Corrosion Green Inhibitor of Mild Steel in Acidic Medium: A Review

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***Abstract*—For the need for development of non- toxic, cost-effective, readily available and eco- friendly corrosion inhibitor, this review deals with the study of various researches related to corrosion inhibition of mild steel with an emphasis on acidic media by green inhibitor. Plant extracts derived from the leaves, flowers, fruits, seeds, and other plant matter from various plants have revealed to have excellent anticorrosive properties. The inhibition efficiency ranged between 30-80% with different inhibitor concentrations in acidic environments. This review provides information about different methods of extract preparation, chemical composition of the various green inhibitor, active component and the corrosion inhibition mechanism of the green inhibitor. the component of inhibitor gets adsorbed on the metal surface and form a barrier film over its surface. It also provides the information about the factors by which corrosion inhibition efficiency of the green inhibitor can affected. It was found that the inhibition efficiency reaches up to a maximum of 90% for green inhibitors in an acidic medium of HCl and H_2SO_4.**

***Index Terms*—acidic medium, corrosion, green inhibitor, mild steel.**

I. INTRODUCTION

Corrosion prevention is an important issue for industrial application of materials. Among numerous corrosion prevention measures, use of corrosion inhibitor has advantages of economy, high efficiency, and facile-feasibility, and has been widely applied in various fields. The effectiveness of an inhibitor to provide corrosion protection depends to a large extent upon the interaction between the inhibitor and the surface. The adsorbed inhibitors can affect the corrosion reaction either by physically blocking the surface or by changing the activation sides of the anodic and cathodic partial reactions of the corrosion process.

Traditionally, evaluation of inhibition performance is primarily conducted by experiment, such as weight loss assessment, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). Several quantum chemical methods and molecular modeling techniques have been developed to correlate the inhibition efficiency of the inhibitors with their molecular properties. The reactivity of the inhibitor is closely linked to their frontier molecular orbitals (MO), including the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO, and other parameters, such as Lewis acid/base hardness and softness.[1]

Green corrosion inhibitors are generally obtained from plant extracts thus they are eco-friendly. Plants, fruits, and peels have been excellent sources of inhibitors. Many natural products have been used in corrosion inhibition as plant extracts like *Chelidonium majus* (Celandine) [2], *Aloe vera* (Aloe Vera) [3], *henna* (Lawsonia Inermis) [4], *Newbouldia leavis* [5],*Carica Papaya* and *Camellia Sinensis* [6], *Euphorbia hirta* [7], *Tithonia diversifolia* [8].

II. LITERATURE

Chung et al. [9] studied *Magnolia kobus* DC. (M. kobus), a prominent Southeast Asian flowering plant species, for its inhibition efficiency against mild steel corrosion in H_2SO_4. The weight-loss and electrochemical study were used for the study. M. kobus shows maximum corrosion inhibition efficiency of 81.96% in 1 M H_2SO_4.

The M. Kobus leaves extract was prepared with methanol. 100 g of powdered plant material was extracted with 1 L of methanol for 72 h with fresh load of methanol for every 24 h. The residue was filtered using Whatman Grade 1 filter paper and evaporated. This extract was dissolved in 1 M H2SO4 to prepare 100, 200, 300, 400, and 500 ppm inhibitor solutions. By the UHPLC analysis, alcoholic extract of the leaves was identified to have 145.80 µg/g of myricetin and 102.32 µg/g syringic acid as prominent components, with a TPC of 95.26 mg/g and a total flavonoid content (TFC) of 25.38 mg/g. Myricetin along with other plant components present in the plant extract contributed to the inhibition process

The surface of mild steel coated with M. Kobus aqueous extract was analyzed by AFM, UV–vis, and FT-IR spectroscopy. These analyses provide strong evidence for the formation of a protective barrier on mild steel in presence of the inhibitor, when immersed in the corrosive medium. The morphology study of mild steel surfaces was done by SEM and EDX. The SEM results show the difference of surface morphology in inhibited and uninhibited systems. The elemental composition provided by EDX, gives a proof of the protective barrier formation on mild steel. PDP curves indicates the mixed type behavior of the inhibitor.

Chung et al. [10] studied phytochemical components of the methanol extract of *Liriope platyphylla* (L. platyphylla) leaves and their inhibition activities on corrosion of mild steel in 1 M H_2SO_4 by electrochemical, gravimetric, and surface analytical techniques. The extract provides maximum 95.66% anticorrosion efficiency at 250 ppm inhibitor concentration.

Fresh leaves of L. *platyphylla* were collected from South Korea, washed, shade dried and powdered. Approximately 300 g of the powdered L. *platyphylla* leaves was soaked in 1 L of methanol at room temperature for 5 days. The solvent was changed at 24 h time intervals. The extract was filtered using same Whatman Grade 1 filter paper, evaporated and dried in a rotatory evaporator to obtain 100 mg/mL of plant extract. The extract contained 299.11mg/g of TPC and 33.88mg/g of TFC. The involvement of the phenols and flavonoids in corrosion inhibition was identified by UHPLC.

The adsorption was enhanced as increasing in inhibitor concentrations but as temperature increases inhibitor efficiency decreases due to the instability of the adsorbed layer of L. *platyphylla* extract on the metal surface.

PDP data revealed the mixed-mode of corrosion inhibition mechanism by electrostatic interactions. Analysis of the surface morphology by SEM, AFM, and FT-IR confirmed the formation of a protective barrier film on the metal surface. The adsorption of the L. *platyphylla* extract can be described by a Langmuir adsorption isotherm.

