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Role of Plants Extract as Corrosion Inhibitor in Various Acidic Medium on Steel Surface

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ABSTRACTL: Application of green corrosion inhibitors, which reduce corrosion rates to the appropriate level with low environmental impact, is one of the emerging key approaches of controlling corrosion in modern society. From the standpoint of environmental compatibility, this research field is undergoing significant developments. Nowadays, due to increasing ecological awareness, corrosion inhibitors are subject to stringent restrictions and regulations enforced by environmental agencies in a number of nations. According to these requirements, these chemicals must be environmentally acceptable and safe. In light of this, intensive research has been undertaken in recent years aimed at development of green corrosion inhibitors from plant extracts. Being readily available, inexpensive, biodegradable, and safe make these substances promising alternatives to the hazardous conventional corrosion inhibitors.

KEYWORDS-Plant, extracts, corrosion, inhibitors, sustainable, steel, acidic

I.INTRODUCTION

Natural extracts have been widely used to protect metal materials from corrosion. The efficiency of these extracts as corrosion inhibitors is commonly evaluated through electrochemical tests, which include techniques such as potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss measurement. The inhibition efficiency of different extract concentrations is a valuable indicator to obtain a clear outlook to choose an extract for a particular purpose. A complementary vision of the effectiveness of green extracts to inhibit the corrosion of metals is obtained by means of surface characterizations; atomic force microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy analysis are experimental techniques widely used for this purpose. Moreover, theoretical studies are usually addressed to elucidate the nature of the corrosion inhibitor—metal surface interactions. In addition, calculations have been employed to predict how other organic substances behave on metal surfaces and to provide experimental work with fresh proposals. This work reports a broad overview of the current state of the art research on the study of new extracts as corrosion inhibitors on metal surfaces in corrosive media. Most constituents obtained from plant extracts are adsorbed on the metal, following the Langmuir adsorption model. Electron-rich regions and heteroatoms have been found to be responsible for chemisorption on the metal surface, whereas physisorption is due to the polar regions of the inhibitor molecules. The plant extracts compiled in this work obtained corrosion inhibition efficiencies above 60%, most of them around 80–90%. The effect of concentration, extraction solvent, temperature, and immersion time were studied as well. Additional studies regarding plant extracts as corrosion inhibitors on metals are needed to produce solutions for industrial purposes.[1,2,3]

The use of corrosion inhibitors is a cost-effective corrosion mitigation strategy for carbon steel. There is an increased focus on developing and using low-cost, biodegradable and environmentally friendly inhibitor formulations. Plant-based extracts have been evaluated in many studies using a multitude of electrochemical methods and characterisation techniques. Although plant extracts appear as promising alternatives for commercially synthesised inhibitor formulations, a significant amount of optimisation is required. The majority of the research on plant extracts does not elucidate the effect of other synergistic combinations in commercial inhibitor formulations. Therefore, further development of plant extracts as corrosion inhibitors is of significant interest.

Carbon steel is extensively used in the oil and gas industry, and due to its mechanical properties and low cost, is the preferred material for pipeline construction. Owing mainly to their much higher costs, it is not normally feasible to replace carbon steel with corrosion resistant alloys in large oil and gas trunklines. However, carbon steel is highly susceptible to corrosion. The presence of CO₂, H₂S and organic acids (acetic acid, propionic acid and formic acid) is

one of the leading causes of corrosion in oil and gas production that can instigate localised or pitting corrosion¹. This review presents an analysis of so-called plant-extract-based green corrosion inhibitors that have been investigated to mitigate CO₂ corrosion. The review is extended to also include plant-extract-based green corrosion inhibitors that were studied for their efficiency to prevent strong acid corrosion by HCl and H₂SO₄ since such products are expected to also prevent weak acid corrosion from CO₂. [4,5,6]

CO₂ corrosion

The problem of sweet corrosion arises from the fact that CO₂ is soluble in the water that comes to the surface with production fluid, and results in the formation of carbonic acid (H₂CO₃) that, although being a weak acid, is still extremely corrosive for carbon steel. The literature identifies iron carbonate (FeCO₃) as the main corrosion product formed at carbon steel under CO₂ corrosive environments. The following cathodic mechanism of CO₂ corrosion has been proposed

