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Survey of Green Corrosion Inhibitor for Metal Surface

Sushmita Gandash¹, Naseeb², Lalit Kumar³, Jyoti Sharma^{4*}

¹Department of Chemistry, Raj Rishi BhartrihariMatsya University Alwar-301001, Rajasthan, India

²Department of Vocational Studies and Skill Development, Central University of Haryana, Jant-Pali Mahendergarh-123031, India

³Department of Computer Science& Application, Maharishi Dayanand University Rohtak-124001, Haryana India 4*Government PG College Tijara, Alwar-301001, Rajasthan, India.

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KEYWORDS Corrosion, plant extract, green inhibitor.	ABSTRACT: Almost every eng corrosion in rece calls for continuo affordable, envir solution to addres and active funct Furthermore, a v variables that infl	gineering profession and aspect of our ent decades. It is seen as a potential pus investigation into potential remedi conmentally friendly, and derived fro ss this problem, according to recent r ional group of green inhibitors are variety of plant extracts that inhibit uence their efficacy.	r everyday lives has suffered harm due to ly catastrophic environmental issue that es. Green corrosion inhibitors, which are m plant extracts, are the most effective esearch. The mechanism, categorization, all explained in detail in this review. corrosion are discussed, along with the

1.1 Introduction

Corrosion is the "deterioration by chemical attack or interaction of oxygen present in environment with metal.Corrosion is an interfacial material (metal, wood, polymer, concrete and ceramic) reaction with its environment that results in material consumption into environmental components, according to the International Union of Pure and Applied Chemistry. Corrosion control of metals and alloys is an expensive process and industries have to spend huge amount to control it. It is estimated that the cost of corrosion in the developed countries is about 3-5% of their gross national product[1]. The direct cost of corrosion for India is U.S. \$26.1 billion (2.4% of the nation's gross domestic product) and the avoidable cost of corrosion is estimated as U.S. \$9.3 billion, which is equivalent to 35% of the direct cost of corrosion [2]. The most effective way to prevent metal surfaces from being destroyed or degraded in corrosive media is to apply corrosion inhibitors[1-3]. These inhibitors have also been utilized effectively in the production of primers and anticorrosive coatings but their toxic nature is a major disadvantage in this direction" [5]. Synthetic organic green inhibitor and inorganic corrosion inhibitor

stringent environmental rules. In order to address this issue in effective manner researchers are looking for eco-friendly, efficient, low cost and less toxic corrosion inhibitors such as plant extracts as substitute of inorganic inhibitors.For this, a variety of plant materials have been utilized. The plant extracts contain active elements like S, N, O, P etc[4-7]. The metal surface is pumped with the lone pair electrons that are present on these elements, preventing the loss of electrons from the metal surface [8,9]. Corrosion of metals and alloy is a common industrial issue for which field of green chemistry provide fertile research. A great interest of research is increasing towards green inhibitor due to their biodegradability, safety, renewability. Natural extract can be outlined back to the 1930's when possibility of using extracts of Chelidoniummajus (Celandine) in H₂SO₄ pickling baths were explored for the first time by Sanyal[1]. Since then, a sufficient number of studies were carried out to test corrosion inhibitor properties of various plants. Despite these enormous studies existing in literature the search for optimal anti-corrosive material has still not ended. "The number of published papers (patents included) over the topic "green corrosion inhibitors", as obtained through a

like lead and chromates have a greater chance of having

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SciFinder® literature review, is represented in the figure 2.1. The increase of publication shows an exponential trend"



Fig. 1: Number of Publications per 20-year-range from 1920 to 2020

Therefore, there is a greater need to create corrosion inhibitory substances that are safe for humans and the environment. Inhibitory qualities of eco-friendly and safe substances have been the subject of growing research since the 1930s, when interest in them first gained traction.[10,11].



Fig. 2: Distribution of research work done on natural product as corrosion inhibitor [12]

Anticorrosive nature of various plant extract has been carried out in H_2SO_4 and HCl solution as explained in literature. Green inhibitor provides a new, less costly and environmentally friendly method to inhibit corrosion. Figure 2.2 shows the division of research done in the last two decennary on various green corrosion inhibitor[12]. It reveals that most of publications are focused on the study of plant extract.

