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Green Corrosion Inhibitors for Copper in HCl and H₂SO₄ Solution - A Review

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Abstract: Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Recently, a huge interest for the use of naturally occurring inhibitors extracted from plants have been emerged. Most of the natural products are non-toxic, biodegradable and readily available due to environmental concerns. The inhibitor is chemically adsorbed on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface. Corrosion of copper and its inhibition was analyzed by weight loss (Gravimetric), effect of temperature and time of immersion methods. Electrochemical methods such as, Potentiodynamic polarization and Electrochemical Impedance Spectra (EIS) were employed. The protective films formed on metal surface have been analyzed by various techniques such as Scanning Electron Microscope (SEM), Energy dispersive X-ray spectrometry (EDS) and Atomic Force Microscopy (AFM), Fourier transform infrared spectroscopy (FT-IR), UV-Visible spectra, X-ray Diffraction spectroscopy (XRD), Energy Dispersive X-ray Spectroscopy (EDX), electrochemical frequency modulation (EFM) techniques. The results obtained from weight loss and electrochemical techniques were in good agreement. In this review paper, research works produced over the past background on the corrosion of copper in various medium and their corrosion inhibition by using a various green inhibitors were presented.

Keywords: Corrosion, Copper, Green inhibitors, Potentiodynamic Polarization, EIS, SEM.

I. INTRODUCTION

Corrosion is a natural phenomenon where metals and alloys try to revert to their more stable thermodynamics form due to reaction with the environment that surrounds them. Corrosion is expensive due to loss of materials or their properties, which leads to loss of time during maintenance, the shutting down of systems, and severe failure of some structures, which in some cases may be hazardous and cause injury. Our economy would be drastically changed if there were no corrosion.

Copper with a reddish orange colour is the fifth most usual metal in the earth's crust which is very useful in pure or alloying form. Copper and its alloys are widely used in industries because of some favourable properties such as good corrosion resistance, high electrical and thermal conductivity, mechanical workability and malleability [1]. Copper and its alloys are highly regarded because of their wide application in production of wire, sheets and pipelines in electronic industries, marine industries, power stations, heat exchangers and cooling towers [2] and recently in the manufacture of integrated circuits [3,4]. Copper is known as a noble metal which provides appropriate corrosion resistance in the atmosphere and in some of chemical environments due to the formation of a protective passive (oxide) film or nonconductive layer of corrosion products on its surface [5].

Corrosion of copper can be caused during this chemical treatment after the scale or oxides have been removed, which implies the dissolution of the metal and the consumption of the acid used. This also implies important economic losses for the industrialists [6]. According to widespread use of copper in different industries, the issue of corrosion and corrosion protection of copper has attracted a lot of attention and many studies have been conducted to date on this issue and are still ongoing.

One of the most practical methods for protection against excessive dissolution of metals by corrosion is use of proper inhibitors [7]. Corrosion inhibitors are substances which when added in small concentration to corrosive media decrease or prevent the reaction of the metal with the media [8]. A lot of work has been done to find and develop different types of organic and inorganic inhibitors. However, some of these inhibitors have disadvantages: high cost, toxic to humans, risk of pollution to the environment. In this context, researchers have to search alternatives by focusing on biodegradable, economical, renewable plant products as corrosion inhibitors that do not present any risk to human health and the environment [9].

The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors” [8]. According to Barakat et al. [10], plant extracts have been used for decades as effective corrosion inhibitors, their property due to their richness in complex organic compounds containing heteroatom’s, aromatic rings and multiple bonds (double and triple bonds) have also been identified as adsorption centres that interact with active sites on the surface of a metal.

There are three types of inhibitors according to mechanism of electrochemical action, such as anodic, cathodic or mixed inhibitors. (i) Anodic inhibitors slow down the oxidation reaction, i.e. by blocking the anodic sites (seat of metal oxidation), which decrease the density of the metal dissolution current and shift the corrosion potential in the positive direction. (ii) Cathodic inhibitors show blocking the cathodic sites (oxygen reduction site in aerated neutral environment or H^+ proton reduction site in acidic environment) which decrease the density of the hydrogen reduction current and which displace the corrosion potential in the negative direction. Cathodic inhibitors are considered safer than anodic inhibitors because they are not likely to promote localized corrosion. (iii) mixed inhibitors which act on both cathodic and anodic reactions. They decrease the speed of both partial reactions with little change in the corrosion potential. The adsorption isotherm can be expressed as the relationship between the rate of recovery of an interface by the adsorbed species and the concentration of the species in solution. There are several models of adsorption isotherms such as Langmuir adsorption isotherm, Temkin adsorption isotherm, Freundlich and Flory-Huggins adsorption isotherm.