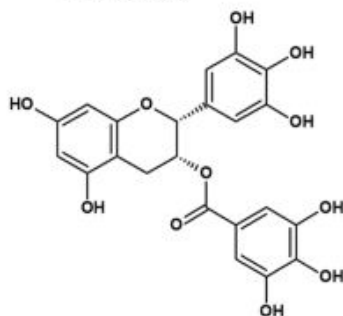
Amongst the various ways of mitigating corrosion (coating, alloying, etc.), the use of chemical compounds known as corrosion inhibitors is one of the most cost-effective corrosion mitigation strategies for carbon steel. A corrosion inhibitor is typically used in small concentrations and essentially minimises the corrosion rate by inhibiting the reaction of metal with its environment. Hence, the use of inhibitors allows low-cost carbon steel to be used as a structural material. An ideal inhibitor is described as one which is composed of low cost, abundant and environmentally friendly constituent [7,8,9]

A synthetic commercial corrosion inhibitor formulation applied in oil and gas production usually contains one or more of the following: quaternary ammonium salts (called quaternary amines in oilfield parlance), fatty acids, fatty amines/diamines, imidazolines, and oxygen, sulfur or phosphorus containing compounds.

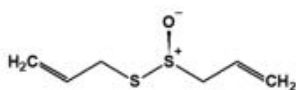
The polar functional groups, commonly present in aforementioned compounds, are regarded as main instigators for the adsorption process. The adsorption behaviour of an organic inhibitor is in turn governed by physicochemical properties of the molecule such as the electronic density of donor atoms²⁴. Durnie et al. conducted various in-depth studies on the adsorption of several different commercial carbon dioxide corrosion inhibitor formulations using quantum mechanical calculations to show that a range of molecular parameters determined the thermodynamic adsorption properties of carbon dioxide corrosion inhibitors. [10,11,12]

II.DISCUSSION

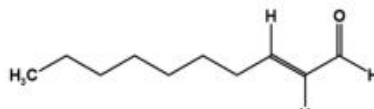
Plants in their entirety are composed of various types of chemicals and out of those, the non-nutritive components responsible for a plant's smell, taste and colour are called 'phytochemicals'. Phytochemicals can be divided into different classes such as terpenoids, polyphenols and organic acids and these groups can further be classified. The non-toxic nature of the majority of the plants and their extracts make them a viable replacement option for toxic organic inhibitors. They are also attractive because of their biodegradable nature that makes their disposal simpler. The extraction process is also relatively simple and economical. Environmentally friendly corrosion inhibitors can be extracted from various parts of a plant such as fruit, leaves, bark, roots, seeds or peels. The inhibitive properties of a plant extract can generally be attributed to the mix of phytochemicals in it, having various functional groups capable of adsorbing on a metal surface. However, it is because of their complex composition that a full understanding of the corrosion inhibition mechanism of biomass extracts is yet to be determined. It is difficult to study the individual and/or combined interactions of organic species with the metal surface without isolating the active constituents of any biomass extract [13,14,15]