1.2 Active Functional Group

Active ingredient of green inhibitor consists of functional group "N, O, S, P or Se" heteroatom through which these are linked to a metallic surfaces. Compounds having electronegative functional group with conjugated multiple bonds and lone pair of electrons have been shown to be most effective [15][25].

The presence of repeated units, such as the "methyl and phenyl groups of the parent chain", as well as an extra substituent group, increases the bonding strength. Due to their ease of attachment to metal surfaces through the non-bonding electron, heterocyclic compounds have also demonstrated better inhibitory efficacy. The polar group and aromatic ring serve as adsorption centres [26]. Table1 shows some list of functional group present in green inhibitor. Some substances naturally originate from plants like benzoic acid, benzotriazole, carbohydrates, thiourea [17], flavonoids[16][27], tannins and tryptaminehave these functional groups as corrosion inhibitors.

Table1: Some functional group in green Inhibitor

Functional group	Name	Functional group	o Name
-OH	Hydroxy	-P-	Phospho
-C-N-C	Amine	-S-	Sulphide
-CONH2	Amide	-S=O	Sulfoxide
-NH2	Amino	-C=S	Thio
-NH	Imino	-SH	Thiol
-COOH	Carboxy	-N=N-N-	Triazole
-C-O-C	Epoxy	-C≡C-	yne
-P=0	Phosphonium	-As-	Arsano
NO2	Nitro	-Se-	Seleno

1.3 Literature Review

1.3.1 Leaves Extract as Corrosion Inhibitor

Singh A. et al.[17] investigated that compared to the Andrographispaniculata other leaf extracts, demonstrated superior inhibitory performance (98%).Strychnosnuxvomica showed greater inhibition (98%) in comparison to the other seed extracts. With a 98% inhibition efficacy, Moringaoleifera has the best mild steel corrosion inhibition among the tested fruit extracts in 1M HCl. The highest inhibitory performance of the examined stem extracts was 95% at 600 ppm for Bacopamonnieri.

Sharma J. & Gandash S. examined the corrosion inhibition behavior of *Brassica juncea* leaves, root extract for aluminium and MS respectively by WL, EIS and PP methods in acidic medium. The inhibitory efficacy was observed up to 80 % and 83% with 1000 ppm extract concentration and at as mixed inhibitor.[6,7]

Ogunleye et al.[18] investigated that "*Luffa Cylinderical* leaf extract (LCLE) act as corrosion

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inhibitors in 0.5 molar hydrochloric acid solution. The constituents of inhibitor were identified by using GC-MS. The LCLE adsorption on mild steel accompanied Langmuir isotherm and pseudo-second order adsorption kinetics. The optimum IE of 87.89% was obtained".

"Weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and Scanning Electron Microscope (SEM) techniques were to examine the inhibition efficacy of used Xylopiaferruginea and Nicotianatabacum leaves extract and partitions in different solvents on the corrosion behavior of mild steel (MS) in 1 M HCl by Amira[30] and Bhawsar J., Olasehinde, et al.[19,20] using. The Langmuir adsorption isotherm adsorption is followed by the adsorption of inhibitors on MS surface. SEM studies demonstrated that the adsorption of inhibitor provided corrosion protection of MS".

The effects of an acid extract from the leaves of the (Mahogany) Khayasenegalensis (LKS) plant were studied by **Ali I. H. et al.**[21] as "inhibitor for the corrosion of C-steel in 1.0 M HCl using weight loss, scanning electronic microscope, polarization curves and electrochemical impedance spectroscopy. The results obtained demonstrate that the extract could be considered as a good corrosion inhibitor for the C-steel in HCl media".

The extract of *Raphanussativus L* (Sinapinethiocyanate, Inhi-ST) as green inhibitor was characterized using ESI-MS, 1H and 13C-NMR and evaluated using "weight loss and potentiodynamic polarization measurement by **Jiang, et al.**[22] The study results indicate that Inhi-ST is an effective green inhibitor for QS corrosion in HClmedium".