- 1) *Plant Materials as Green Inhibitors:* Corrosion inhibitors are used various parts of the plant extracts such as, Leaves [19,22,24,25,28,29,31,33-36,42,46,50,51], Seeds [16,33,45], Fruits [20,37,48], Branches [33], Fruits [20,37,48], oil [32,44], Roots [33] and Plant extract [23,39,43].
- 2) *Plant Extracts used:* Various solvents like double distilled water [39,40,], Alcohol [11,14,16,19,25,31,34,36,37,41,43,47,51] and Acetone [26,27] were used for making extract of the plant materials.
- 3) *Medium:* In this Review, for making plant extracts in HCl [11-38] and H_2SO_4 [39-55] environment has been investigated.
- 4) *Methods:* Various methods such as Weight loss method [11-15,17-20,24-29,31-40,42,43,45,47,50-55], Potentiodynamic polarization [15,17,18,21-27,29-32,34,36,39-47,52,54,55], EIS [15,17,18,21,23,25,26,29-31,34,39-42,44,47,48,52,55] and Kinetic parameters: Rate constant and Half- life period [51] were used for investigation of corrosion mechanism and to calculate the percentage of inhibition efficiency of green inhibitors. Metal surface analysis is confirmed by various surface morphological studied, like SEM [12,14,16,17-19,25-28,31,40,41,46-48,52,54,55], AFM [12,17,52,54,55], FT-IR spectroscopy [11,14,18,19,25,30,36,46,55], UV spectroscopy [19,36], EDX [17,19,22,25,26], EDS [12], AAS [26], MDS [54], Ion chromatography [26], XRD [19], XPS [46,49,54,55], OMT [43], EFM [18] and quantum mechanical study [17,18,22,30,48,49,53] were used.
- 5) *Adsorption isotherms:* The adsorption isotherm model for phyto-chemicals present in various green inhibitors extract into the metallic surface has been studied. For this, different kind of adsorption isotherms, such as Langmuir [11-20, 23,27,28,3-38,39,41,43-49,52-55], Freundlich [25,28,29,42,50,51], Frumkin [42], Temkin [19,20,21,28,51] and Flory-Huggins [28,39,43,47] adsorption isotherms were suggested. A list of various plant extract used as green corrosion inhibitors for Copper was shown in Table-1 and in Table-2.

Table- 1. Green corrosion inhibitors for copper in HCl solution.

(Wl = Weight loss, pp = Potentiodynamic Polarization, EIS = Electrochemical Impedance Spectroscopy)

No.	Inhibitor	Medium	Methods	Findings	I.E. (%)	Ref.
1	<i>Acacia nilotica</i>	0.5 N HCl	Weight loss with temperatures. Fourier transforms infrared spectroscopy (FT-IR).	Langmuir isotherm.	85.84 Wl	11
2	<i>Alginate biopolymer</i>	1.0 M HCl	Weight loss. Potentiodynamic polarization and EIS methods. Scanning electron microscopy (SEM), Energy dispersive X-ray spectrometry (EDS) and Atomic Force Microscopy (AFM) techniques. Quantum calculations.	Cathodic inhibitor. Langmuir isotherm.	78.20 Wl 83.06 PP 82.12 EIS	12
3	<i>Aloe vera Barbadensis Gel</i>	HCl	Weight loss with temperature.	Langmuir adsorption Isotherm. A first order type of mechanism.	-	13