O.A. Akinbulumo et al. [11] investigate the *Euphorbia heterophylla L.* extract as a corrosion inhibitor for mild steel in 1.5 M HCl by gravimetric method at RT as well at elevated temperature. The thermodynamics parameters and adsorption mechanism also investigated. The activation energy, enthalpy change, and entropy change were calculated. It was observed that the inhibition efficiency decreased as the temperature increased, and the activation energy decreased as the inhibitor concentration increased. The adsorption study demonstrated that the data confirmed to the Langmuir, Flory-Huggins, El-Awary's, and Temkin isotherms, with the Flory-Huggins model providing the best fit.

The adsorption of *Euphorbia heterophylla L.* is feasible and spontaneous. *Euphorbia heterophylla* L extract is more effective at a temperature below 343 K.

P. Muthukrishnan et al. [12] studied the *Ficus hispida* leaf extract (FHLE)-Stigmasterol as a corrosion inhibitor for mild steel in 1 M HCl by using weight loss measurement, PDP and EIS techniques. The maximum 90% IE was achieved with 250 ppm of FHLE at 308 K.

F. *hispida* leaves were dried and ground well into fine powder. 20 g of dried and powdered leaves was extracted with absolute ethanol in Soxhlet apparatus for 12 h. The extract was filtered and heated on a water bath at 60 C until most of the ethanol evaporated. 0.8 g of the ethanol extract was digested in 1 liter of 1 M HCl solutions. From the stock solution (0.8 g/l), plant extracts test solutions were prepared at concentrations of 50, 100, 150, 200 and 250 ppm. Stigmasterol was confirmed as the major component of *F. hispida* by GC–MS.

The IE of the inhibitor decreases as temperature increases. IE increases as the activation energy of corrosion process increases in inhibited system. Cathodic and anodic polarization curves revealed that

FHLE acts as a mixed-type inhibitor. The adsorption of FHLE on the mild steel surface follows the Langmuir adsorption isotherm. The ΔG^{o}_{ads} indicates Physisorption onto the mild steel surface.

E. Baran et al. [13] studied the IE of the methanol extract of *Gentiana olivieri* and its fractions on the corrosion of mild steel in a 0.5 M HCl solution using PDP and EIS. Surface analyses (SEM/ EDX) were carried out. Thermodynamic parameters (Ea, ΔH, ΔS, ΔG) were also examined.

The aerial parts of *G. olivieri* were collected at the flowering stage from Turkey, and dried. The dried and powdered plant samples (250 g) were extracted with methanol (99.9%) (5×1L) at room temperature. The extract was filtered and concentrated using a rotary evaporator. The concentrated extract was then dissolved in distilled water at 60ºC and was filtered to remove lipophilic substances and chlorophyll. Afterwards, this solution was extracted with ethyl acetate and n-butanol. The organic solvents were removed. The methanol (MeOH) extract was fractionated into three fractions, ethyl acetate fraction, n-butanol fraction and water fraction.

The chemical compositions of the methanol extract and its fractions were identified by HPLC and FT-IR spectroscopy.

The adsorption of the *G. Olivieri* extracts on the metal surface obey the Langmuir adsorption isotherm. Anodic and cathodic polarization curves indicate that the extract and its fractions are mixed-type inhibitors. The thermodynamic parameters demonstrated the adsorption mechanism is a combination of physisorption and chemisorption, predominantly physisorption.

The study showed that the ethyl acetate and water fractions partially lose their inhibitory effect after an immersion time of 24 h, which is not in the case for the methanol extract and its n-butanol fraction. The study, shows that the methanol extract and its n-butanol fraction, containing the high amounts of gentiopicroside and isoorientin, can be used as effective inhibitors against the corrosion of mild steel. EIS showed maximum IE OF 93.7% at an inhibitor concentration of 800 ppm.

O.O. Joseph et al. [14] studied the efficiency of ***Lecaniodiscus cupanioides*** leaves extract on the degradation behavior of normalized and annealed mild steels in 0.5 M HCl by gravimetric and PDP measurements. Also study the effect of extract concentration and exposure time on corrosion behavior.

The leaves of *Lecaniodiscus cupaniodes* were air dried and ground into powder weighing about 4kg. Soaked the dried leaves powder in ethanol for five days and filtered. The resulting extract solution was left for about 60 hours to evaporate the ethanol. A variation of 1 - 5ml of the extract concentration was used for the tests.

Weight-loss measurements were taken at two-day intervals for a total period of 34 days. The inhibitive effect of the extract diminished with exposure time for annealed mild steel. The corrosion rate of normalized mild steel was generally higher than that of annealed mild steel, both in the presence and absence of the inhibitor. The corrosion rates of the two heat-treated steels were significantly influenced by the concentration of *Lecaniodiscus cupanioides* extract.

The study revealed that *Lecaniodiscus cupaniodes* performed effectively to inhibiting the corrosion attack on the heat-treated steels in 0.5 M HCl medium with an average inhibition efficiency of 90%.

Y. Liu et al. [15] studied **ginger extract** as an environmentally friendly inhibitor in simulated concrete pore (SCP) solutions. The inhibition efficiency of ginger extract was studied by stereo-microscope and various electrochemical techniques like SEM, XPS, EDX, etc.