A research study on inhibitive performance of "*Coleus forskohlii* leaf extract on mild steel corrosion process in 1.0 M HCl aqueous solution proposed that the *Coleus forskohlii leaf* extract is a mixed type inhibitor. Several methods such as mass loss, Tafel polarization, EIS have been adapted for the study. Adsorption process obey Langmuir model. SEM and EDS were used to explore the efficiency of inhibitor". **Ali. et al**[23]. found that inhibitive effectiveness increased with increase in inhibitor concentration.

Xie G. et al[24] investigated the use of electrochemical techniques to study the anticorrosion behavior of Anthocleistadjalonensis (A. djalonensis) leaf extract and mixture on steel submerged in an HCl solution. The study was conducted between 0.1 and 0.4 g/L at a variety of temperatures. Maximum inhibitory efficiency was determined to be 93% at concentrations of 0.4 g/L.

Inzunza R. G. et al. [36] examined "the inhibitive action of an ethanol extract from the leaves of *Pachycormus discolor* (EEPD) on carbon steel corrosion in 1 M HCl at different temperatures; gravimetric method and electrochemical tests were conducted. Potentiodynamic Polarization result classified the extract as mixed type inhibitor. Ethanol extract obey Langmuir adsorption isotherm". With increase in temperature inhibition efficiency increases which showed 94.52% IE at 25° C and 97.89% at 75° C.

The inhibitive effect of the *Saracaindica* (Asoka), *Xylopiaferruginea*, henna (*LawsoniaInermis*) leaves and olive leaf extract on "the corrosion of mild steel in potable water was investigated by **Amira**, et al.,[30]Chaudhari, et al.,[37] and Jamshidnejad, et al[25] using weight loss, open circuit potential measurements, SEM and potentiostatic polarization techniques. The threshold concentration of the inhibitor was found to be 500 ppm'. This concentration of inhibitor shows an inhibition efficiency of 92.4%".

The leaf extracts of *Centellaasiatica* (CE) was tested as green inhibitor for "corrosion of mild steel in 0.5 M H_2SO_4 by **Shivakumar S. S. et al.**[26] using gravimetric, Polarization and Electrochemical Impedance Spectroscopy (EIS) measurements. With increase in extract concentration inhibition efficiency increases. A superior inhibition efficiency of 95.08% was observed for 1200 ppm at 303K. Polarization measurement exhibited that CE extract function as mixed type inhibitor. SEM was used for surface analysis".

"Inhibition efficiency of *Brassica oleracea* extract on pipeline steel corrosion in 0.5 M H_2SO_4 was evaluated by **Ngobiri N. C. et al.** using electrochemical techniques. The result revealed that with increase in extract concentration and temperature inhibition efficiency increases to a point and decrease with further

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increase in extract concentration and temperature". It was found that *Brassica oleracea* has an excellent inhibition efficiency and mixed type inhibition behaviour[27].

"The action of ethanol (EEAA), acid (AEAA), and toluene (TEAA) extracts from Artemisia annua and Artemisinin(ATS) on corrosion of mild steel in H₂SO₄medium was investigated by Okafor P. C. et al. using gravimetric and gasometric techniques. The result revealed that extract and ATS act as good inhibitor. %IE followed the trend: EEAA > AEAA > TEAA > ATS directly proportional and to inhibitors concentration and inverse to temperature. The adsorption of inhibitor obeys the Langmuir isotherm. Physisorption mechanism of inhibition is proposed"[28].

Amamra S. et al. evaluatedThymus vulgaris extracts have antioxidant activity as measured by DPPH, ABTS, and electrochemical method. Result showed that Thymus vulgaris possess essential antioxidant activity[29].

Since organic inhibitor are ecofriendly so preferred to inorganic ones. One of the corrosion inhibitor *MyrmecodiaPendans* was investigated by **Pradityana A. et al.** [43] on used "pipe of carbon steel API 5L Grade B in 3.5% NaCl solution using Polarization and Electrochemical Impedance Spectroscopy. For chemical characterization Fourier Transform Infrared (FTIR) were used. From the result it was explored that the addition of 400 mg/L inhibitor provide higher inhibition efficiency".