4	<i>Azadirachta indica</i>	0.5 N HCl	Weight-loss with time, SEM and FT-IR.	Langmuir adsorption isotherm.	97.72 W1	14
5	<i>Calligonum comosum</i>	2 M HCl	Weight loss. potentiodynamic polarization and EIS methods.	Mixed-type inhibitor. Langmuir adsorption isotherm.	80.06 W1 90.36 PP	15
6	<i>Capparis decidua</i> seeds	0.5 M HCl	SEM.	Langmuir adsorption isotherm.	94.60 W1 51.11 EIS	16
7	Chitosan	1 M HCl	Weight loss, polarization and EIS measurements. SEM, EDX spectrometry and AFM studies. quantum chemical and molecular dynamics simulation approaches.	Cathodic inhibitor. Langmuir adsorption isotherm.	87.34 PP 86.75 EIS	17
8	Chitosan	0.5 M HCl	Weight loss, potentiodynamic polarization, EIS and EFM measurements. SEM and FT-IR spectroscopy. quantum chemical calculations.	Mixed-type inhibitor. Langmuir adsorption isotherm.	-	18
9	<i>Cnidioscolus chayamansa</i> leaves	1.0 N HCl	Weight loss with time and temperature. UV, FT-IR, XRD and EDX, SEM spectral techniques.	Langmuir and Temkin adsorption isotherms.	70.57 W1	19
10	<i>Coccinia Grandis</i> Fruit	1 N HCl	Weight loss with temperature.	Langmuir and Temkin adsorption isotherms.	57.00 W1	20
11	<i>Egyptian licorice extract</i>	0.1 M HCl	Potentiodynamic polarization, EIS methods	Mixed-type inhibitor. Temkin adsorption isotherm.	89.55 PP 81.22 EIS	21
12	<i>Emilia sonchifolia</i> (ES) leaf extract	2 M HCl	Potentiodynamic polarization measurement, EDX emission spectroscopy and surface examination techniques. Computational simulations. Quantum chemical calculations and molecular dynamics simulations.	Mixed- type inhibitor.	99.75 PP	22
13	<i>Ephedra sarcocarpa</i> plant extract.	2 M HCl	Potentiodynamic polarization and EIS.	Langmuir adsorption isotherm.	94.50 PP	23
14	<i>Eucalyptus</i> leaves	1 M HCl	Weight loss measurements. galvanostatic polarization and surface characterization techniques.	Mixed-type inhibitor predominantly cathodic.	-	24
15	<i>Leucas Aspera</i> (MLA) leaf	HCl	Weight loss with time and temperature. potentiodynamic polarization, and EIS. Field emission SEM and EDX spectrometry analysis, FT-IR Spectra.	Mixed-type Predominant cathodic inhibitor. Freundlich isotherm	86.96 W1 87.33 PP 67.91 EIS	25
16	<i>Mangrove Tannin</i>	0.5 M HCl	Weight loss method, potentiodynamic polarization, EIS, SEM along with EDX, atomic absorption spectroscopy (AAS) and ion chromatography (IC).	Cathodic inhibitor. Langmuir adsorption isotherm.	72.80 W1 82.40 PP 87.60 EIS	26

17	<i>Mangrove Tannin</i>	1.0 M HCl	Weight loss, potentiodynamic polarization and SEM analysis.	Cathodic inhibitor Langmuir adsorption isotherm.	68.80 PP	27
18	<i>Momordica balsamina</i> Linn.(African Pumpkin) Leaf Extract	0.8 M HCl	Weight loss with temperature. SEM.	Langmuir, Freundlich, Flory-Huggins and Temkin adsorption isotherms.	71.43 Wl	28
19	<i>Morinda tinctoria</i> leaves	0.5 M HCl	Weight loss with time and temperature. potentiodynamic polarization and EIS methods .	Freundlich isotherm.	65.39 PP 79.77 EIS	29
20	<i>Phosphatidylcholine</i> (PC) extracted from egg yolk	1 M HCl	Potentiodynamic polarization and EIS methods. FT-IR spectroscopic quantum chemical results.	-	96.40 PP 99.30 EIS	30
21	<i>Prosopis Cineraria</i> Leaves	0.5 N HCl	Weight loss with time. Potentiodynamic polarization and EIS. SEM.	Anodic inhibitor. Langmuir adsorption isotherm.	74.88 Wl 94.10 PP 75.26 EIS	31
22	<i>Sesum indicum</i> oil	0.5 N HCl	Weight loss. potentiodynamic polarization	Mixed-type inhibitor. Langmuir adsorption isotherm.	80.00 Wl 86.70 PP	32
23	<i>Tecomella undulata</i> Root –branches- leaves- seeds	1 N HCl	Weight loss with temperature.	-	Root-86.72 Wl Branches-89.27 Wl Leaves-86.13 Wl Seeds-93.84 Wl	33
24	Tea Leaves	0.01,0.1, 0.5 and 1.0 M HCl	Weight loss, potentiodynamic polarization, EIS and SEM.	Cathodic inhibitor, Langmuir adsorption isotherm	93.00 Wl 99.00 PP	34
25	<i>Terminallia-cattapa</i> leaf extract	0.5 M HCl	Weight loss with temperature.	Langmuir adsorption isotherm.	72.72 Wl	35
26	<i>Wrightia tinctoria</i> leaves extract	1.0 M HCl	Weight loss with time and temperature. UV, FT-IR and SEM.	Langmuir adsorption isotherm.	87.87 Wl	36
27	<i>Ziziphus mauritiana</i> fruit.	0.5 N HCl	Weight loss with time. FT-IR spectroscopy.	Langmuir adsorption isotherm.	88.52 Wl	37
28	<i>Zenthoxylum alatum</i>	0.1 M HCl	Weight loss measurement and potentiometry polarization technique.	Langmuir adsorption isotherm.	98.28 Wl 95.80 PP	38

