise in temperature,

supporting the proposed physisorption mechanism [179].

### Copper

Copper is a relatively noble metal, which is known to have attractive physical properties such as high electrical and thermal conductivities and mechanical workability [180, 181]. Copper metal is used in many industries like heat exchanger, condenser, electrical wiring, connectors and printed circuit boards. Many plant extracts have been reported as green corrosion inhibitors on copper in various corrosive media such as *Azadirachta* [182], *Cannabis* [183], *Zanthoxylum* [184], *Herba alba* [185] and *Calligonum comosum* [186]. *Capparis spinosa* extract is known to contain several organic compounds such as sterols, flavones, oxygenated heterocyclic constituents, alkaloids and isothiocyanate glycosides [187]. The corrosion inhibition efficiency of this extract on the corrosion of copper in 1 M NaOH solution was investigated [188]. Polarization measurements showed that the extract acts as a mixed-type inhibitor. Four different herbal compounds, *Pimpinella anisum*, *Carum carvi*, *Cuminum cyminum* and *Hibiscus sabdariffa* have been tested as green corrosion inhibitors for copper exposed to 0.5 M NaCl [189].

Corrosion inhibitive effects of *Withania somnifera* extract [190], *Chenopodium* extract [191], *Alchemilla vulgaris* extract [192], *Nerium oleander* extract [193] and *Myrrh* extract [194] were studied on copper in acidic environment. Extracts of *Ziziphus lotus* were experienced as a corrosion inhibitor of copper in sea water using polarization methods and weight loss measurements [195]. Majority of molecules in *Ziziphus lotus* extract are vitamin C, vitamin A, vitamin E and linoleic acid. Synergistic effect of barium chloride on the corrosion inhibition efficiency of aqueous lupine seed extract on copper in 2 M HNO<sub>3</sub> acid solution has been investigated [196].

### Miscellaneous

The essential oil of *Artemisia herba alba* has been extracted and tested as an inhibitor of lead corrosion in 0.1 M Na<sub>2</sub>CO<sub>3</sub> medium [197]. Zinc is one of the most important non-ferrous metals which find extensive use in metallic coating. Zinc corrodes in a solution with pH lower than 6 and higher than 12.5, but within this range the corrosion rate is very slow [198]. Under aggressive conditions, zinc metal undergoes corrosion, gaining white colored rust [199]. The inhibiting effect of *Ailanthus altissima* aqueous extract as a corrosion inhibitor for zinc in 0.5 M HCl, has been evaluated [120]. Results

revealed that this extract acted as a mixed-type inhibitor and adsorbed onto the zinc surface following Temkin isotherm. *Slanum nigrum* extract has been tested as an eco-friendly green inhibitor for zinc in 3.5% NaCl and 16 ppm Na<sub>2</sub>S solution [121].

### CONCLUSION

The research work on the corrosion inhibition of metals in various corroding media using a variety of natural compounds is presented in this review article. Plant extracts were the most studied natural products. A wide variety of solvents were used to prepare extracts of the leaves, seeds and stems of the respective plants. The inhibition efficiency of the green corrosion inhibitors tested increased with concentration. An increase in temperature resulted in the lower efficiency of the tested products. Although a number of plants and their phytochemical leads have been reported as anticorrosive agents, the vast majority of plants have not yet been properly studied for their anticorrosive activity. For example, of the nearly 3,00,000 plant species that exist on the earth, only a few (less than 1%) of these plants have been completely studied relative to their anticorrosive activity. Thus, enormous opportunities exist to find out novel, economical and eco-friendly corrosion inhibitors from these source of natural products.

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