"The effect of *Culcasiascandens* leaf extract on the corrosion of mild steel in 2 M HNO₃medium was analysed by **Nkop E.J. et al.** using weight loss or gravimetric technique at 303K, 323K and 343K for 30 minutes. Corrosion rate increase with more addition of extract concentration and rise in temperature. Adsorption of leaf extract follow Langmuir isotherm". Minus value of adsorption free energy shows that the inhibition involves spontaneous adsorption on the metal surface that aids in physical adsorption[30].

Corrosion inhibition properties of *Brassica Oleracea* (Cabbage) extract was evaluated by **Kumar R. S. et al.**

using weight loss method. Based on the corrosion treatment, the measuring investigation revealed that Brassica oleraceaextract had outstanding ability [31].

"An aqueous extract of Sidaacuta leaves (SAL) was prepared and its influence on corrosion inhibition of aluminium in 1N NaOH solution was studied by Sirajunnisa A. et al. using chemical and electrochemical methods. The result showed that with increase in concentration of Sidaacuta leaves extract, efficiency increases. Electrochemical inhibition measurement revealed that SAL extract act as mixed type inhibitor. SEM studies confirmed the protective film formed on surface of aluminium" [32].

"The effect of *Aegle marmelos* leaves (AML) extract on the corrosion inhibition of aluminium in 1 N NaOH solution was investigated by **Prabha K. L. et al.** using chemical and electrochemical techniques. The investigation revealed that inhibition efficiency increases up to 800 ppm concentration and further increase in extract concentration decrease efficiency from 87.6 to 84.7%". The study showed that AML act as mixed type inhibitor. Surface of aluminium determined by SEM[33].

The effect of aqueous extract of "*Tridaxprocumbens* leaves (TPL) on corrosion of aluminium in 0.5 NaOH solution was studied by **Kiruthiga G. et al.** using chemical and electrochemical techniques. It was found that with increase in extract concentration inhibition efficiency increases. Electrochemical measurement disclosed that TPL extract function as mixed type inhibitor. Protective film formed on surface of aluminium was confirmed using SEM studies" [34].

1.3.2 Oil as Corrosion Inhibitor

Inhibition behavior linseed oil amide (LOA) for MS in hydrochloric acid was measured by **Yang, et al**.[35]through "gravimetric, Potentiodynamic Polarization, Electrochemical Impedance Spectroscopy (EIS) and scanning electron microscopy". Measurements of weight loss show that theCorrosion rate was affected by the inhibitor's concentration. and that it decreased with an increase in the LOA inhibitor concentration. After 96 hours of immersion, the www.jchr.org

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superior inhibition efficiency is maintained above 90%, indicating the LOA inhibitor's long-term efficacy.

"Using weight loss, polarisation curves (Tafel, Stern & Geary as well as Stern methods), electrochemical impedance spectroscopy, **Bensouda Z. et al.** investigated the *MenthaPiperita* essential oil (MPEO), rich in anthraquinone, 1-(p-fluorophen) as the major compound (42.8%) as a corrosion The inhibitory effectiveness was observed to grow with rise in inhibitor concentration, reaching around 87% at 0.7 g L⁻¹ of MPEO, but the rise in temperature was in favour of its sluggish decrease.The adsorption data followed to Langmuir isotherm model and involved both physisorption. SEM technique testified the formation of protective film on to the metal surface"[36].

1.3.3 Peels Extract as Corrosion Inhibitor

YuliYetri, et al.[2]examined"the effect of polar extract of cacao (Theobroma cacao) peels to the inhibition of corrosion, adsorption properties and mechanical properties in 1.5M HCl solution on mild steel. Methods of weight loss, potentiodynamic impedance to determine the corrosion rate and efficiency of inhibition, as well as tensile and hardness testing for mechanical properties was conducted with the concentration of extract (0.5-2.5) % by an interval of 0.5%. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to examine the surface morphology of the samples (AFM). A technique called energy dispersive X-ray spectroscopy (EDX) was employed to analyse the surface's chemical composition.Corrosion rate is reduced and efficiency is increased with the rise in extract concentration".