6) Active Phytoconstituents Present in Green Inhibitors

- a) *In HCl Media:* Plant extraction products are acts as a good potential corrosion inhibitor for Copper in HCl media. The active constituents of green inhibitors are varied from one plant species to another species but their structures are closely related to their number of organic molecules, e.g., *Acacia nilotica* [11,56] contains Terpenoids, Tannins, alkaloids, Saponins, Glycosides, Nitrogen, phosphorus. Gallic acid, Chlorogenic acid, galloylated flavan-3,4-diol (leucocyanidin), catechin and 7,3',4',5,-tetrahydroxyflavan3,4-diol have been reported from the pods. *Aloe vera Barbadosensis Gel* [12,57] contain compounds such as salicylates, magnesium lactate, acemannan, lupeol, campesterol, sterol, linolenic, aloctin and anthraquinones. *Azadirachta indica* (AZ) extract [14,42,58] contain saponin, tannin, alkaloid, glycoside, anthraquinone and flavonoid. *Cnidioscolus Chayamansa* leaves [19] contain hydrocyanic glycosides, Flavonoids, Terpenoids, Glycosides, Steroids, Alkaloids, Carbohydrates, Amino acid and Tannins. *Egyptian licorice extract* [21] contain Glycyrrhizic acid and glabridin. *Mangrove Tannin* [26,27,59] contain mainly four flavanoid monomers, namely: catechin, epicatechin, epigallocatechin and epicatechin gallate. *Prosopis Cineraria* leaves [31,60,61] contains specigerine, steroids such as campesterol, cholesterol, sitosterol, stigmasterol, Tricosan-1-ol, Methyl docosanoate, Diisopropyl-10,11-dihydroxyicosane-1,20- dioate. Amino acids isolated from leaves and pods are Aspartic acid, Glutamic acid, Serine, Glycine, Histidine, Threonine, Arginine, Alanine, Proline, Tyrosine, Valine, Methionine, Cysteine, Isoleucine, Leucine, Phenylalanine and Lysine. *Sesum indicum* oil [32] contains lignans such as sesamol, sesamin and sesamol. The percentage composition of fatty acid is 44%, stearic acid 4.2%, palmitic acid 9% and arachidic acid 0.7%. Tea Leaves contain [34,62] polysaccharides, volatile oils, vitamins, minerals, purines, alkaloids (e.g.caffeine) and polyphenols (catechins and flavonoids). *Wrightia tinctoria* leaves [36] mainly contain flavonoids, alkaloids, saponins, and triterpenes. *Ziziphus mauritiana* fruit [37,63] contain phytochemicals such as fructose, glucose and galactose organic acids, citric, malonic and malic identified and other organic components such as tannins, phenolic compounds and flavonoids phenolic compounds identified are vanillic acid, ferulic acid and p-hydroxybenzoic acid, gallic acid.
- b) *In H₂SO₄ Media:* Plant extraction products are acts as a good potential corrosion inhibitor for Copper in H₂SO₄ media. The active constituents of green inhibitors are varied from one plant species to another species but their structures are closely related to their number of organic molecule,e.g., *Allium sativum* [40] contain Diallyl disulfide (26.623%), Trisulfide, methyl2-propenyl (16.459%) and Trisulfide, di-2-propenyl (34.104%). *Arghel* [41,64] contains Argelosides, Glycoside, Choline, Phytosterols, Flavonoids and Amyrine. *Cannabis* Plant [43, 65] contain cannabidiol-type (CBD) and cannabinol, endogenous cannabinoids anandamide (AEA), 2- arachidonoyl glycerol (2-AG). *Cinnamon* essential oils [44] contain 86.21% of CiO with Trans-cinnamaldehyde (46.30%), δ -cadinene (8.16%) and β -Cubebene (5.20 %). *Citrullus colocynthis* Fruits [45,66] contain Alkaloids, flavonoids and saponins compounds. *Myrianthu sarboreus* leaves [51] contain Alkaloid, Flavonoid, Saponin, Tannin, Terpenoids and Carbohydrates. *Newbouldialaavis* extracts [53] contain lapachol and newbouldiaquinone. Papaya leaves extract [55] contain DL-ascorbic acid (DLA), 5,7-Dimethoxy-chromen-2-one (DCO), 2-Amino-4- methylsulfanyl-butyric acid (AMB), 3,4-Dithydroxy-benzoic acid (DBA.), 2-Hydroxy-succinic acid (HSA), 3-[3-(3,4-Dihydroxy-phe nyl)-acryloxy]-1,4,5-trihydroxy-cyclohexanecarboxylic acid (DTA).