The ginger was washed and squeezed through a plant presser to acquire the ginger extract. The ginger extract was passed through a 1.25 mm sieve and dried at 60 °C in an oven to obtain the dried ginger extract powder. The ginger extract powder was mixed into to a 0.1 mol/L sodium hydroxide solution at a dosage of 6%. In order to allow the effective components of ginger extract powder to be fully dissolved, the low frequency ultrasonic operation on ginger extract mixture was carried out with ultrasonic transducer for 5 min, and then the extract was placed at room temperature for 24 h. After proper filtration and precipitation. The ginger extract prepared is a kind of well-dispersed suspension

The main phenolic constituents [6- Gingerol; 8-Gingerol; Cyclocurcumin; 1-hydroxy-1, 5-bis (4-hydroxy- 3- methoxyphenyl) pentan-3-one; 1-hydroxy-1, 5-bis (4- hydroxy- 3, 5-

dimethoxyphenyl) pentan- 3- on; Arginine] of the ginger extract were confirmed by LC-MS.

The results from the stereo-microscope and electrochemical measures matched well with each other and indicate that the ginger extract was an efficient corrosion inhibitor in reducing chloride-induced corrosion. At the later corrosion stages, with the induction of a certain concentration of chloride ions, the ginger extract inhibited the corrosion mainly by restraining the anodic reaction. According to the experiment results, the ginger extract can be classified as an effective mixed-type corrosion inhibitor.

The ATR-FTIR and XPS confirmed the formation of the carbonaceous organic film on the steel bar and also gave some information about elements and chemical bonds of the adsorbed layer formed on the steel surface.

G. Bahlakeh et al. [16] reported the *Peganum harmala* (Esfand) seed extract as effective corrosion inhibitors for mild steel in 1 M HCl. To study the corrosion inhibition behavior, electro chemical methods (EIS and polarization), surface analyses (AFM, SEM and contact angle) and theoretical studies (MD, DFT and MC) were performed.

To get the extract of inhibitor, 30 gm *Peganum harmala* seed was added to 1 liter distilled water and then mixed for 3 h (at 70 °C). Finally, the mixture was centrifuged and the extract solution was kept in an oven at 70 °C overnight to extract powder. Four levels of 200, 400, 600 and 800 ppm *Peganum harmala* seed extract powder were added to 1 M HCl solution and mixed to get clear solution.

The presence of many adsorption sites and functional groups, i.e., O-H, C=O, C=N, C-H, N-H, and C-N, in component of the extract like harmaline ($C_{13}H_{15}ON_2$), harmalol and harmane were confirmed by UV–Visible and FT-IR test results.

From EIS and polarization tests, the IE of the inhibitor was 95%, by mixed anodic/cathodic prevention mechanism. The adsorption of the extract component on the steel surface, obeying the Freundlich adsorption isotherm. The adsorption of the inhibitor was confirmed from the EIS and surface studies explorations.

A. Berrissoul et al. [17] studied the use of *Lavandula mairei Humbert* extract (LM) as inhibitor for mild steel corrosion in 1 M HCl solution. The corrosion IE was examined via weight loss and electrochemical measurements, SEM, and XPS techniques. The corrosion IE increased with the increase of LM concentration up to maximum 92% at 303 K for a 400 ppm concentration.

A quantity of 40 gm of the aerial's parts powder of *Lavandula mairei Humbert* was macerated with 200 mL of ethanol for 24 h at room temperature using a magnetic stirrer. The extract was then shacked, filtered and evaporated in a rotating evaporator to dryness. This extract is characterized by a presence of Quercetine-3-glu curonide (72.8%) as major compound. The others main components were identified as Rosmarinic acid (9.3%) Chicoric acid (8.7%) and Acacetin-acetyl glucoside (4.7%) by HPLC-UV-ELSD-MS techniques.

Polarization measurements show that the LM ethanol extract acts as a mixed-type inhibitor. The adsorption of LM ethanol extract on a metal surface complies with the Langmuir adsorption isotherm. From the SEM and EDX analysis it was observed that the inhibition properties of this extract are associated with creation of a protective film on the sample surface. XPS shows chemical interactions between the major component of LM extract and the mild steel surface. C=O and C-O-H group attached on the sample surface indicates that the inhibitor was chemisorbed on the sample surface.

DFT method showed a good correlation between experimental data and the electronic properties of the major component of the inhibitor. MD simulation shows that LM has a high capacity to occupy a large percentage of the surface area of Fe (110) in the acidic medium. It also shows that the increase in temperature has a negative influence on the adsorption configurations.

A. Berrissoul et al. [18] studied the corrosion behavior of mild steel (MS) in 1 M HCl and its inhibition by the aqueous extract of *Artemisia Herba Alba* (AHA), by different types of techniques and methods namely: Weight loss, EIS, PDP, SEM, EDX, XPS. The highest IE obtained was 92% for 400 ppm of AHA aqueous extract in 1 M HCl at 303 K.

The AHA plant was dried at room temperature for one week. The aqueous extract of AHA leaves was obtained using the microwave assisted extraction for 30 min. The extracted solution was then filtered and dried at 313 K until the water from the extract evaporates. The powdered extract obtained was used as green corrosion inhibitor to prepare required solutions. The phytochemical screening showed the presence of flavonoids, saponins, tannins and alkaloids as components of the extract.

SEM, EDX, and XPS measurements have shown that surface deterioration and damages have been decreased by AHA inhibition action. Moreover, the composition of the protective film confirmed the presence of AHA extract on the metallic exposed surface.

Quantum chemical parameters that have been obtained from the DFT method showed a good correlation between experimental data and the electronic properties of the major component. MD technique shows the major component of AHA extract has a high capacity to occupy a large percentage of the surface area of metal in the acidic medium. The increase in temperature has a negative influence on the adsorption configurations by increasing the interaction energy with the inhibitor.