"The electrochemical impedance measurements of aqueous brown onion peel extract on the corrosion reaction of carbon steel in 1 mol L⁻¹HCland Fuji apple peel extract in saline medium was studied by **Ferreira**, **et al.**[37], Vera, R. et. al.[38] and found that the Rct values increased in the presence of inhibitor reaching 94% of inhibition efficiency in the presence of 300 mg L⁻¹ of the onion extract and 90% at 1000 ppm concentration of apple peel extract".

"The inhibitory effects of *pomegranate* peel extracts (PPE) on mild steels corrosion in hydrochloric acid (HCl) solution was studied by **Sorkhabi H. A. et**

al.using Polarization, mass loss, and Electrochemical Impendence techniques". The result revealed that inhibitory efficiency increased with increased in extract concentrations[39].

"The inhibition efficacy of *Manilkarazapota* fruit peel (MZFP) extract on the corrosion of MS in 1.0 N HCl has been examined by **Petchiammal A. et al.**throughPotentiodynamic Polarization and Electrochemical Impedance Spectroscopy (EIS) measurements. The inhibition efficiency was enlarged with rise of inhibitor concentration and achieved maximum of more than 93% for both methods". The result revealed the extract as mix type inhibitor[40].

"Papaya peel extract has been investigated as corrosion inhibitor on aluminium alloy in 1 M HCl using EIS and PDP". Supreme inhibition efficacy of 98.1 % was gained at 2.0 g/L concentration of PPE. Surface morphology was examined by SEM and AFM[42].

1.3.4 Root Extract as Corrosion Inhibitor

Nnanna, et al.[43]examined the efficacy of the aqueous extracts of *Pentaclethramacrophylla Bentham* root "on corrosion of MS in 0.5 M KOH solution through the weight loss measurement at room temperature and concentration effects. Potentiodynamic polarization method was employed to evaluate corrosion rate and inhibition efficiency. A *Pentaclethramacrophylla Bentham* root extract concentration of 0.3 g/L in 0.5 M KOH resulted in a corrosion inhibition efficacy of 84.02%. Corroded metals were characterized by energy dispersive X-ray spectroscopy and scanning electron micrograph techniques".

Valerianawallichii root extract has been investigated by **Haldhar et al.**[44] for "mild steel in 0.5 M H₂SO₄ as corrosion inhibitor through weight loss, EIS, Potentiodynamic polarization, SEM, AFM, UV-visible spectroscopy and FT-IR. The study exhibited that root extract act as excellent inhibitor up to a maximum inhibition efficiency of 93.47% for mild steel at 500 mg L⁻¹ concentration in 0.5 M H₂SO₄ at 298 K temperature. The phytochemical constituents of root extract possess oxygen atoms and π electrons that facilitate adsorption on to the metal surface. The fact that this extract adheres to the Langmuir adsorption isotherm and operates as a mixed type inhibitor was validated by

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polarization research. Surface study confirm the protective layer formation on to the metal surface in the presence of inhibitor".

Nagiub et al.[45] studied "the effect of aqueous beet root extract (BRE) on the corrosion of mild steel in 1.0 M HCl using both gravimetric and electrochemical technique SEM, UV and EDAX. An increase in corrosion inhibition was observed with increase in inhibitors concentration. The percentage of inhibition reaches up to 83.79% at concentration 0.3034 gL⁻¹ at room temperature and 71.11% at 328 K. The adsorption study was found to agree with Langmuir adsorption isotherm. Polarization study showed that BRE acts as mixed type inhibitor".

Ekeke et al.[46]applied a gravimetric approach to test the effect of Mangiferaindica ethanol extract on tin (Sn) metal surface corrosion in 0.5 M hydrochloric acid and at room temperature. The effectiveness of inhibition increases with concentration. The greatest inhibitory efficiency of 99.98% was obtained at 1.0 g/L of extract concentration. The corrosion rate of the tin samples at higher extract concentrations gradually decreased over the course of the days.