Table- 2. Green corrosion inhibitors for copper in H₂SO₄ solution.

(Wl = Weight loss, pp = Potentiodynamic Polarization, EIS = Electrochemical Impedance Spectroscopy)

No.	Inhibitor	Medium	Methods	Findings	I.E. (%)	Ref.
1	<i>Alhagi maurorum</i> plant extract	0.5 M H ₂ SO ₄	Weight loss, Potentiodynamic polarization (PP) and EIS.	Cathodic-type inhibitor, Langmuir, Flory–Huggins adsorption isotherms. kinetic–thermodynamic model,	87.90 Wl 83.40 PP 88.00 EIS	39
2	<i>Allium sativum</i>	0.5 M H ₂ SO ₄	Weight loss with temperature. Potentiodynamic polarization. EIS. Surface analysis by SEM/EDX.	Cathodic inhibitor.	97.00 Wl 94.60 PP 94.80 EIS	40
3	<i>Arghel</i>	0.5 M H ₂ SO ₄	Potentiodynamic polarization and EIS measurements. SEM.	Mixed-type inhibitor. Langmuir's isotherm.	93.26 PP 76.84 EIS	41
4	<i>Azadirachta indica</i> leaves	0.5 M H ₂ SO ₄	Weight loss and polarization techniques.	Frumkin adsorption isotherm.	86.40 PP	42