Klícia Carla et al. [19] studied *Glycine Max* (Soybean) meal extract, act as corrosion inhibitor for mild steel in 0.5 M H_2SO_4 solution by weight loss measurements, EIS, and PDP technology. Additionally, SEM and XPS were used respectively to characterize morphologically and chemical composition of the surface.

The soybean meal underwent a pre-grinding treatment. From the soybean meal powder, two corrosion inhibitors were obtained, aqueous extract (AE) by infusion and its HMWF by diafiltration. Another investigated inhibitor was the aqueous extract of the commercial soy protein (CIP) which was extracted by infusion. IE obtained in the presence of these extracts followed the trend AE < HMWF < CIP.

NMR analysis confirmed the presence of carbohydrates and proteins in the analyzed AE, HMWF and CIP samples. SDS-PAGE analysis showed that the majority proteins present in AE as well as its HMWF and CIP, are glycinin and β-conglycinin.

The results of the EIS analysis show that the added extracts modified the electric double-layer structure, which could be attributed to the molecules adsorption present in AE, its HMWF and CIP onto the metal/solution interface. The XPS analysis confirmed the presence of coating on the steel surface by N containing species from soybean extracts. The of SEM also confired the adsorption of the constituent of soybean extracts. There was a reduced surface roughness compared with the uninhibited condition.

There was a decrease in inhibition efficiency only at high temperatures. The % IE kept constant with temperature indicates chemical adsorption of the constituent molecules of aqueous extract. The highest IE obtained was 85.2% for 800 ppm of aqueous extract in 0.5 M H_2SO_4.

A. Dehghani et al. [20] studied the corrosion inhibition characteristics of green inhibitors based on Chinese gooseberry fruit shell extract on mild steel in 1 M HCl solution by EIS, PDP, SEM, AFM and contact angle tests. Computational methods DFT and MC/MD simulations were also applied.

Chinese gooseberry fruit shell was collected from the north of Iran and then dried under shadow and finally grinded to obtain powder. 30 gm of Chinese gooseberry shell powder was poured into 1000 ml of deionized water. The resulting solution was mixed for 3 h at 70 °C and filter. The solution was centrifuged for 10 min at 4000 rpm to a clear solution. At 50–60°C the solution was dried for 24 h, a powdered extract was obtained which was subsequently used for preparation of the test solutions. The extract powder was analyzed by FT-IR and UV–visible analyses. The Chinese gooseberry fruit shell extract contains components like sucrose, maltose and folate.

EIS tests indicated that IE increased with inhibitor concentration and reached to 92% for 1000 ppm inhibitor concentration. The Chinese gooseberry fruit shell extract behaved as a mixed type inhibitor and controlled both anodic and cathodic reactions with a little cathodic prevalence. SEM and AFM analyses indicated that an increase in the concentration of the inhibitor led to the greater formation of a protective layer on the mild steel surface. The contact angle measurements reflected that, upon adding the extract into the corrosive solution, the hydrophobicity of the surface increased.

The computational MC and MD simulations evidenced the adsorption of the Chinese gooseberry fruit shell extract components over the mild steel. computational outcomes proposed significant role of nitrogen/ oxygen/ aromatic ring containing folate compound, considered phytochemicals. The DFT-based computations delivered the highest proton affinity of various polar heteroatoms, especially nitrogen atoms.

Peipei Kong et al. [21] studied the inhibition performance of polyaniline (PANI)/chitosan (CTS) on mild steel corrosion in 0.5 M HCl by electrochemical techniques like PDP and EIS, quantum chemical calculations, and morphological observations by SEM.

Polyaniline solution was added to the chitosan solution and stirred for 30 min to form a homogeneous solution. An ammonium persulfate solution was added dropwise to a homogeneous solution for 1 h at 0 5 °C. The molar ratio of oxidant to monomer was 1:2, the polymerization reaction carried out at 0-5 °C for 6 h. The precipitated composite was collected by filtering and washing with water and ethanol, then dried.

Polarization results revealed that PANI/CTS acted as a mixed-type inhibitor, primarily suppressed cathodic processes. EIS measurements indicated that increasing the concentration of PANI/CTS results in an increase in R_{ct}, the addition and increasing inhibitor concentration, the frequency ranges with the maximum phase angle, the low-frequency impedance values increased, showing effective adsorption of inhibitor molecules. Quantum chemical calculations suggested that the electron-donating nitrogen, oxygen atoms, –C=N groups, and aromatic ring of PANI/CTS are responsible for the adsorption.

A. Sedik, D. Lerari, and A. Salci [22] studied the Dardagan Fruit (DF) as corrosion inhibitor for mild steel in 1 M HCl solution using PDP and EIS and surface analysis techniques. The surface of mild steel was examined by SEM AFM and EDX.

From the EIS measurements it was show that the inhibitor is acting by a simple blocking effect without affecting the mechanism of this reaction. The capacitive loops are slightly depressed as semi-circular shape with a center under the real axis. This refers to frequency dispersion that is attributed to the adsorption of inhibitor molecules at the metal surface, formation of porous layer and heterogeneity of the electrode surface. The contact angles measurement indicates that the addition of DF increases the hydrophobicity of the metal surface.