1.3.5 Biomass Waste as Corrosion Inhibitor

Consequence of *Aloe Vera* gel and *Hunteriaumbellata* seed husk extracts on MS corrosion in 1 molarHCl solution has been demonstrated by **Dahiya S**.[47] and **Alaneme, et al.**[47,48] using "weight loss, electrochemical, and Tafel polarization. These results were accompanied by 'atomic force microscopy (AFM) and scanning electron microscopy (SEM)'. At an ideal concentration of 200 ppm, the inhibitor demonstrated >90% inhibition efficiency and the lowest corrosion rate".

"Corrosion inhibition efficiency of turmeric and ginger extract on MS in acidic medium was studied by Al-Fakih A.M.[4] and El-Sabbah, et al.[49] using gravimetric and potentiodynamic polarization measurements and field emission scanning electron microscopy (FESEM). As inhibitors concentrations rise, the IE% rises as well to attain 92 and 91% at 10 g/L of turmeric and ginger, respectively. The Langmuir adsorption isotherm is obeyed by the inhibitors' adsorption on mild steel surfaces. Turmeric acts as a better corrosion inhibitor compared to ginger".

"Corrosion inhibition characteristics of extract of rice husk ash on MS in 1 M HCl and H_2SO_4 was carried out by **Alaneme, et al.**[50] using mass loss, inhibition efficiency, SEM, atomic adsorption spectroscopy (AAS), FT-IR spectroscopy and surface analysis as bases for assessing the inhibition and adsorption properties of the extract in the acid solutions. The efficiency of the extract in HCl (96%) was noted to be more than in H_2SO_4 (86%) solution. Langmuir model was found to be better fitted than the Freundlich".

The alcoholic extracts of plants namely *Lyciumshawii*, *Teucriumoliverianum*, *Ochradenusbaccatus*, *Anvilleagarcinii*, *Cassia italica*, *Artemisia sieberi*, *Carthamustinctorius*, and *Tripleurospermumauriculatum* grown in Saudi Arabia were examined by **Al- Otaibi**, et al.[1] on MS in 0.5 M HCl media through the open circuit potential (OCP).

In a 1 mol L⁻¹HCl media for mild steel, **Cordeiro et al.'s**[51] investigation into the anticorrosive properties of coffee husk aqueous extract (1) and its high molecular weight fraction (2). According to gravimetric tests, the inhibitory effectiveness (IE) of both inhibitors rose with immersion time and extract concentration, reaching IE values of 89.2% and 90.3% for 800 mg L⁻¹ of inhibitors (1) and (2), respectively, after 24 hours.

"The inhibitive action of tobacco rob water extract (TRE) on corrosion of N80 steel in HCl solution was studied by **Guo Y., et al.**[52] using gravimetric, electrochemical measurement, and surface analysis. Maximum inhibition efficiency of 91.5% is achieved with 750 mg·L⁻¹ of TRE in 1M HCl at 60 °C. Polarization curves disclose that the TRE acts as a mixed type inhibitor".

"Corrosion inhibition efficiency of curcuma was studied Gadow, et al.[53] using weight by loss, potentiodynamic polarization, EFM andEIS measurements. Potentiodynamic measurements indicated that; Curcuma considers a mixed-type inhibitor for α -brass in 1.0 M HCl".

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"Inhibition ability of green tea extract (GTE), Jasmine tea extract and *Pulicariaundulata* (PU) on the C38 steel (CS) in 1.0 M HCl was evaluated by **Salghi, et al.[54], Tang, J. et. al.[55] and Fouda, et. al.[56]** using different methods such as: gravimetric,Potentiodynamic Polarization (PDP) and EIS methods at various temperatures. EIS results indicate the increase of resistance transfer (Rt) while double layer capacitance (Cdl) decrease in the rise of green tea extract (GTE) concentrations".

"The protection mechanism by *Heterophragmaadenophyllum* extract against Fe-C steel in acidic medium was investigated by **Pahuja P. et al.** using weight loss, EIS and PP techniques". The maximum protection value was found about 96% at 600 ppm concentration. Surface morphology by SEM-EDX, AFM, XPS indicated good adsorption capability[57].