5	<i>Cannabis</i> Plant	0.5 M H ₂ SO ₄	Weight loss. potentiodynamic polarization and EIS, optical micrograph techniques.	Cathodic-type inhibitor. Langmuir and Flory Huggins adsorption isotherm. Kinetic-Thermodynamic model.	96.00 PP 91.00 EIS	43
6	<i>Cinnamon</i> <i>essential oil</i>	0.5 M H ₂ SO ₄	Polarization and EIS	Cathodic-type inhibitor. Langmuir adsorption isotherm.	89.60 PP 87.24 EIS	44
7	<i>Citrullus</i> <i>colocynthis</i> Fruits	1 M H ₂ SO ₄ ,	Weight loss with time and temperature. Electrochemical polarization methods.	Mixed-type inhibitor. Langmuir adsorption isotherm.	90.58 W1 98.41 PP	45
8	<i>Davidia</i> <i>involucrata</i> leaf extract (DLE)	0.5 M H ₂ SO ₄	Potentiodynamic polarisation measurements. FT-IR and X-ray photoelectron spectroscopy (XPS). SEM and AFM. quantum chemical calculation and molecular dynamics simulation.	Langmuir adsorption isotherm.	90.00 PP	46
9	<i>Fenugreek</i> extract	2 M H ₂ SO ₄	Gravimetric, Linear polarization and EIS measurements. SEM.	Langmuir and Flory-Huggins isotherm.	76.56 W1 84.18 EIS 83.81 PP	47
10	<i>Idesia</i> <i>polycarpa</i> maxim fruits extract	0.5 M H ₂ SO ₄	EIS and SEM techniques. Quantum chemical calculation.	Langmuir adsorption model. physisorption and chemisorption.	93.80 EIS	48
11	Losartan Potassium	0.5 M H ₂ SO ₄	Potentiodynamic polarization. Surface morphological observation by X-ray photoelectron spectroscopy (XPS), quantum chemical calculation and molecular dynamics (MD) simulation.	Mixed-type inhibitor. Langmuir adsorption model.	-	49
12	<i>Morinda</i> <i>tinctorial</i> leaves extract	0.25 M H ₂ SO ₄	Weight loss with temperature and Potentiodynamic polarization.	Mixed-type inhibitor. Freundlich adsorption isotherm.	< 60 W1 49.61 PP	50
13	<i>Myrianthus</i> <i>arboreus</i> leaves	2 M H ₂ SO ₄	Weight loss method at various time and temperatures. Rate constant (k) and half-life parameters.	Freundlich and Temkin adsorption isotherms. First order reaction.	97.67 W1	51
14	<i>Myrtus</i> <i>communis</i>	0.5 M H ₂ SO ₄	Weight loss with time. Potentiodynamic polarization, EIS, AFM and SEM methods.	Mixed- type inhibitor. Langmuir adsorption isotherm.	88.50 PP 90.70 EIS	52
15	<i>Newbouldia</i> <i>laevis</i> extracts	0.5 M H ₂ SO ₄	Gravimetric with temperature. Quantum Chemical calculations.	Langmuir isotherm.	77.53 W1	53
16	<i>Papain</i> <i>freeze</i> dried	H ₂ SO ₄	Weight loss with temperature. Potentiodynamic polarization measurements. AFM and SEM. XPS. Molecular dynamics simulations (MDS).	Mixed-type inhibitor. Langmuir adsorption isotherm.	95.00 W1	54
17	Papaya leaves extract	H ₂ SO ₄	Weight loss with temperature. Potentiodynamic polarization, EIS. FT-IR, SEM, XPS and AFM techniques.	Mixed-type inhibitor. Langmuir adsorption isotherm.	92.90 PP 95.50 EIS	55

- 7) *Mechanism of Corrosion Inhibition:* In acidic solutions, transition of the metal/solution interface is attributed to the adsorption of the inhibitor molecules at the metal/solution interface, forming a protective film. The rate of adsorption is usually rapid, and hence, the reactive metal surface is shielded from the acid solutions [67]. The adsorption of an inhibitor depends on its chemical structure, its molecular size, the nature and charged surface of the metal, and distribution of charge over the whole inhibitor molecule. In fact, adsorption process can occur through the replacement of solvent molecules from the metal surface by ions and molecules accumulated near the metal/solution interface. Ions can accumulate at the

metal/solution interface in excess of those required to balance the charge on the metal at the operating potential. These ions replace solvent molecules from the metal surface, and their centres reside at the inner Helmholtz plane. Since all the different parts of plant extract possess several heteroatoms containing active constituents, therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies.

II. CONCLUSION

In this review paper, research works produced over the past background on the corrosion of copper in various medium and their corrosion inhibition by using a different green inhibitors were presented. Various solvents are used to formulate extracts of fruits, flower, leaves, seeds, roots, peels, bark, stem and seed oil. Weight loss (gravimetric) with time and temperature effect are common methods to investigate the corrosion rate and inhibition efficiency for the evaluate green (natural) inhibitors. According to extracted results from corrosion tests, the increase in the concentration of corrosion inhibitor in the bulk of the solution (to an optimum concentration) and also increase in immersion time result in improving corrosion inhibition performance. The increase in temperature usually leads to a decrease in corrosion inhibition efficiency. Some studies were performed using Potentiodynamic polarization and EIS, for finding which type of inhibitor, whether it is anodic or cathodic or as mixed type. To study surface analysis of protective film formed on metal various study such as SEM, AFM, FT-IR, EFM, AAS, UV-Spectroscopy, EDX, XRD, EDS, LPR, XPS, MDS and Quantum Chemical study (HOMO and LUMO) of the molecular modeling were used. According to some author's adsorption isotherm occurred through the Langmuir, Freundlich, Temkin, Frumkin and Flory-Huggins. Kinetic-thermodynamic model. All the results obtained from EIS, LPR, and weight loss are in good agreement with each other.

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