Phenolics

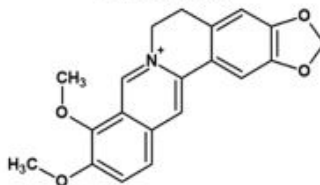
Epigallocatechin gallate

Essential oils

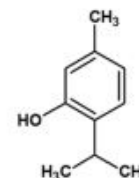
Allicin

Saponins

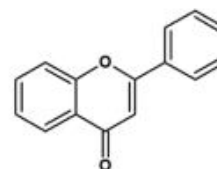
Trans-2-decenal

Alkaloids

Berberine

Terpenoids

Thymol

Flavonoids

Flavone

III.RESULTS

Plants are sources of naturally occurring compounds, some with complex molecular structures and having different chemical, biological, and physical properties. The naturally occurring compounds are mostly used because they are environmentally acceptable, cost effective, and have abundant availability. These advantages are the reason for use of extracts of plants and their products as corrosion inhibitors for metals and alloys under different environment [13]. Plant extracts have potential to replace synthetic organic and inorganic inhibitors given their success story in literature. The mechanism of action of green inhibitors depends on the structure of the active ingredient and thus many researchers have to date postulated many theories to explain this phenomenon [2,16]. Different plant extracts can be used as corrosion inhibitors commonly known as green corrosion inhibitors. In the present review, we have worked on the extracts of *Camellia sinensis*, *Datura stramonium*, *Moringa oleifera*, *Cocos nucifera*, *Gongronema latifolium*, *Acalypha torta* and *Curcuma longa* as corrosion inhibitors. III.I EXTRACTS OF *CAMELLIA SINENSIS* (GREEN AND BLACK TEA) Yahaya et al., [17] investigated the inhibitive behavior of Green Tea Extracts (GTE) and Black Tea extracts (BTE) on mild steel in acidic environment using gravimetric and spectroscopic methods. Results showed that the inhibition efficiency of both extracts increases with increasing the concentration of extract and decreases with increasing the temperature. Maximum inhibition efficiency of 83.1 and 81.7% were obtained for GTE and BTE respectively at 0.25g/L inhibitor concentration. Adsorption behavior of both inhibitors on the mild steel surface obeyed the Langmuir adsorption isotherm and they inhibited the corrosion of mild steel by adsorption mechanism where the adsorption process involved was spontaneous, exothermic and physisorptive.[16,17,18] The FTIR spectra also indicated the formation of active compound-Fe complex. GTE and BTE from *C. sinensis* thus represent potential and inexpensive environment friendly corrosion inhibitors for mild steel in acid environment. The effect of *C. Papaya* (pawpaw) leaves and *C. Sinensis* (tea) extracts as an organic green inhibitor on the corrosion of $\alpha \beta$ (duplex) brass (65-35% Cu-Zn alloy) in 1M HNO₃ (nitric acid) was studied by [18] at ambient Temperature. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The tea extract was obtained from the green tea leaves. The results obtained showed effective corrosion inhibition of the extracts on the brass test specimens in the 1M nitric acid used. The different combined extracts concentrations also gave good corrosion inhibition performance. They also exhibited effective corrosion reactions synergism. The test specimen (duplex brass) gave some appreciable corrosion resistance in the test environment. In another study carried out by [19], the effect of green tea extract as an organic „green“ inhibitor on the corrosion of mild steel in dilute sulphuric acid was studied at ambient temperature. Weight loss/corrosion rate and potential measurement techniques were used for the experimental work. The tea extract was obtained from the green tea leaves. The results obtained showed effective corrosion inhibition of the extract on the mild steel test specimens in the different concentrations of sulphuric acid used. There was no apparent significant difference in the corrosion inhibition performance of the selected extract's concentrations. The

different acid strength used did not give any clear adverse corrosive effect on the performance of the inhibitor. III.II DATURA STRAMONIUM LEAF EXTRACT D. stramonium leaf extract as corrosion inhibitor in 1M HCl acid solution was assessed using phytochemical screening, atomic absorption spectroscopy (AAS), gravimetric (mass loss), and electrochemical (Tafel and potentiodynamic polarization) methods [20]. The extract was found to efficiently inhibit the corrosion process and the inhibition efficiency increased with increasing extract concentration (over 400% increases) at room temperature. The maximum inhibition efficiency of DSLE in 1M HCl was found to be 98.69% at 0.5g/l concentration. The potentiodynamic polarization results revealed that DSLE functioned as mixed type inhibitor acting on both the anodic and cathodic sites (but predominantly anodic control). The AAS analysis shows that the concentration of Fe²⁺ in the electrolyte decreases with increase in the extract concentration. The adsorption studies of the extract on the metal surface showed that there was a physisorption process as the concentration increases and the chemisorption process is also prevalent. The adsorption studies fitted the assumptions of Temkin and Freundlich isotherm models.[19,20,21]