Al-Senani, et al.[58] investigated the effectiveness of Juniperusprocera[59] waste and date palm tree extracts as carbon steel corrosion inhibitors in 1 M HCl. The extracts were effective inhibitors, as demonstrated by the electrochemical studies. The adsorption data fit Langmuir isotherm model.

Sair et al. used "electrochemical impedance spectroscopy (EIS) and Potentiodynamicpolarisation techniques to investigate the inhibitory effects of date palm waste extract as a natural inhibitor on corrosion of 304 stainless steel in a 1M HCl solution. Results classified the extract as mixed type inhibitor with an anodic predominance, 91.1% inhibition efficiency"[60].

The application of "Barley Agro- Industrial waste as corrosion inhibitor for stainless steel and wheat straw for aluminium has been studied using mass loss, EIS, PP, SEM technique. The inhibitor acted as mixed inhibitor and exhibit an efficiency of up to 97%"[61,62].

Faiz M. has been investigated corrosion inhibitive effect of crude extract from *Cryptocaryanigra* and its alkaloids for MS in 1 M HCl through EIS and PP techniques. SEM analysis supports the development of a barrier coating over the MS surface. The study showed highest inhibition efficiency of 91.05%[63].

1.4 Methods

To measure the effectiveness of a green inhibitor's inhibition, metal strips must first be prepared and refined with emery paper of various grades until they have a mirror finish and then completely cleaned with solvents (distilled water, acetone). "The important methodologies for measuring inhibition efficiency in the literature are weight loss measurement (WLM), Electrochemical impedance Spectroscopy (EIS), linear resistance and Potentiodynamic polarization polarization". Scanning electron microscope has been used to determine surface morphology. Adsorption isotherm and computational study is also useful in determining the mechanism of adsorption and corrosion inhibitor behavior of green inhibitors.

1.4.1 Weight loss method

The simplest method to determine the corrosion rate is the weight loss method. It includes subjecting fresh, weighed coupons of selected metal to corrosive conditions for a given time frame, washing the corrosion products off, and weighing the coupons to calculate weight loss. The corrosion rate (in mm per year), surface coverage, corrosion inhibition efficiency $\eta\%$ is calculated using following equations (1) -(3) respectively[6-9]. In both the absence and presence of green inhibitor, the effectiveness of the inhibitor in preventing corrosion attack on metal coupons is evaluated.

$$CR = \frac{W_1 - W_2}{At}$$
(1)

$$\theta = \frac{W_1 - W_2}{W_1}$$
(2)

$$\eta\%_0 = \frac{W_1 - W_2}{W_1} \times 100$$

(3)

"Where CR = corrosion rate (mm per year), $W_1 =$ weight loss in the absence of inhibitor, $W_2 =$ weight loss

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in the presence of inhibitor, A = metal coupons surface area (cm^2), T= immersion time (hour)".

1.4.2 Potentiodynamic polarization

PDP additional electrochemical-based is an measurement technique for corrosion inhibition effectiveness, corrosion rate, and protection mechanism. It is used to assess a metal's vulnerability to cervices and other forms of localized corrosion. Utilizing three electrodes in an electrochemical cell-main electrode, a reference electrode, and a counter electrode-all of which are submerged in a experimental solution with known volume-is the fundamental laboratory setup. In most cases, saturated calomel electrode and Ag/AgCl aqueous electrode are utilized as reference electrodes, while platinum electrode[64] and graphite rod[65] are employed as counter electrodes. The metal being studied for corrosion serves as main electrode. The reference electrode measures and regulates the system's voltage while the counter electrode measures current (I). The metal's open circuit potential (EOCP) varies as the electrochemical process begins. A steady value is measured once equilibrium has been reached, and a PDP scan is then performed[6-9]. "A Tafelplot is then created by putting a potential from a value lower than the original measured EOCP to a higher potential (between -0.25 and +0.25V)".Plots are used to measure the corrosion current (icorr) and corrosion potential (Ecorr).Corrosion rate and $\eta\%$ is calculated using equation 4 and equation 5 respectively.

$$CR = \frac{i_{corr} \times \kappa \times EW}{\rho \times A}$$
(4)
$$\eta\% = \frac{i_{corr}^{0} - i_{corr}^{1}}{i_{corr}^{0}} \times 100\%$$
(5)

"Where κ = conversion factor, EW = equivalent weight (g), $\rho = \text{density}$ (g/cm³), A = sample area, i_{corr}^0 and i_{corr}^1 = i_{corr} density values in the absence and presence of inhibitor respectively".