DF is a good corrosion inhibitor for mild steel protection in 1 M HCl solution by reducing the rates of both anodic and cathodic reactions. The IE of the inhibitor depends on its concentration. The highest IE is 90% at 3000 ppm in 1 M HCl. The inhibition efficiency increases with the increasing immersion time and reaches 97%. The inhibitor molecules adsorb homogeneously on the metal surface and form a protective film.

The surface of mild steel was examined by SEM and AFM. A significant reduction in the surface roughness was observed in the inhibitor-containing corrosive media compared to uninhibited corrosive media. The elemental composition of the surface after exposure to test solutions was analyzed with the help of EDX, compounds bearing S, N, O, those are considered to be active centers for adsorption process. Surface analysis measurements and the electrochemical results confirm a protective and well-distributed film over the metal surface.

A. Dehghani, G. Bahlakeh, and B. Ramezanzadeh [23] studied the corrosion retardation potential of *Tamarindus indiaca* (fruite) aqueous extract for MS in 1 M HCl experimentally (EIS, PDP, SEM, AFM and contact angle) and theoretically (basic atomic/electronic scale tools).

30 gr *Tamarindus indiaca* was added to 1 lit of deionized water. The solution was mixed continuously for about 3 hours at temperature of 70 °C. Then, the solution was filter and the clear solution was centrifuged for 5 min in 4000 rpm power. After spilling the solution in pet dish, the solution was heated for 24 hours at 70 °C. The solid residue was obtained after evaporation of the solvent and used as inhibitor.

PDP measurement shows that *Tamarindus indiaca* extract operated as a combined anodic/cathodic inhibitor prevalence to cathodic inhibition. The electrochemical measurements indicates that the inhibitor protect the mild steel from corrosion without changing the reaction mechanism. The i_{corr} value reduced in presence of the inhibitor and gives 85% IE in acidic solution. Also, the weight loss measurements depicted 93% efficiency after 4 h exposure to 1 M HCl media at 25 °C. The temperature effect on the inhibition efficiency concluded that inhibition reaction is endothermic.

Based on the AFM micrographs it was shown that HCl solution containing 800 ppm *Tamarindus indiaca* extract led to the most smoothened MS surface. The DFT explorations highlighted that the aromatic rings and oxygen heteroatoms behaved as influential local sites for molecular adsorption.

K. Muthukumarasamy et al. [24] studied the ethanolic extract of *Thunbergia fragrans* as a significant corrosion inhibitor of mild steel in 1 M HCl by using weight loss method and electrochemical analysis.

The fresh plants were dried under shade and crushed into powder. 200 g of the powdered plant material was soaked with 500 mL of ethanol for six hours. Then the extract was reflux, the resulting solution was filtered and concentrated to obtain the extract.

The corrosion inhibition efficiency increases with increase in concentration. 500 ppm inhibitor concentration was sufficient to show maximum corrosion inhibition of 81%. The weight loss data indicated that the adsorption of *Thunbergia fragrans* extract on mild steel obeys Langmuir adsorption isotherm. The interaction between the inhibitor and the mild steel surface was observed using SEM coupled with EDS. SEM and EDS also indicated that the inhibition followed the Langmuir adsorption mechanism. Tafel studies revealed the mixed type of action of inhibition. The Nyquist plots was found to increase with increase in the inhibitor concentrations. It indicated that the corrosion was a charge transfer process. The R_{ct} values increase with increase in inhibitor concentration, indicating considerable surface coverage by the inhibitor molecules through strong bonding to the metal surface. The phytoconstituents of the extract were adsorbed on mild steel surface and block the corrosion sites.

M.R. Rathod et al. [25] studied the *Dolichandra unguis-cati* leaves extract (DUCLE) to utilize it as corrosion inhibitor for mild steel in 1 M HCl solution. Mass-loss, PDP, and EIS measurements were applied in the evaluation. At 300 ± 1K, the highest %IE of 93.61 in 1M HCl at an optimized inhibitor concentration of 760 ppm.

Dolichandra unguis-cati plant leaves were washed, dried under sun light, and ground to a fine powder. 30 grams of leaf powder was taken in the extraction tube and extracted with 300 ml of ethanol using the soxhlet apparatus. The extract containing excess ethanol was expelled by a rotary-evaporator, and a stock solution was prepared. FT-IR spectrum of DUCLE indicated the existence of a monomeric hydroxyl group.

From polarization curves, it can assume that DUCLE functions as a mixed type of inhibitor. EIS demonstrates that with a rise in the inhibitor concentration, the resistance enhance but the value of C_{dl} reduce that assists the DUCLE adsorption. The results obtained from SEM images recommend that corrosion inhibition appears through the adsorption process. The ΔH^o_{ads} value is -17.45 kJ mol^{-1}, the negative value of ΔH^o_{ads} suggests that the adsorption is exothermic. The ΔG^o_{ads} values lie between -31.585 and -32.45 kJ mol^{-1} are negative, smaller than -40 kJ mol^{-1}, indicate physisorption as well as chemisorptions, and also show that the adsorption process is spontaneous.

The corrosion product of the surface of mild steel is IR active and attributed to the presence of DUCLE. The SEM images show that the change in surface morphology during the corrosion is least affected in the presence of inhibitors. From the FT-IR, AFM, and contact angle studies it was revealed that the interaction of inhibitors on the surface of mild steel through the adsorption process. The coating makes the surface of mild steel hydrophobic and thereby prevents corrosion progression

C.M. Fernandes et al. [26] studied the marine sponge *Ircinia strobilina* crude extract (ISCE) as a corrosion inhibitor for mild steel in 1 M HCl. The corrosion behavior was evaluated using weight loss method, PDP, LPR, EIS, AFM and DRIFT.