Raja and Sethuraman [21] studied the extract of D. stramonium as a possible source of green inhibitor for corrosion of MS in HCl and H₂SO₄ media at different temperatures. The anticorrosion effect was evaluated by conventional weight loss studies, electrochemical studies (Tafel polarization, ac impedance) and SEM studies. The studies reveal that the plant extract acts as a good inhibitor in both the acid media and better in H₂SO₄ medium. Tafel polarization method indicate that the plant extract behaves as a mixed mode inhibitor. Double layer capacitance and charge transfer resistance values derived from Nyquist plots obtained from ac impedance studies give supporting evidence for the anticorrosive effect. III.III COCOS NUCIFERA LINN The corrosion inhibitive effect of coconut water as an ecofriendly inhibitor for the corrosion control of mild steel in 0.5 Molar solution of H₂SO₄ acid have been investigated using the weight loss method which is considered more informative than other laboratory techniques [22]. The studies were carried out using 30-110ml of the coconut water. The test coupons were totally immersed in the corroding medium containing various concentration of the inhibitor at the time intervals of 24-192 hours. The results obtained showed that the concentration of the inhibitor in the corrodent impacted differently on the test coupons. The corrosion rate was found to decrease while the inhibitor efficiency increases as the inhibitor concentration was increased. The work reported maximum inhibition efficiency of 89.07% and 81.57% at the concentration of 90ml and 110ml for 24hours and 48hours immersion time respectively. The study showed that coconut water possesses inhibiting properties for reducing the corrosion of mild steel in the acidic medium. In another study, Vijayalakshmi et al., [23] investigated the inhibitive effect and adsorption properties of petiole extract obtained from destructive distillation of C. nucifera for the corrosion of mild steel in 0.5 M H₂SO₄ and 1 M HCl using mass loss, polarization and electrochemical impedance techniques of monitoring corrosion. The results obtained indicate that petiole extract of C. nucifera behaves as good inhibitor for the corrosion of mild steel in 0.5 M H₂SO₄ and 1 M HCl. Activation energy of thermodynamic parameter was evaluated from temperature studies result. The adsorption of the inhibitor on mild steel surface was found to be spontaneous, endothermic and consistent with the assumptions of Langmuir adsorption isotherm. The electrochemical measurements reveal that the petiole extract behaved like mixed type inhibitor. Efforts are made to analyze the effectiveness of petiole extract of coconut palm in industrial processes. III.IV MORINGA OLEIFERA LEAF EXTRACT The inhibiting effect of M. oleifera leaf extract on the corrosion of a reinforced steel bar in 2M solution of HCl was studied using gravimetric, gasometric and potentiodynamic polarization techniques [24]. The study revealed that as the concentration of the extract increases, the inhibition efficiency increases in all three investigation scenarios. 1.0 g/l attained the efficiency of 92.31 % after 120 hours exposure during gravimetric measurement. The volume of the hydrogen gas evolved reduces with an increase in the exposure time during the gasometric test. It was noted that the extract slowed down the corrosion rate and the rate at which the hydrogen gas evolved. The formation of an adsorption layer on the surface of the metal reduces the rate at which hydrogen gas is evolved, which is a function of the concentration of the extract. Potentiodynamic polarization results revealed that the M. Oleifera leaf extract modifies the mechanism of anodic dissolution and cathodic hydrogen evolution. It was also observed that the corrosion current density decreases with the increase in the concentration of the extract.[22,23,24] This decrease in corrosion is due to increased blocking of the metal surface by adsorption of the leaf extract. Investigation on corrosion inhibiting abilities of M. oleifera and Lettuciae dibelialis in acidic medium by weight loss method were carried out [25]. The significance of the corrosion inhibition in the 1N, 2N HCl medium and 1N, 2N H₂SO₄ medium has been discussed. The corrosion rate was found to decrease with increase in concentration of both the inhibitors in HCl medium. But the corrosion rate was observed to be high in the presence of inhibitors in H₂SO₄ medium. III.V GONGRONEMA LATIFOLIUM EXTRACT Onwumelu and co-workers [26] studied the corrosion inhibition effect of methanol extract of Gongronema latifolium mild steel in HCl solution using gasometric methods at 303K, 313K and 323K. The inhibition efficiency was found to increase as the concentration of extracts increased from 0.1%w/v to 0.5%w/v and decreased with increase in temperature. The maximum efficiency of inhibition was found to be 77.17% at 303K. Values of activation energy for the inhibited system were greater than the values obtained for the uninhibited system. Physical adsorption mechanism