(

After addition of inhibitor "cathodicTafel slope (Bc), anodic Tafel slope (βa) shifted to lower value indicating the inhibitor inhibited by cathodic reaction and anodic reaction" which further signifying that inhibitor acted as mixed type[66].

1.4.3 **Electrochemical impedance spectroscopy**

Another electrochemical method for estimating polarization resistance is EIS. It monitors how the electrochemical system reacts to a weak AC voltage provided at various frequencies. Based on the reaction process, a similar circuit is built using the electrochemical response. When compared to weigh loss measurement, an EIS spectrum runs in a matter of minutes. Similar to PDP, Thiscalculation is carried out in a "three-electrode electrochemical cell with minor potential disturbances between 5 and 50 mV of AC voltage across frequency ranges from 100 kHz to 10 MHz [67].Nyquist plot is obtained from the value of frequencies that correspond to real (Z') and imaginary (Z") impedance value. Electrical double -layer capacitance and n % value" can be determined using Eq. 6 and 7 respectively.

$$C_{dl} = \frac{1}{2\pi\omega_{max}R_{ct}}$$
(6)
$$\eta\% =$$

"Where ω_{max} = maximum frequency of impedance imaginary quantity (rad/s), $R_{ct(i)}$ and $R_{ct(o)} = R_{ct}$ in the presence and absence of green inhibitor respectively".

 $\frac{R_{ct(i)}-R_{ct(o)}}{100\%} \times 100\%$

R_{ct(i)} (7)



Fig. 3 Nyquist plot for mild steel in 0.5 M H₂SO₄ in the absence and presence of various concentration of Solanum surattense extract (Reprinted: haldhar 2021)

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An increase in Nyquist plot diameter (as given in fig 3)[66] with increase in inhibitors concentration shows that inhibitive film strength increases as corrosion rate decreases. [68]. Significant increase in Rct in green inhibitor presence results in adsorption of inhibitor particles on the metal surface and have high corrosion preventionefficacy[69]. The Nyquist plot shows a drop in diameter with rising solution temperature, indicating a reduction in corrosion inhibition rate [70].

1.5 Conclusion

"Many plants extract have been examined as corrosion inhibitors for different alloy and metal such as carbon steel, mild steel, Aluminium, tin and copper in Sulphuric acid, hydrochloric acid and sodium chloride solution. However, some extract exhibits excellent inhibitive property even at low concentration. Many variables such as concentration, extraction solvent, temperature and immersion time can be explored to evaluate a plant extract as corrosion inhibitor". It is reported that the effect of natural extract become towards lower inhibition efficiency at high temperature. "The effectiveness of inhibitor should be examined by at least two electrochemical technique such as PP, EIS, WLM and others. There are few properties of organic green inhibitors responsible for protection of metal, such as adsorption type and formation of protective film onto the surface of metal. Phytochemicals mostly heterocyclic compounds are suitable for interaction with metal surface and hence for the inhibition of corrosion. For adsorption mechanism and inhibitor-metal interaction, theoretical studies (DFT and MD) are mostly used. Plant extract obtained inhibition efficiency around 80-90%. This study revealed that green corrosion inhibitor can be used as an alternative of conventional inhibitor. As green inhibitors are less costly, easily available and environmental friendly compare to the carcinogenic and harmful inhibitor. In recent years, there has been a considerable interest towards organic green corrosion inhibitor made from waste biomass such as leaf, stem, peel and seeds. The most important challenge is to isolate the main component that has an inhibition efficiency more than 90% according to the norm NRF-005-PEMEX-2009".

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