The sponge *Ircinia strobilina* was collected by scuba diving. Samples were stored in ethanol (EtOH) until laboratory analyses. The EtOH extract was removed and the sponge tissue was further extracted by static maceration with a mixture of methanol and ethyl acetate (MeOH/AcOEt) (1:1) for one week. After being removed from the MeOH/AcOEt extract, the sponge tissue was extracted over again with a mixture of MeOH/AcOEt (1:1). After evaporation under vacuum, the three extracts were combined giving the *Ircinia strobilina* crude extract (ISCE) with 16.46% yield.

From the chemical characterization of the ISCE by LC-HRMS, identification of 16 components of the extract was made, which have structural characteristics, which is necessary to adsorb on the metal surface and form a protective film. Surface characterization and DRIFT supported it.

The lowering the E_a from the blank HCl solution to the inhibited, indicated characteristic of the chemisorption process. The formation of an ordered stable film is also corroborated by the more negative value of entropy in the presence the inhibitor, suggesting a more orderly system. the positive values of enthalpy reflected that the process of metal dissolution is an endothermic process.

EIS and LPR corroborate with each other. The anticorrosive efficiency increases as the concentration of the inhibitor increases. The mechanism of inhibition occurs through adsorption on the metal surface. PDP curves shows that the prevention of mild steel dissolution, being a mixed type inhibition process. The adsorption process obeys the Langmuir Adsorption isotherm even at higher temperatures.

S. Abdelaziz et al. [27] studied the extract of *Arbutus unedo L.* plant leaves as a green corrosion inhibitor of mild steel in hydrochloric acid. Various experimental and theoretical techniques have been used to confirm its corrosion protection property.

The freshly collected *Arbutus unedo L.* plant leaves were washed and dried in a dry and ventilated place. Marinated extraction method is used, as. this method requires neither special equipment nor a special location. Moreover, it operates at low temperatures, which is an ideal technique to minimize any potential degradation of active components. A quantity of 300 g was macerated with 250 ml of EtOH/water (70/30: v/v) mixture for 24 h at room temperature. This operation was performed three times. The resulting solution was filtrated and evaporated under a vacuum at reduced pressure to obtain *Arbutus unedo* L. extract. The resultant extract was dried to get solid powder. The aqueous extract is rich in polyphenol and flavonoid compounds which were determined by the quantitative aluminum chloride colorimetric method.

EIS, LPR and PDP were used as for electrochemical analyses. The surface characterization of inhibited and uninhbited mild steel surface was carried out by SEM. To support the experimental study, theoretical approaches were used. DFT and MD simulations were used to assess the active sites of adsorption of the major leaves extract components and their interaction with the mild steel surface. The addition of the extract even at low concentration increases significantly IE with a maximum of 91.72% for 500 ppm of leaves extract at room temperature.

The value of ΔG^{o}_{ads} confirmed the combination of chemical and physical adsorption. The pKa analysis revealed that the neutral form of the two main constituents (Quercetin, Catechin) of the leaves extract is predominant in the corrosion inhibition in an acidic environment. Mulliken charges analysis and Fukui functions indicate that the most active sites of the main constituents of the extract are heteroatoms and conjugated double bonds of aromatic rings. According to MD simulation, the Quercetin molecule was adsorbed spontaneously in parallel to the metal surface, leading to a strong interaction to cover the total surface.

Inhibitor (plant extract)	Maximum inhibition efficiency	Inhibition concentration	Corrosive medium
Alcoholic extract of Magnolia kobus	81.96 %	500 ppm	1M H_2SO_4
Liriope plytyphylla	95.66 %	250 ppm	1M H_2SO_4
Euphorbia heterophylla L.	-	-	1.5M HCL
Ficus hispida leaf extract	90.00 %	250ppm	1M HCL
Gentiana olivier (Alcoholic extract)	93.70 %	800 ppm	0.5M HCL
Lecaniodiscus cupanioides	90.00 %	2000 ppm	0.5M HCL

Ginger extract	89.00 %	200 - 800 ppm	1M HCL
Peganum harmala	95.00 %	800 ppm	1M HCL
Lavandula mairei Humbert extract	92.00 %	400 ppm	1M HCL
Artemisia Herba Alba	92.00 %	400 ppm	1M HCL
Glycine max (soybean)	85.20 %	800 ppm	0.5 M H_2SO_4
Chinese gooseberry fruit shell	92.00 %	1000 ppm	1M HCL
Chitosan	-	-	0.5M HCL
Dardagan fruit	97.00 %	3000 ppm	1M HCL
Tamarindus indiaca (fruit)	93.00 %	800 ppm	1M HCL
Thunbergia fragrans	81.00 %	-	1M HCL
Dolichandra unguis-cati	93.61 %	760 ppm	1M HCL
Ircinia strobilina crude extract	82.00 %	2000 ppm	1M HCL
Arbutus unedo L. plant	91.72 %	500 ppm	1M HCL

III. CONCLUSION

- From the above discussion, it is concluded that many natural plant extracts are effective against mild steel corrosion in acidic medium.
- Weight loss, electrochemical impedance, and potentiodynamic polarization techniques were generally used to confirm corrosion inhibition.
- There is need for further work on the exploration of these materials in other corrosive environments such as carbon dioxide, Sulphur dioxide, and hydrogen sulfide.
- Further research should also be focused on the extraction and structural elucidation of active plant extracts to ascertain to help understand the process of corrosion inhibition.
- Scale-up experiments for industrial applications also need to be done so as to commercialize these natural extracts to effectively replace the conventional chemicals currently used to control corrosion.
- Various factors such as inhibitor concentration, corrosion rate, temperature effects, and adsorption mechanisms of certain plant inhibitors have been examined.
- It is observed that corrosion inhibition typically rises with increasing inhibitor concentration.
- Temperature has been found to directly influence corrosion inhibition in instances.
- Adsorption mechanisms generally adhere to Langmuir adsorption, although Freundlich adsorption has been observed in some cases as well.