was proposed for the adsorption of the inhibitor from the trend of the inhibition efficiency with temperature and the values of E_a , and ΔG_{ads} obtained. The adsorption of *G. latifolium* extract on the surface of the mild steel followed Langmuir, Freundlich and El-Awardy adsorption isotherms. Extract of *Gnetum africanum*, *Gongronema latifolium* *Chromolena odoratum* was investigated as corrosion inhibitor of stainless steel in 1M HCL and H₂SO₄ using conventional weight loss [27]. Results were obtained at intervals of 24, 48, 72 and 96 hours respectively. The corrosion rate and inhibition efficiency were calculated. The results revealed that all the plant extract act as inhibitors in the acid medium while *C. odoratum* proved to be better corrosion inhibitor than *G. africanum* and *G. latifolium* extract as it recorded the highest inhibition efficiency of 90.95% in 1M HCL for 20 ml concentration. III.VI ACALYPHA TORTA AND CURCUMA LONGA LEAF EXTRACT The inhibitive action of ethanol extract of *Acalypha torta* leaves (EAL) on corrosion of mild steel in 1 M HCl solution was investigated by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, chronoamperometric measurements, and scanning electron microscopic observations [28]. The adsorption of EAL on mild steel follows a Langmuir adsorption isotherm, and the activation parameters governing the adsorption process were calculated and discussed. Polarization measurements reveal that the EAL acts as a mixed-type inhibitor. The inhibition efficiencies obtained from weight loss measurements and electrochemical tests were in good agreement. The inhibitor property of *C. longa* L. extract in different concentrations of simulated refinery wastewater (0.05% - 2% wt) and at various temperatures (30, 35 and 40 °C) was investigated using weight loss method [29]. The results showed that the presence of about 1.2 % (v/v) of curcuma extract gave about 84% inhibition indicating its effectiveness on mild steel corrosion in simulated refinery wastewater, besides the adsorption process on the mild steel surface obeyed the Langmuir adsorption isotherm. III.VII CENTROSEMA PUBESCENS AND BRASSICA OLERACEA CAPITATA LEAF EXTRACT Reference [30] investigated the influence of *Centrosema pubescens* leaf extract on electrochemical corrosion behaviour of MS in stimulated acidic medium. The presence of secondary metabolites including flavonoid, tannins, anthraquinones, terpenoids, alkaloids, phenols and saponins were revealed. The FTIR also revealed aromatics and functional groups such as R-OH, C=O, C-O and C-H which are attributes of good inhibitors. They also evaluated the performance of the extracts was evaluated using gravimetric method of monitoring corrosion rate in different concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 w/v. *C. pubescens* gave an inhibition efficiency of 74.91%. *Chinweuba* [31] focused on inhibition action of *B. o. capitata* extract on mild Steel and Zinc corrosion in 2.0M H₂SO₄ solution using weight loss technique. [25,26,27]The results obtained indicate the decrease in the corrosion rate of the metal as the concentration of the extract increase. Inhibition efficiency was found to increase with *B. o. capitata* concentration. Optimum inhibition efficiency (IE) for mild steel and Zinc were found to be 97.1% and 91.3% respectively at 50ml volume of the extract.[28,29,30]

IV.CONCLUSION

Corrosion of metals is the major problem in industries. Considering environmental and ecological reasons, green inhibitors are found to be effective. The above discussion show that the natural plant extracts are very efficient for Mild steel corrosion protection, and we can use green inhibitor in replacement of other chemical which used for control corrosion, green inhibitors are eco – friendly, and also very less expensive, in feature we can use the plant extract as corrosion inhibitor to protect our environment.[31]

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