IV. ABBREVIATION

AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflection fourier transform infrared spectroscopy
C_{dl}	Double layer capacitance

CIP	Commercially isolated soy protein
DFT	Density functional theory
DRIFT	:eflectance Infrared Fourier Transform Spectroscopy
E_a	Activation energy
EDX	Energy dispersive X-ray spectroscopy
EDS	energy dispersive spectrum
EIS	Electrochemical impedance spectroscopy
ELSD	Evaporative Light Scattering Detector
FT-IR	Fourier transform infrared spectroscopy
ΔG^o_{ads}	Free energy of adsorption
GC-MS	Gas chromatography mass spectroscopy
ΔH^o_{ads}	Adsorption enthalpy
HMWF	High molecular weight fraction
HPLC	High performance liquid chromatography
IE	Inhibition efficiency
LC-MS	Liquid chromatography mass spectroscopy
LC-HRMS	Liquid chromatography high resolution mass spectroscopy
LPR	Linear Polarization Resistance
MC	Monte carlo
MD	Molecular dynamics
MS	Mass Spectrometry
PDP	Potentiodynamic polarization
PZC	Potential of zero charge
R_{ct}	charge transfer resistance
RT	Room Temperature
SDS-PAGE	Sodium dodecyl sulphate polyacrylamide gel electrophoresis analysis
SEM	Scanning electron microscopy
TFC	Total Flavonoid Content
TPC	Total Phenolic Content
UHPLC	Ultra high pressure liquid chromatography
UV-vis	Ultraviolet visible
XPS	X-ray photoelectron spectroscopy

REFERENCES

[1] I.B. Obot, D.D. Macdonald, Z.M. Gasem, "Density Functional Theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: An overview, Corrosion Science" (2015).

[2] M. M. Motawea, A.El-Hossiany, A. S. Fouda, "Corrosion Control of Copper in Nitric Acid Solution using Chenopodium Extract", *Int. J. Electrochem. Sci.*,14 (2019) 1372.

[3] R. T. Vashi , H. G. Chaudhari, "The Study of Aloe-Vera gel Extract as Green Corrosion Inhibitor for Mild Steel in Acetic acid", *International Journal of Innovative Research in Science, Engineering and Technology*, 6 (2017) 22081.

[4] H.G. Chaudhari, R.T. Vashi, "The study of Henna leaves extract as green corrosion inhibitor for mild steel in acetic acid", *J Fundam Appl Sci.*, 8(2) (2016), 280.

[5] Nnanna A. L., Nwadiuko C.O., Ekekwe D. N., Ukpabi F. C., Udensi C. S., Okeoma B. K., Onwuagba N. B., and Mejeha M. I., "Adsorption and inhibitive properties of leaf extract of newbouldia leavis as a green inhibitor for aluminium alloy in H_2SO_4", *Americ. J. Mat. Sci.*, 1(2) (2011) 143.

[6] Loto C. A. and I. Popoola A. P., "Effect of cola a cuminata and camellia sinensis mixed extracts on the corrosion inhibition of mild steel in 0.5M sulphuric acid", *Int. Electrochem. Sci.*, 7 (2012) 2983.

[7] Nnanna A. L., Anozie I. U., Avoaja A. G. I., Akoma C. S. and Eti E. P., "Comparative study of corrosion inhibition of aluminium alloy of type AA3003 in acidic and alkaline media by euphorbia hirta extrac" Afric. J. Pure Appl. Chem., 5(8) (2011) 265.

[8] Alaneme K. K. and Olusegun S. J., " Corrosioninhibition performance of lignin extract of sunflower(Tithonia Diversifolia) on medium carbon low alloy steelimmersed in H2SO4 solution", *Leonardo J. Sci.*, 11(20) (2012) 59.

[9] Ill-Min Chung, Ramalingam Malathy, Rameshkumar Priyadharshini, Venkatesan Hemapriya, Seung-Hyun Kim, Mayakrishnan Prabakaran, "Inhibition of mild steel corrosion using Magnolia kobus extract in sulphuric acid medium", *Materials Today Communications*, 25 (2020) 101687.

[10] Ill-Min Chung, Venkatesan Hemapriya, Seung-Hyun Kim, Kanchana Ponnusamy, Natarajan Arunadevi, Subramanian Chitra, Mayakrishnan Prabakaran, and Mayakrishnan Gopiraman,"Liriope platyphylla extract as a green inhibitor for mild steel corrosion in sulfuric acid medium", *Chemical Engineering Communications*, 208 (2021) 72.

[11] Olatunde Alaba Akinbulumo, Oludare Johnson Odejobi, Ebenezer Leke Odekanle, "Thermodynamics and adsorption study of the corrosion inhibition of mild steel by Euphorbia heterophylla L. extract in 1.5 M HCl", *Results in Materials*, 5 (2020) 100074.

[12] P. Muthukrishnan, P. Prakash, B. Jeyaprabha, K. Shankar, "Stigmasterol extracted from Ficus hispida leaves as a green inhibitor for the mild steel corrosion in 1 M HCl solution", *Arabian Journal of Chemistry*, 12 (2019) 3345.

[13] Evrim Baran, Ahmet Cakir, Birgu¨l Yazici, "Inhibitory effect of Gentiana olivieri extracts on the corrosion of mild steel in 0.5 M HCl: Electrochemical and phytochemical evaluation", *Arabian Journal of Chemistry*, 12 (2019) 4303.

[14] O.O. Joseph, O.S.I. Fayomi, O.O. Joseph, O.A. Adenigba, " Effect of lecaniodiscus cupaniodes extract in corrosion inhibition of normalized and annealed mild steels in 0.5 M HCl", *Energy Procedia*, 119 (2017) 845.

[15] Yongqi Liu, Zijian Song, Wanyi Wang, Linhua Jiang, Yingjie Zhang, Mingzhi Guo, Fengyan Song, Na Xu, " Effect of ginger extract as green inhibitor on chloride-induced corrosion of carbon steel in simulated concrete pore solutions", *Journal of Cleaner Production*, 214 (2019) 298.

[16] Ghasem Bahlakeh, Bahram Ramezanzadeh, Ali Dehghani, and Mohammad Ramezanzadeh, "Novel cost-effective and high-performance green inhibitor based on aqueous Peganum harmala seed extract for mild steel corrosion in HCl solution: Detailed experimental and electronic/atomic level computational explorations", *Journal of Molecular Liquids*, 283 (2019) 174.

[17] A. Berrissoul, A. Ouarhach, F. Benhiba, A. Romane, A. Zarrouk, A. Guenbour, B. Dikici, and A. Dafali, "Evaluation of Lavandula mairei extract as green inhibitor for mild steel corrosion in 1 M HCl solution: Experimental and theoretical approach", *Journal of Molecular Liquids*, 313 (2020) 113493.

[18] A. Berrissoul a, E. Loukili , N. Mechbal , F. Benhiba , A. Guenbour, B. Dikici , A. Zarrouk , A. Dafali, "Anticorrosion effect of a green sustainable inhibitor on mild steel in hydrochloric acid", *Journal of Colloid and Interface Science*, 580 (2020) 740.

[19] Klícia Carla de Santana de Lima, Victor Magno Paiva, Daniel Perrone, Beatriz Ripper, Grazieli Simões, Maria Luiza M. Rocco, Amanda Garcez da Veiga , Eliane D'Elia, "Glycine max meal extracts as corrosion inhibitor for mild steel in sulphuric acid solution", *j mater res technol* , 9(6) (2020) 12756.

[20] Ali Dehghani, Ghasem Bahlakeh, Bahram Ramezanzadeh, "A detailed electrochemical/theoretical exploration of the aqueous Chinese gooseberry fruit shell extract as a green and cheap corrosion inhibitor for mild steel in acidic solution", Journal of Molecular Liquids, 282 (2019) 366.

[21] Peipei Kong, Huixia Feng, Nali Chen, Yong Lu, Shiyou Li and Peng Wang, "Polyaniline/chitosan as a corrosion inhibitor for mild steel in acidic medium", *Royal Society Of Chemistry Adv.*, 9 (2019) 9211.

[22] A. Sedika, D. Lerari, A. Salci, S. Athmani, K. Bachari, I.H. Gecibesler, R. Solmaz, " Dardagan

Fruit extract as eco-friendly corrosion inhibitor for mild steel in 1 M HCl: Electrochemical and surface morphological studies”, *Journal of the Taiwan Institute of Chemical Engineers*, 107 (2020) 189.

[23] Ali Dehghani, Ghasem Bahlakeh, Bahram Ramezanzadeh, Mohammad Ramezanzadeh, “ Electronic/atomic level fundamental theoretical evaluations combined with electrochemical/surface examinations of Tamarindus indiaca aqueous extract as a new green inhibitor for mild steel in acidic solution (HCl 1 M)”, *Journal of the Taiwan Institute of Chemical Engineers*, 102 (2019) 349.

[24] Kalaiselvi Muthukumarasamy, Sakunthala Pitchai, Kesavan Devarayan, Lawrence Nallathambi, “Adsorption and corrosion inhibition performance of Tunbergia fragrans extract on mild steel in acid medium”, *Materials Today: Proceedings*, 33(7) (2020) 4054.

[25] Manohar R. Rathod, S.K. Rajappa, B.M. Praveen, D.K. Bharath, “Investigation of Dolichandra unguis-cati leaves extract as a corrosion inhibitor for mild steel in acid medium”, *Current Research in Green and Sustainable Chemistry*, 4 (2021) 100113.

[26] Caio Machado Fernandes, Thayssa da S. Ferreira Fagundes, Nazir Escarpini dos Santos, Talita Shewry de M. Rocha, Rafael Garrett, Ricardo Moreira Borges, Guilherme Muricy, Alessandra Leda Valverde, Eduardo Ariel Ponzio, “Ircinia strobilina crude extract as corrosion inhibitor for mild steel in acid medium”, *Electrochimica Acta*, 312 (2019) 137.

[27] S. Abdelaziz, M. Benamira, L. Messaadia, Y. Boughoues, H. Lahmar, “A. Boudjerda, Green corrosion inhibition of mild steel in HCl medium using leaves extract of Arbutus unedo L. plant: An experimental and computational approach”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 619 (2021) 126496.

NOTE:
As this is a review paper so no new data were generated or analyzed in this study. All data discussed are available in the cited literatures.